DEVELOPMENT OF FILTRATION TECHNOLOGIES FOR EFFECTIVE, COST-EFFICIENT AND ROBUST WATER TREATMENT

by

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Declaration

I, the undersigned, hereby declare that this thesis, entitled, *‘Development of filtration technologies for effective, cost-efficient and robust water treatment',* is entirely my own work. The thesis has not been submitted in whole or in part to any other University or Institution. All sources used have been acknowledged and referenced in the text.

Maebh Grace

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Abstract

The provision of high quality, potable water in a sustainable and effective manner is a key challenge for water engineers, scientists, and policy makers. Urbanisation and industrial development, along with population growth, intensification of agriculture and climate change, has increased the strain on current potable water supplies in the developed world, not only in terms of supply, but also by way of introducing new contaminants into the abstraction waters. Emerging contaminants, alongside increasingly stringent environmental legislation, make the maximum allowable concentrations for various contaminants within potable water more difficult to achieve. Although the situation is improving, over 660 million people worldwide still do not have access to improved water supplies. Sustainable and robust solutions that ensure effective water treatment for a variety of contaminants, while also being low cost and low maintenance, are required.

Metals and nutrients continue to enter source water supplies by anthropogenic and natural sources. While metals can be damaging to human health, nutrients can lead to excessive microbial activity. The presence of organic matter in source waters also challenges water treatment plants (WTPs), as disinfectants used post-treatment can trigger a reaction with organic matter to create toxic by-products. These can develop both in the WTP and along the distribution network, and long-term exposure can be detrimental to human health. This is a major problem in Ireland and elsewhere, and to date, no cost-effective and sustainable solution has been found.

Various technologies are being developed to target problem contaminants, including coagulation systems, gas transfer systems, oxidation technologies, and membranes. Although these may be effective, they may also require high capital investment, be subject to fouling, and require expert maintenance. In addition, costly treatment systems are not feasible for smaller water treatment facilities and developing countries. Instead, a move towards more traditional contaminant removal and retention mechanisms, such as adsorption and filtration, may be more sustainable. Such technologies, in tandem with the use of alternative filter media, such as waste products and locally sourced material, can improve the sustainability of WTPs while not negatively impacting performance.

This study aimed to address the issue of contaminant removal, by designing a filter that could fit into the current model of a WTP, and which could remove a variety of contaminants including metals, nutrients, and disinfection by-product precursors. The technology incorporated the use of waste materials to reduce cost and maintain sustainability, and was comprehensively tested at laboratory-scale and pilot-scale.

A number of waste products and local materials were first tested at bench-scale, using a variety of common water contaminants to assess their adsorptive capacities. The media tested included coarse sand, zeolite, granular activated carbon (GAC), pyritic fill, Bayer residue, bottom ash, fly ash, and granular blast furnace slag. Following this, laboratory-scale stratified filters were constructed, comprising some of the most successful media from the bench-scale study: fly ash, Bayer residue, zeolite, sand, and GAC. The filters were evaluated for treatment performance and media clogging potential.

The results obtained from the laboratory-scale study led to a re-design for the pilot-scale study, which was operated at a WTP that used lake water as its potable water source. The WTP was chosen as it had a history of formation of disinfection by-products. Two filter configurations were examined under intermittent and constant loading rates, and comprised combinations of sand, Bayer residue, GAC, and pyritic fill. While each of the alternative designs proved more successful than a standard sand filter, a filter configuration comprising sand, GAC, and pyritic fill, proved most effective in dissolved organic carbon removal under a continuous loading regime.

These studies show that waste products can be used in filtration technologies, where adsorption is a key mechanism, thereby reducing overall capital and maintenance requirements. Adsorption isotherms are instrumental in the design of bespoke filters, and this study found that it is possible to target the removal of specific contaminants, depending on the constituents of the source water. This study presents a simple, low-maintenance design to reduce the concentration of key contaminants in potable water, and addresses a major problem for WTPs.

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Nomenclature

1/n	Freundlich intensity parameter
A	Cross sectional area
Al	Aluminium
Al_2O_3	Aluminium oxide
ANOVA	Analysis of variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
b	Constant related to the heat of sorption
B_1	Constant related to the heat of adsorption
BS	British Standards
C&D	Construction and demolition
Ca	Calcium
CaO	Calcium oxide
CCP	Coal combustion products
Cd	Cadmium
C_e	Equilibrium contaminant concentration in the pore water
CEC	Cation exchange capacity
Cl	Chlorine
Cr	Chromium
Cu	Copper
d	Day
d_{10}	Effective size
DBP	Disinfection by-products
dH/dZ	Change in hydraulic gradient
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EAA	European Aluminium Association
EC	Emerging contaminants
EPA	Environmental Protection Agency
EPS	Extracellular polymer substances
ESB	Electricity supply board

EU	European Union
FAO	Food and Agriculture Organisation in the United Nations
Fe	Iron
Fe_2O_3	Iron oxide
GAC	Granular activated carbon
GBS	Granular blast furnace slag
GGBS	Ground granular blast furnace slag
h	Hour
HAA	Haloacetic acids
HCl	Hydrochloric acid
Hg	Mercury
HLR	Hydraulic loading rate
ICP-MS	Inductively coupled plasma mass spectrometry
ISF	Intermittent sand filter
K	Potassium
K	Langmuir equilibrium constant
K_2O	Potassium oxide
K_2PO_4	Dipotassium phosphate
K_A	Measure of the affinity of the contaminant for the media
KCl	Potassium chloride
K_F	Freundlich capacity factor
K_{fs}	Field-saturated hydraulic conductivity
KNO_3	Potassium nitrate
K_s	Saturated hydraulic conductivity
K_t	Equilibrium binding constant
K_v	Virgin hydraulic conductivity
l	Height of sample
La(III)	Lanthanum
LOI	Loss on ignition
M	Million
M	Molar
MAC	Maximum allowable concentration
Mg	Magnesium

MgO	Magnesium oxide
Mn	Manganese
MnO	Manganese oxide
N	Nitrogen
Na	Sodium
Na_2O	Sodium oxide
NaOH	Sodium hydroxide
NH_4^+-N	Ammonium-nitrogen
NH_4Cl	Ammonium chloride
Ni	Nickel
NO_2^--N	Nitrite-nitrogen
NO_3^--N	Nitrate-nitrogen
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
P	Phosphorus
P_2O_3	Phosphorus trioxide
PAC	Powdered activated carbon
Pb	Lead
PE	Population equivalent
PO_4^{3-}-P	Ortho-phosphorus
Q	Flow rate
q_i	Quantity of contaminant adsorbed per gram of media
q_{max}	Maximum amount of contaminant that can be adsorbed onto the media
R	Gas constant
RO	Reverse osmosis
SDWA	Safe Drinking Water Act
SEM	Scanning electron microscope
SI	Statutory Instrument
SiO_2	Silica
SO_4	Sulfate
t	Tonne
T	Absolute temperature in degrees Kelvin

TEC	Total exchange capacity
THM	Trihalomethanes
TiO_2	Titanium dioxide
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
UN	United Nations
UNICEF	United Nations International Children’s Emergency Fund
USA	United States of America
UV	Ultra-violet
UVA_{254}	Ultra-violet absorbance at 254 nm
WHO	World Health Organisation
WWTP	Wastewater treatment plant
WTP	Water treatment plant
XRD	X-ray diffraction
z	Head of water
ZFA	Zeolite synthesised fly ash
Zn	Zinc
$ZnCl_2$	Zinc chloride
ΔG°	Adsorption energy

1 Introduction

1.1 Background

Clean drinking water is a concern for every nation in the world, and although many improvements have been made in the purification of water worldwide, 663 million people currently lack access to improved drinking water sources (WHO/UNICEF, 2015). The trend of improvement is more focused on urban areas, with 80% of those lacking access living in rural areas. This indicates the need for a sustainable solution for the treatment of drinking water, which can be easily implemented at both large and small scale, and can be adaptable to the variety of contaminants that may be present in water.

In the developed world, much of the pressures on drinking water supplies are as a result of population growth, urbanisation, agriculture, climate change, and industrial development (Shannon et al., 2008). Certain industries also require higher standards of water purification than is demanded by legislation. In addition, as technology and health care standards improve, emerging contaminants (ECs) and toxins are being discovered in water supplies (USEPA, 2012). A solution to these issues must harness purification methods without causing harm to the environment, and must be as cost-efficient as possible.

Disinfection is an integral part of the drinking water treatment process, and is the most beneficial stage for maintaining good human health (EPA, 2011a). However, the use of chemical disinfectants can bring about the creation of toxins referred to as disinfection by-products (DBPs) (Hendricks, 2011). These can differ depending on the constituents of the raw water, but are most commonly caused by a reaction with natural organic matter (NOM). Over 600 different DBPs have been recognised, very few of which have been legislated for in water treatment (Deborde and von Gunten, 2008; Hrudey, 2009). These toxins can have severe consequences on health, and those of which are monitored have been the cause of many regulatory exceedances in recent years (EPA, 2015a).

Many new technologies have focused on DBP removal, including oxidation techniques, air-stripping and membrane filtration (Lamsal et al., 2012; Wang et al., 2015). Some technologies require pre-disinfection (Liu et al., 2012), although this does not guarantee that DBPs will not form if further disinfection is applied along the distribution network. Other technologies, such as membrane filtration, are prone to fouling, which means that costly maintenance may be required (Tian et al., 2013).

This study investigated the performance of filters containing various novel, locally available materials, operated under intermittent and constant loading rates, for the removal of NOM, metals, and nutrients from water, and compared their performance against sand filters, which are conventionally used in water treatment plants (WTPs).

1.2 Knowledge gaps targeted

The study aims to address several key gaps in drinking water treatment:

- The formation of trihalomethanes (THMs), a DBP, in drinking water supplies is a major emerging issue in Irish drinking water supplies (Irish Times, 2016). Conventional methods of treatment used to avoid this problem are costly, unsustainable, or ineffective. This study proposes to use what are conventionally considered ‘waste’ materials, placed in filters to solve this problem. While some of the media examined in this thesis have been examined for their adsorption potential previously, this study is the first to optimise their use in pilot-scale filters, based on the results of tests at bench- and laboratory-scale.
- Much of the current research into preventing DBPs at the tap, focus on removing DBPs from water after formation, and focuses solely on DBPs. This study focuses on precursor removal, while maintaining effective nutrient and metal removal to ensure an all-encompassing treatment.
- Although there has been investigations into the utilisation of waste products, there are some locally available products which have not been investigated in terms of water treatment. This study aims to harness the waste products and create a sustainable technology for drinking water treatment, and brings the focus back to older, more robust technologies, but redesigns to make them applicable to the present day.

- The occurrence of clogging in a filter greatly reduces its capacity for treatment, and can render it hydraulically impractical. However, clogging in terms of drinking water treatment is not well researched. This study investigates the clogging of both novel media and sand, and the influence of loading regime on clogging occurrence.

1.3 Research aims

The overall objective of this study was to use new knowledge and insights to design a cost-efficient, robust, and sustainable water filtration technology. The specific aims undertaken to achieve this objective were:

- To select of a variety of media, using both locally sourced materials and known adsorbents for drinking water treatment.
- To test these media for adsorption potential, using a number of key water contaminants.
- To carry a smaller number of media forward from bench-scale to laboratory and pilot-scale, and logically design a filter configuration to target specific contaminants.
- To investigate clogging mechanisms, and redesign based on these results.
- To investigate of the redesign at an outdoor location, using lake water as its source to analyse performance under real conditions.
- To examine organic matter removal, combined with UV_{254} as a method of assessing DBP formation potential, and to monitor nutrients and metals where possible.

1.4 Experimental Procedures

A literature review of current practises for drinking water processes was undertaken, with a focus on DBP formation and removal mechanisms, as well as traditional contaminants. Filtration was chosen for further study as it is a robust, sustainable technology and has a scope for change by using different types of filtration media. A further literature review was undertaken to identify alternative media which may have the potential for use in water filters.

Adsorption experiments were carried out on a variety of media, including coarse sand (as a control), zeolite, granular activated carbon (GAC), pyritic fill, Bayer residue ('red mud'), bottom ash, fly ash, and granular blast furnace slag (GBS). The media were first tested for their adsorption capacity for a number of drinking water contaminants, nutrients (nitrate-nitrogen (NO_3^--N), ortho-phosphorus (PO_4^{3-}-P), ammonium-nitrogen (NH_4^+-N)), dissolved organic carbon (DOC), and metals (aluminium (Al), copper (Cu)). Following this, temperature, time and pH effects on adsorption were examined.

Based on the results of the bench-scale experiments, laboratory-scale filters were designed, constructed and operated under both intermittent and constant hydraulic loading regimes. One filter configuration comprised Bayer residue, zeolite, and coarse sand; and the other comprised fly ash, GAC, zeolite, and coarse sand. A control was also constructed comprising unstratified fine and coarse sand, and operated under both loading regimes. The filters were fed with a synthetic water mix containing organic carbon (C), Al, NO_3^--N, and NH_4^+-N. Effluent samples were collected bi-weekly and tested for these water quality parameters. After 90 days of operation, the filters were deconstructed and the clogging mechanisms were investigated.

Given the occurrence of clogging in the laboratory-scale filters, a redesign was necessary before a pilot-scale trial. The redesign comprised two three-layer filters, containing sand, GAC, pyritic fill; and sand, Bayer residue, and pyritic fill. The study control comprised unstratified sand, constructed as per current regulations. These filters were operated at a WTP using lake water as its source, which had high concentrations of organic matter. Samples were taken weekly or bi-weekly, and the filters were instrumented with sample ports at the media interfaces to allow for analysis of removals within each layer. Organic carbon and UV_{254} were the primary tests completed, to assess potential for formation of disinfection by-products. Nutrient testing was also carried out. Finally, filter deconstruction was carried out to assess where organic matter accumulation had occurred.

1.5 Structure of dissertation

Chapter 2 reviews challenges and progress in drinking water, along with sources and relevant legislation. It reviews common contaminants, their removal mechanisms and drinking water treatment processes. Chapter 2 also discusses alternative treatment technologies, and the use of waste products as alternative media for water treatment.

Chapter 3 investigates the adsorptive properties of media for Cu, Al, NO_3^--N, NH_4^+-N, DOC, and P. Media used included bottom ash, fly ash, granular blast furnace slag (GBS), pyritic fill, sand, zeolite, and granular activated carbon (GAC). This allowed the media selection to be narrowed down before being tested in filter form.

Chapter 4 investigates two filter designs at laboratory-scale. The first design consisted of a three-layer stratified filter (each layer had a depth of 0.33 m) containing (downwards from the filter surface) Bayer residue, zeolite and coarse sand. The second design was a four-layer filter, with equal layers of 0.25 m-deep media, containing (downwards from the filter surface) fly ash, GAC, zeolite and coarse sand. The chapter investigates filter performance, in relation to removal of NO_3^-N, NH_4^+-N, Al, and organic C, and the clogging characteristics associated with the filters.

Chapter 5 investigates two improved filter configurations at pilot-scale. Each configuration is a three-layer stratified filter, with one containing coarse sand, Bayer residue, and pyritic fill; and the other containing coarse sand, GAC, and pyritic fill. The filters were operated at a WTP, using lake water as its source. Dissolved organic carbon was the primary contaminant of issue in the lake water, and is the focus of this chapter.

Finally, in Chapter 6, the conclusions from the study are presented, along with recommendations for future research.

1.6 Contribution to Existing Knowledge

1.6.1 Journal Papers (Published)

Grace, M.A., Healy, M.G., and Clifford, E. (2015). Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water. Science of the Total Environment 518–519: 491 – 497.

Grace, M.A., Healy, M.G., and Clifford, E. (2016). Performance and surface clogging in intermittently loaded and slow sand filters containing novel media. Journal of Environmental Management 180: 102-110.

Grace, M.A., Clifford, E, and Healy, M.G. (2016). The potential for the use of waste products from a variety of sectors in water treatment processes. Journal of Cleaner Production 137: 788-802.

1.6.2 Journal Paper (Under Review)

Grace, M.A., Clifford, E, and Healy, M.G. (2016). Performance of novel media in stratified filters to remove organic carbon from lake water.

1.6.3 Conference Papers (In Proceedings)

Grace, M.A., Clifford, E. and Healy, M.G. (2015). A novel filtration configuration for targeted humic acid removal from drinking water. IWA Speciality Conference on Natural Organic Matter, Malmö, Sweden, 7-10 September.

The journal and conference papers can be found in Appendix A.

2 Literature Review

2.1 Overview

Water is an essential part of life, and is necessary for the promotion of good health and wellbeing. In the developing world, the supply of clean water is often compromised or unavailable. In the developed world, population growth and industrial expansion puts extra strain on existing resources and can introduce new pollutants into the water cycle. The development of sustainable and robust technologies, to tackle the issues of potable water supply, is a necessary step to maintain and improve global water access. This chapter discusses drinking water legislation, contaminants, and treatment processes, with a specific focus on filtration. Filtration is a cost-effective and efficient method of contaminant removal. Potential improvements to the filtration process include introducing alternative types of filter media, a variety of which are discussed.

Some of the contents of this chapter have been published in the Journal of Cleaner Production (Grace, M.A., Clifford, E, and Healy, M.G. (2016). The potential for the use of waste products from a variety of sectors in water treatment processes. Journal of Cleaner Production 137: 788-802).

2.2 Drinking Water

In 2010, the United Nations (UN) addressed the general assembly on the issue of the human right to water and sanitation, acknowledging that each state is responsible for the protection of all human rights (United Nations, 2010). Currently, more than 90% of the global population has access to improved supplies (Figure 2.1). However, as many as 663 million people remain without access to acceptable water supplies (WHO/UNICEF, 2015). Countries in the developing world continue to lag behind the developed world, with the lowest levels of improved drinking water sources occurring in the least developed countries, as designated by the UN (WHO/UNICEF, 2015).

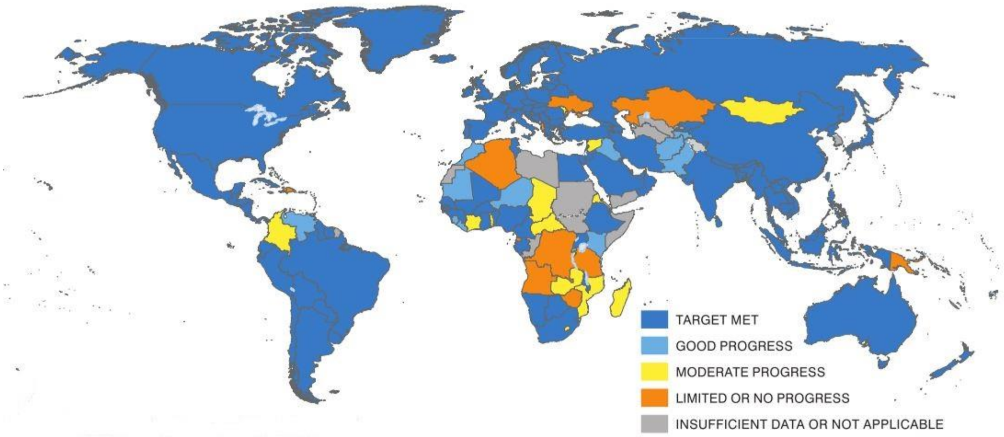

Figure 2.1 State of water improvement progress worldwide (WHO/UNICEF, 2015).

2.2.1 Sources

Although the Earth's suface is made up of about 70% water, only 3% of that is freshwater. The most common source for drinking water in the USA is surface water (Figure 2.2) (i.e. rivers and lakes), which comprises just 0.3% of the world's water supply (Shammas and Wang, 2011). Rainfall and snow meltwater that soaks through soil can be defined as groundwater, and collects in underground storage reservoirs known as aquifers (EPA, 2015b). Groundwater comprises 37% of the USA public water systems, and is generally available at the point-of-use, unlike surface water (Shammas and Wang, 2011). In Europe, rivers and groundwater provide 46% and 35% respectively, of the total water demand (European Commission, 2015a). In Ireland, over 81% of drinking water has a surface water source (EPA, 2015c). Saline water can be used for drinking water, but freshwater is more desirable for ease of treatment, although in some instances, saline water is the only available source (Subramani and Jacangelo, 2015).

Figure 2.2 Lake water is commonly used as a surface water source (Photo taken at test site in Chapter 5).

The contaminants found in abstraction waters vary widely depending on the source. Groundwater is generally more pure, and is less influenced by anthropogenic activities than surface water supplies (Shammas and Wang, 2011). However, groundwater is commonly influenced by the rock and soils through which it passes. In Ireland, only 1.5% of groundwater bodies were classified as having a poor chemical status, which was due to either phosphate or historical mining contamination (EPA, 2015b). Groundwater that collects in karst areas may contain calcium (Ca), magnesium (Mg), and bicarbonate, resulting in "hard" water.

Surface water can be contaminated from any upland activities including agricultural, industrial, and household wastewaters. This can lead to the introduction of contaminants such as nutrients, pesticides, pharmaceuticals, and metals. The flow of water across the landscape allows for the uptake of natural contaminants, including organic matter and naturally occurring metals and minerals. Irish river and lake monitoring has found that 53% of monitored bodies are of "satisfactory" ecological status, and 43% of lakes achieved "high" or "good" status (EPA, 2015b). Rivers are most commonly polluted by agriculture and municipal sources, and lake pollution is recognised as eutrophication caused by nutrient loading.

2.2.2 Regulations and Legislation

The legislation governing drinking water in Europe is the Drinking Water Directive (European Communities Council Directive 98/83/EC on the quality of water intended for human consumption, which was amended to include Commission Directive (EU) 2015/1787), which aims to supply clean water in order to safeguard human health from contamination of drinking water (European Commission, 2016; European Communities, 1998). The Directive outlines 48 parameters which must be frequently monitored and maintained at minimum standards by all EU states, and includes chemical, microbial and indicator parameters (Table 2.1).

In Ireland, public drinking water supplies are regulated by the Environmental Protection Agency (EPA), and the supplies are operated by Irish Water, a subsidiary of a commercial semi-state company. The legislation governing the quality of drinking water is Statutory Instrument No. 278 of 2007, European Communities (Drinking

Water) (No. 2) Regulations 2007, which is adapted from the Drinking Water Directive. The legislation covers the duties of suppliers, points of compliance, duties in relation to water on premises, monitoring functions of supervisory authorities, records, protection of human health, and intervention by supervisory authority among others, as well as detailing the parametric values and specifications (SI No 278 of 2007).

The World Health Organisation (WHO) has also published a document on the standards of drinking water, entitled, "Guidelines for drinking-water quality" (WHO, 2011). This document is commonly used as a basis on which governing bodies set their own regulations. It outlines the safest level of drinking water quality for life-long consumption, management strategies, and how to plan system development and health-based targets. The document also includes microbial and chemical aspects of drinking water treatment, and contains fact-sheets on the potential contaminants that may occur in a water supply.

In the USA, drinking water quality is regulated by the Safe Drinking Water Act (SDWA). The SDWA gives the United States EPA (USEPA) the authority to develop national standards for drinking water. The water quality standards are then regulated by the USEPA or, where permitted, state drinking water programmes (USEPA, 2002). The parametric limits, which are set out in the National Primary Drinking Water Regulations, are very similar to those of the European Communities Directive (USEPA, 2009). Differences in allowable concentrations for relevant contaminants have been stated in the text below.

2.3 Drinking water parameters and removal mechanisms

Although the Drinking Water Directive mentions 48 specific contaminants (Table 2.1), this section addresses those of which were measured in this study. Those addressed in this study were chosen based on exceedances reported by the Irish EPA in recent years (EPA, 2015c, 2012a). This included a selection of inorganic ions and organic particles.

Table 2.1 Monitored drinking water contaminants (SI No 278 of 2007).

	Parameter	**MAC**	**Unit**
1	Escherichia coli (E.coli)	0	/100 mL
2	Enterococci	0	/100 mL
3	Acrylamide	0.01	μg L^{-1}
4	Antimony	5	μg L^{-1}
5	Arsenic	10	μg L^{-1}
6	Benzene	1	μg L^{-1}
7	Benzo(a)pyrene	0.01	μg L^{-1}
8	Boron	1	mg L^{-1}
9	Bromate	10	μg L^{-1}
10	Cadmium	5	μg L^{-1}
11	Chromium	50	μg L^{-1}
12	Copper	2	mg L^{-1}
13	Cyanide	50	μg L^{-1}
14	1,2-dichloroethane	3	μg L^{-1}
15	Epichlorohydrin	0.1	μg L^{-1}
16	Fluoride		
	(a) fluoridated supplies	0.8	mg L^{-1}
	(b) supplies with naturally occurring fluoride	1.5	mg L^{-1}
17	Lead	10	μg L^{-1}
18	Mercury	1	μg L^{-1}
19	Nickel	20	μg L^{-1}
20	Nitrate	50	mg L^{-1}
21	Nitrite	0.5	mg L^{-1}
22	Pesticides	0.1	μg L^{-1}
23	Pesticides - Total	0.5	μg L^{-1}
24	Polycyclic aromatic hydrocarbons	0.1	μg L^{-1}
25	Selenium	10	μg L^{-1}
26	Tetrachloroethene and Trichloroethene	10	μg L^{-1}
27	Trihalomethanes - Total	100	μg L^{-1}
28	Vinyl chloride	0.5	μg L^{-1}
29	Aluminium	200	μg L^{-1}
30	Ammonium	0.3	mg L^{-1}
31	Chloride	250	mg L^{-1}
32	Clostridium perfringens	0	/100 mL
33	Colour	no abnormal change	
34	Conductivity	2500	μS cm^{-1} at 20°C

35	Hydrogen ion concentration	≥6.5 and ≤9.5	pH units
36	Iron	200	µg L^{-1}
37	Manganese	50	µg L^{-1}
38	Odour	No abnormal change	
39	Oxidisability	5	mg L^{-1} O_2
40	Sulphate	250	mg L^{-1}
41	Sodium	200	µg L^{-1}
42	Taste	No abnormal change	
43	Colony count 22°	No abnormal change	
44	Coliform bacteria	0	/100 mL
45	Total organic carbon	No abnormal change	
46	Turbidity	No abnormal change	
47	Tritium	100	Bq L^{-1}
48	Total indicative dose	0.1	mSv $year^{-1}$

2.3.1 Nutrients

2.3.1.1 Nitrogen

Nitrogen (N) can be present in water as NH_4^+-N, NO_3^--N and NO_2^--N and organic nitrogen. The maximum allowable concentration (MAC) for NH_4^+-N in drinking water is 0.3 mg L^{-1}. The presence of NH_4^+-N in WTPs can have a negative impact on (i) disinfection by resulting in increased chlorine (Cl) consumption or reducing the effect of Cl-based disinfection systems (Wilczak et al., 1996) and (ii) both pH and dissolved oxygen (DO) concentrations in the distribution system (Feng et al., 2012). The MAC for NO_3^--N in drinking water is 11 mg L^{-1}. Nitrate can enter drinking water abstraction sources from anthropogenic sources, generally from municipal wastewater treatment plants (WWTPs) where denitrification was incomplete, and from agricultural land (EPA, 2012a). Nitrate was responsible for the failure of 4 water supplies in Ireland in 2014 (EPA, 2015c). The MAC for NO_2^--N in drinking water is 0.2 mg L^{-1}, and its presence has also been linked to blue-baby syndrome (Fan and Steinberg, 1996). Nitrogen is most commonly removed at filtration stage by a combination of biological mechanisms and adsorption, with the biological activity occurring at the surface of the filters.

2.3.1.2 Phosphorus

Phosphorus is not currently legislated for under drinking water quality legislation. However, given that most potable water uses surface- or ground-water as its abstraction source, P is likely to be found in abstraction waters. The Water Framework Directive (2000/60/EC; EC, 2000) states the threshold concentration of P in waters to be 0.035 mg L^{-1}. However there is a likelihood that certain locations in the EU, for example where agricultural P leaching occurs, will not meet this objective, based on current trends (EPA, 2015b). Phosphorus causes detrimental eutrophication effects when present in surface water sources. Phosphorus is also likely to cause problems in the water distribution network, with excessive concentrations increasing microbial growth (Miettinen et al., 1997).

2.3.1.3 Removal mechanisms

Nutrient removal mechanisms can occur in a number of ways. The most common method for N removal from wastewater is a series of biological reactions, nitrification followed by denitrification. Nitrification involves the conversion of ammonia to nitrites and nitrates, and requires aerobic conditions. Denitrification is the conversion of nitrates to nitrogen gas, and requires anoxic conditions (Hendricks, 2011). Denitrification does not always occur in wastewater treatment plants, and combined with agricultural leaching, meaning NO_3^--N and NO_2^--N are the most commonly found nitrogen ions in abstraction water. Recommended technologies for NO_3^--N and NO_2^--N removal include ion exchange, reverse osmosis, and electro-dialysis (Vesilind et al., 2010). Adsorption has also proved successful for NO_3^--N uptake from aqueous solutions, using a variety of media including activated carbon, sepiolite, and other low-cost materials (Cengeloglu et al., 2006; Zhang et al., 2013).

Phosphorus removal can be carried out by biological and chemical processes. Biological P removal is a wastewater treatment process and requires anaerobic and aerobic conditions (Metcalf and Eddy, 2003). Chemical processes include precipitation, whereby metal ions can be added to wastewater to bind to P anions, which in turn create a settleable precipitate (Hendricks, 2011), and adsorption where the anion binds to sorption material (Egemose et al., 2012). Materials with a high silica and alumina content have proved successful for P adsorption (Agyei et al., 2002).

Other methods such as membrane filtration, reverse osmosis, and magnetic separation have also been used successfully for P removal (Nguyen et al., 2015).

2.3.2 Metals

Metals are most likely to enter drinking water abstraction sources by anthropogenic sources, such as mining, drainage, road runoff, corrosion of pipes (EPA, 2015a), and by industrial processes (Mohod and Dhote, 2013). In legislation, each metal has a different MAC, depending on the severity of the effects on human health. For example, the MAC of Al is 200 µg L^{-1}, chromium (Cr) is 50 µg L^{-1}, Cu is 2 mg L^{-1}, lead (Pb) is 10 µg L^{-1}, and iron (Fe) is 200 µg L^{-1}. The presence of lead was found in 39 drinking water supplies in Ireland in 2014 (EPA, 2015c). The presence of metals in water can be associated with many physiological illnesses attacking the major organs of the human body (Mohod and Dhote, 2013).

2.3.2.1 Removal mechanisms

Metal removal is mainly carried out by chemical processes. Common recommended treatments include coagulation/filtration, adsorption, ion exchange, and reverse osmosis (Vesilind et al., 2010). Metals can be co-precipitated with P if conditions allow, and it can be achieved using hydroxide and sulphide. pH control is important when attempting to achieve metal precipitation and can vary from metal to metal (Metcalf and Eddy, 2003). Many different ion exchange materials can be used for metal removal, although pH is critical. These include zeolites, cation and anion resins, chelating resins, and biomass (Metcalf and Eddy, 2003). Other successful metal removal techniques include coagulation-flocculation, flotation and electro-chemical methods (Fu and Wang, 2011).

2.3.3 Natural Organic Matter

The majority of WTPs use groundwater or surface water, which can contain fluctuating amounts of TOC, as their source. Organic carbon enters water bodies by leaching from land, particularly from peatlands, and can fluctuate depending on temperature, disturbance of peat, rainfall and depth to water table (Grand-Clement et al., 2014; Sutherland et al., 2015). Organic carbon in a WTP can increase disinfection demand, act as a precursor to DBPs, and be responsible for membrane fouling and corrosion (Matilainen et al., 2010; Velten et al., 2011).

2.3.3.1 Disinfection by-products

Disinfection by-products are responsible for the majority of non-compliance with regulatory standards in many WTPs in Ireland (Water_Team, 2012). Of 973 public water supplies in Ireland, 59 had reported exceedances in 2014 (EPA, 2015c) Disinfection by-products occur when dissolved particles in water react with disinfection chemicals, such as Cl (Kim et al., 2002). The presence of DBPs in drinking water has numerous suggested ill-effects on human health. These include bladder cancer, genetic mutations, and foetal abnormalities (Grellier et al., 2015; Richardson et al., 2007). There are over 600 identified DBPs, but most are not currently regulated (Deborde and von Gunten, 2008; Hrudey, 2009). The most common forming DBPs occur when NOM reacts with Cl, forming compounds such as THMs and haloacetic acids (HAA) (Deborde and von Gunten, 2008). Currently, HAA, bromate, chlorite, and THM are regulated in the USA, where the MACs are 0.06. 0.01, 1.0 and 0.08 mg L^{-1}, respectively (USEPA, 2009). However, to date, THM and bromate are the only DBPs regulated by the EU, where the limit for THM is 0.1 and the limit for bromate is 0.01 mg L^{-1} (SI No 278 of 2007).

The composition of NOM is important when assessing the potential for formation of DBPs (Tran et al., 2015). Natural organic matter is commonly measured as organic carbon, either total (TOC) or dissolved organic carbon (DOC). Natural organic matter compounds, such as humic or fulvic acids, can be measured by various fractionation techniques including particle size distribution, molecular weight distribution and fluorescence excitation emission matrix (Matilainen et al., 2011; Tran et al., 2015). Dissolved organic carbon is the organic matter that can pass through a 0.45 μm filter, and its composition varies depending on the source. It is the most concerning element, as the smaller particles are more difficult to remove in standard treatment processes such as coagulation or straining (Matilainen et al., 2010), and as the dissolved particles are more likely to form DBPs (Gopal et al., 2007). In this case it is necessary to introduce biological and adsorption processes, thus the need for depth filtration.

2.3.3.2 Removal mechanisms

As chlorinated DBPs are the most commonly occurring, many water treatment entities are looking towards other disinfectants such as ozone, ultraviolet radiation, chlorine dioxide, and chloramination (Hendricks, 2011). The Drinking Water Directive does not state the preferred method of disinfection, but that contamination from DBPs is kept as low as possible without compromising the microbial disinfection quality (SI No 278 of 2007). The biggest disadvantage of switching from Cl to another disinfectant is that most, if not all, other forms of disinfectants also lead to the formation of DBPs, or require a further chemical disinfectant (EPA, 2012b). These are not all regulated, but may still have a negative impact on human health. A more sustainable approach is to investigate either the removal of the formed DBPs or to achieve more efficient NOM removal during the water treatment process. Removing NOM will minimise DBP formation along the distribution network. However, if the network contains any source of organic matter, DBPs can reoccur if Cl needs to be added to maintain free Cl residual at the furthest point (EPA, 2012b). This is a relevant concern for Irish WTPs where the network storage could be greater than two days (EPA, 2012b).

Some of the methods used for DBP removal require a pre-disinfection stage. Following this, techniques such as air-stripping, advanced oxidation, ultra-violet treatment, and powdered and activated carbon are used (WHO, 2011). This must be followed by a post-treatment disinfection stage to maintain microbial decontamination, and is not an attractive option for most WTPs. Other techniques aim to improve conventional treatment processes, such as using zeta potential analysis. This allows for optimisation of the coagulation process based on NOM concentrations (Sharp et al., 2006). Flotation techniques are effective in precursor removal, either with dissolved air or floating microspheres (Jarvis et al., 2011). Granular activated carbon has been successfully used to adsorb both DBP and the precursor, NOM (Gopal et al., 2007), and can be retrofitted to operational filters. However, GAC can exhaust with high levels of NOM, and may incur high expenditure. Precursors have also been removed using combinations of ion exchange and coagulation (Metcalfe et al., 2015). Membrane filtration is also effective at NOM removal, though high levels can cause irreversible fouling, rendering the membrane unsuitable for use (Zularisam et al., 2006).

As research into the process of DBP formation and removal intensifies, there has been much investigation into NOM fractionation and characterisation, to specify which molecules are more likely to react with Cl, and to form DBPs (Tran et al., 2015). A disadvantage to this approach is that the methods used to fractionate NOM are generally costly and/or require specific expertise. A more accessible indicator is the relationship between ultraviolet absorbance at a wavelength of 254 nm (UVA_{254}) and DOC, known as specific ultraviolet absorbance (SUVA). It can be used to investigate the potential for formation of DBP by acting as an indicator of the aromaticity and hydrophobicity of the water (Anumol et al., 2015; Christy et al., 1999), as it is most commonly found that the hydrophobic organic compounds have higher THM reactivity than hydrophilic organic compounds (Tran et al., 2015). It also has the practical advantage of using commonly available laboratory instruments (Hua et al., 2015).

2.4 Drinking water treatment processes

Although many new technologies are being developed to target specific and emerging contaminants, the conventional WTP remains a popular choice for water supply entities. The conventional treatment process typically encompasses screening, softening, coagulation and flocculation, sedimentation, filtration, and disinfection. Fluoridation also occurs in some states. Following disinfection, water is pumped to a storage reservoir, and from there is distributed out through the pipe network.

2.4.1 Screening

Screening occurs at the abstraction point (Figure 2.3), just before pumping, and requires the water to flow through at least one screen size. The screen ensures that leaves, twigs, and rags do not enter the pumps or pipes, which could lead to breakdowns and clogging (Hendricks, 2011). The screens can be lifted and cleaned manually or mechanically, depending on the size of the plant.

Figure 2.3 Screen at the abstraction point of a surface water source (Photo taken at test site of Chapter 5).

2.4.2 Softening

Softening is only necessary where the source water is hard (caused by the presence of minerals such as Ca and Mg) (Vesilind et al., 2010). Ion exchange can be used to achieve softening, but the most common method is chemical precipitation in the form of lime soda addition (Hendricks, 2011).

2.4.3 Coagulation and flocculation

Coagulation and flocculation are required to remove the colloidal particles from water, particularly necessary for surface water. Coagulation occurs by charge neutralisation and bridging. Charge neutralisation makes the particles less stable and more available for collision. Bridging involves smaller particles becoming attached to macro-molecules already formed (Vesilind et al., 2010). Coagulants such as alum and ferric, along with a polymer, are added to the water and mixed. These particles have an electrostatic charge which must be chemically altered to allow the formation of larger particles, 'flocs', which will then settle out naturally (Vesilind et al., 2010). The mixing causes flocculation, whereby the micro-particles colloid and aggregate to form flocs (Hendricks, 2011). Coagulation is an important process for TOC removal. However, where TOC concentrations are high but comprise low molecular weight particles, coagulation less effective at removing TOC (Edzwald, 1993).

2.4.4 Sedimentation

Sedimentation is the next step of the water treatment process. It involves the water entering a gravity settling basin, where it remains for sufficient time, to allow the flocs formed in the previous step to settle out (Figure 2.4). Baffles are sometimes used to allow the particles to achieve maximum settling velocity (Vesilind et al., 2010). Lamella separators, plates at an inclined plane, can also be used to aid in the settling process (Hendricks, 2011). The solids are removed at the base of the settling basin, and the resulting sludge is transported to a dewatering facility.

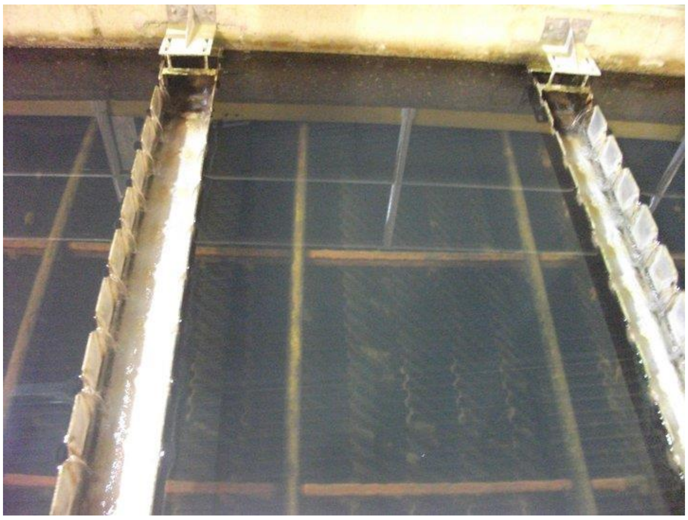

Figure 2.4 A sedimentation basin with angled lamella.

2.4.5 Filtration

Filtration is the next step in the conventional treatment process, and will be discussed in more detail in Section 2.5. Drinking water filtration is generally carried out using rapid gravity sand filters or slow sand filters (Vesilind et al., 2010).

2.4.6 Disinfection

Disinfection is the final step in drinking water purification processes, and its use has been responsible for a major reduction of water-borne illnesses (EPA, 2011a). Disinfection is required to destroy micro-organisms and pathogens, and makes water suitable for human consumption. Removal of micro-organisms is likely to occur at previous stages, such as filtration, but these must be followed by disinfection. The disinfectant must successfully destroy the cell, disrupt the metabolism or inactivate reproduction of the pathogen (EPA, 2011a).

The most common disinfectant is Cl, which can be released into the water as a gas, which oxidises organic material including micro-organisms (Vesilind et al., 2010). Irish regulations state that there must be a free Cl residual maintained throughout the distribution network, until the furthest point of consumption. The presence of biofilms along the network requires super-chlorination at the treatment plant and/or Cl boosts at various points along the line (EPA, 2011a). As mentioned previously, a significant disadvantage of the use of Cl, is the creation of toxic DBPs. This has encouraged the use of alternative disinfectants and processes, such as ozone and membrane filtration.

Failures of the disinfection process result in issuing of 'boil water notices' and draw much media attention. *Cryptosporidium* oocyst, a protozoa, outbreaks of which have occurred in Irish drinking water in recent times, are not readily inactivated by Cl (EPA, 2011a). For this reason, it is necessary in certain areas to have either membrane filtration, ozone, or ultraviolet radiation as another disinfection process (EPA, 2011b).

2.4.7 Fluoridation

In Ireland, the addition of fluoride to public drinking water supplies is required under the Health (Fluoridation of Water Supplies) Act, and Irish Water implement the process (EPA, 2015c). Where fluoridation occurs, it is the last process in the treatment system, and must be dosed at concentrations resulting in 0.6-0.8 mg L^{-1} (Irish Expert Body of Fluorides and Health, 2007). Where fluoride is present in groundwater, the maximum concentration must not exceed 1.5 mg L^{-1} (SI No 278 of 2007). Fluoride is added to aid dental health by reducing the occurrence of cavities, but is a controversial issue (Blinkhorn et al., 2015; Calderon, 2000; Warren and Saraiva, 2015).

2.5 Removal mechanisms and filtration technologies

While the focus of the current study is adsorption, contaminant removal mechanisms can be categorised as physical, chemical, and biological (EPA, 1995), thus using the full depth of the filter.

2.5.1 Physical mechanisms

Physical filtration mechanisms comprise sieving and straining. These occur when larger particles either settle on the top of the filter surface or become trapped in the media as water travels through. Over time, straining can add to the head loss of the filter, and contribute to clogging (EPA, 1995). Embedding is another physical mechanism, whereby a particle can become embedded in the media (Hendricks, 2011). Physical mechanisms are specific to the particle size of the contaminant, and will only be effective on particles bigger than the smallest pore spaces in the media bed. It occurs both on the filter surface and down through the filter depth.

2.5.2 Adsorption

Adsorption is the most common chemical contaminant removal mechanism. Adsorption is a surface phenomenon, and can be defined as the process whereby substances in solution (adsorbate) are accumulated on a suitable interface (adsorbant) (Metcalf and Eddy, 2003). Adsorption most commonly refers to organic molecules and particles such as viruses and bacteria (Hendricks, 2011). Temperature, kinetics, pH, and the nature of the adsorbate and adsorbant can affect adsorption (Ali and Gupta, 2006). At adsorption equilibrium, the adsorption and desorption rates are equal. Molecules have the ability to desorb when they have sufficient thermal energy to break the attachment bond. As a result, if the temperature rises, a higher proportion of molecules will possess the energy required to break the attachment bond and the fraction of adsorbent coverage is less than at a lower temperature (Hendricks, 2011). Electrostatic attraction, a form of adsorption, is another chemical mechanism, whereby ions attach to the surface of a media, such as an ion exchange resin (Hendricks, 2011).

Adsorption isotherms, such as those developed by Langmuir, Freundlich, Elovich and others (Ali and Gupta 2006; Foo and Hameed 2010), may be used to model adsorption. However, it has been shown that the maximum adsorption capacity, as calculated by the Langmuir model, does not always correlate with removal in a complex reaction system (Arias et al., 2001). Nonetheless, in literature it is applied in over 95% of liquid-phase adsorption systems (Foo and Hameed, 2010).

2.5.3 Biological

Biological removal mechanisms are mainly used in the treatment of wastewater rather than drinking water, although NOM removal by biological methods has been investigated (Hendricks, 2011). The biological activity occurs on the surface of a filter, with the build-up of a biomass layer, a biofilm referred to as the “schmutzdecke” (EPA, 1995). Biological treatment also refers to some nutrient removal mechanisms, such as nitrification and denitrification.

2.5.4 Slow sand filters

Slow sand filtration (Figure 2.5) dates back to the early 1800s, where it was used to treat water from the River Thames in London (EPA, 1995). It is a passive process which occurs without the need for frequent operator intervention (Hendricks, 2011). While rapid gravity filtration technologies became more prominent over time, slow sand filtration has proved to be more effective at the removal of microbial contaminants (EPA, 1995). Slow sand filtration appeals more to communities of less than 5000 population equivalent (PE) due to labour costs of processing sand (Hendricks, 2011).

The filtration process in the slow sand filter involves the development of a biomass “schmutzdecke” (Yongabi et al., 2011). This layer can sometimes lead to the clogging of the filter, and may require the top 5-30 mm to be scraped off periodically. For effective filtration this layer must be fully developed, at which point it can be expected to remove cysts, oocysts, algae, bacteria, viruses, parasite eggs and other organic debris (Hendricks, 2011). The particles in a slow sand filter have an effective size of between 0.15 – 0.3 mm and the filters operate at a flow rate of between 0.1 – 0.3 m^3 m^{-2} h^{-1} (WHO, 2011).

Hydraulic design considerations of a slow sand filter are ten-fold: (i) backfill of the sand bed and headwater after scraping (ii) distribution of raw water without filter erosion (iii) uniform collection of treated water (iv) drainage of the headwater for sand bed scraping (v) installation of overflow weir below top level of filter box (vi) measurement of flow to the filter (vii) controlling filter flow (vii) measurement of headloss through the filter bed (ix) provision for filter plumbing and (x) to avoid negative pressures within the sand bed (Hendricks, 2011).

Limitations of a slow sand filter include not reducing the true colour of the water sample (EPA, 1995), and that due to the smaller flow rate, a larger footprint may be required for large WTPs. Despite the limitations of a slow sand filter, it is clear that the design is economically viable for smaller population equivalents.

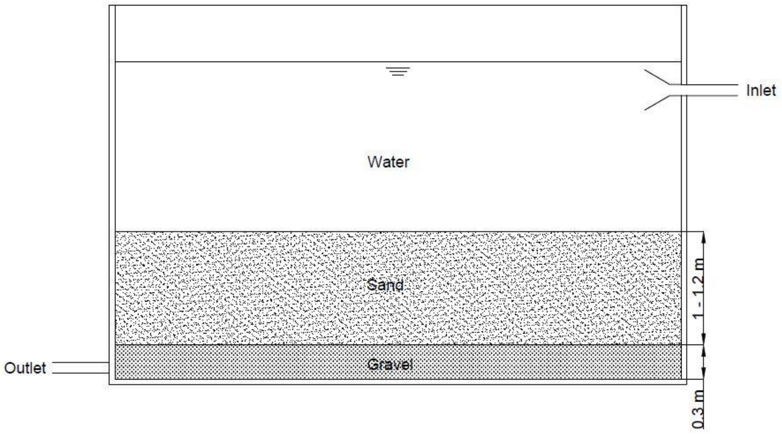

Figure 2.5 Schematic of a slow sand filter.

2.5.5 Rapid gravity filters

Rapid Gravity Filtration works by using the head of water above the filter to ensure a high flow rate. The system operates using two principles, straining and depth filtration. Straining involves the retention of large particles that would not otherwise pass through the media and depth filtration involves the retention of floc particles that attach to media grains (Hendricks, 2011). In rapid gravity filtration, gravity controls flow although in Ireland it is advised to limit flow to between 5 and 7.5 m h^{-1} (EPA, 1995).

Rapid sand filters also go through a backwashing process (Figure 2.6) whereby the flow direction is reversed to loosen the sand particles and remove accumulating particles. The reverse flow must be of a sufficient velocity to fluidise the bed of media. This will dislodge the solid particles by scrubbing and hydraulic shear (Hendricks, 2011). If the filter is not backwashed it can clog, which causes an increase in the head loss down through the filter. The clogging, in turn, can lead to a “breakthrough”, whereby none of the solids are removed by the filter (EPA, 1995). It can be rare to find biodegradation in a rapid sand filter, particularly with plants with a pre-chlorination cycle. This is because the disinfection and backwash does not allow for the build-up of a proper biofilm layer (Chuang et al., 2011).

Figure 2.6 Backwashing of a rapid gravity filter.

The three characteristics of a filter cycle for rapid gravity filtration are chemical conditioning (ripening), steady-state, and breakthrough, after which the filter is no longer viable as a treatment process. When designing a rapid gravity filtration system, the design objectives are to ensure an economical length of run (defined as the period before breakthrough or terminal head loss) and to maximise net water production, i.e. the total water production per unit area after backwash requirements, filter to waste and other support functions (Hendricks, 2011). Typical filter media characteristics for rapid gravity filtration are displayed in Table 2.2.

Table 2.2: Filter media characteristics (EPA, 1995).

Material	**Size Range (mm)**	**Specific Gravity**
Conventional Sand	0.5-0.6	2.6
Coarse Sand	0.7-3.0	2.6
Anthracite/Coal	1.0-3.0	1.5-1.8
Gravel	1.0-50	2.6

2.5.6 Intermittent filters

Intermittent sand filtration (ISF), most commonly used for the treatment of wastewater, involves the water being dosed periodically onto the surface of the sand filter either in recirculation or in single pass mode (Healy et al., 2007). An ISF differs from a rapid sand filter in that there are periods of the day in which there is no wastewater being loaded onto the filter surface and the water is not being pushed through by a rising head of water as the cycle proceeds (Cowan and Middlebrooks, 1980). Equal distribution of the water over the surface of the filter is advantageous, as it forces air vertically into the filter (Schwager and Boller, 1997).

Not all the filter volume in conventional filters is available for biological activity, so it is important to try to distribute the water properly. The only biologically active layer of an ISF is the top layer, which will be only centimetres thick. It is comparable to the schmutzdecke of a slow sand filter and is where all the biological degradation of nutrients occurs (Latvala, 1993). Intermittent sand filters may be buried or open; however with a buried filter, top soil slows down air diffusion. Open filters allow enhanced air access and easier control of the filter surface, but do not allow land use above the filter surface (Schwager and Boller, 1997).

2.5.7 Clogging mechanisms

Clogging is defined as head loss across a filter until a predetermined design limit is reached (EPA, 1995). Clogging mechanisms in sand filters for the treatment of wastewater (Hatt and Fletcher, 2008; Leverenz et al., 2009) and vertical flow constructed wetlands, which operate in a similar way to filters (Hua et al., 2010; Knowles et al., 2011; Pedescoll et al., 2009; Turon et al., 2009), have been well researched. However, clogging mechanisms in filters for drinking water treatment have not been examined to the same extent. Biological clogging has been the main focus of the research to date (Kildsgaard and Engesgaard, 2002; Mauclaire et al., 2004; Thullner et al., 2002); however, clogging may also occur by chemical and physical mechanisms (Le Coustumer et al., 2012; Mauclaire et al., 2004). This may be particularly relevant for water filters. Chemical clogging can affect the shapes and stabilities of the pores in the media, in turn, affecting the flow paths (Baveye et al., 1998). Adsorption of substances and metal precipitation from the influent water may also contribute to clogging within filters (Noubactep et al., 2010). Physical clogging may result from compaction due to loads on the surface of the filter and migration of the fine media into the filter. Therefore, the use of a particularly fine media at the surface may result in a filter cake forming at the media-water interface, contributing to physical clogging (Baveye et al., 1998). Where organic carbon is a component of the influent water (Figure 2.7), clogging is expected due to the extracellular polymer substances (EPS) in humic acid, which attach and form a gel-like, hydrophilic structure as the humic acid accumulates (Tanner et al., 1998), increasing the retardation of flow within the filter (McKinley and Siegrist, 2011).

Figure 2.7 Evidence of clogging in a sand filter.

Clogging of filter media may be investigated in a number of ways. One of the most common methods is to measure the saturated hydraulic conductivity (K_s) (Le Coustumer et al., 2012; Pedescoll et al., 2009; Rodgers et al., 2004). As the filter clogs over time, K_s decreases (Knowles et al., 2011). This can be measured using either a falling head test (ASTM, 2007) or constant head test (British Standard Institution, 1990a), depending on the permeability of the media under consideration. Other common methods of analysis include loss-on-ignition (LOI), chemical analysis of the media at different depths throughout the filter, scanning electron microscopy (SEM) of the biofilm layer, and X-Ray diffraction (XRD) analysis (Knowles et al., 2010; Nivala et al., 2012; Pedescoll et al., 2009; Rodgers et al., 2004).

Clogging becomes evident in filters as surface ponding occurs (for intermittent filters) and the outflow flow rate decreases (Knowles et al., 2011). It is important to ascertain how deep the clogging layer is within the filter, as the filter can be regenerated and the hydraulic conductivity restored. This may be accomplished by replacing the clogging layer of the filter with fresh media (Mauclaire et al., 2004). Current guidelines advise the removal and re-sanding of slow sand filters once a predetermined design head loss has been reached (EPA, 1995). However, re-sanding beyond the clogging layer leads to excessive and unnecessary cost.

2.6 Alternative treatment technologies

Some of the main alternative technologies for potable water treatment are listed in Table 2.3, along with their advantages and disadvantages.

Table 2.3 Alternative treatment technologies, with advantages and disadvantages (Edzwald, 2010; Hendricks, 2011; Metcalf and Eddy, 2003; National Research Council, 1999).

Technology	Advantages	Disadvantages
Reverse Osmosis (RO)	• Removes colour, hardness, sulphates, nitrate, sodium, organics • Can reduce the need for chemical addition • Smaller footprint than a conventional plant • Can be used as a disinfection step • Reduced labour requirements	• Requires a pre-treatment • Results in a concentrate stream requiring disposal • May be subject to reversible and irreversible fouling • Membranes require regular cleaning • Expensive compared to conventional treatment
Membrane filtration	• Removes organics, TSS • Can be a pre-treatment step for RO • Can reduce the need for chemical addition • Smaller footprint than a conventional plant • Can be used as a disinfection step depending on membrane size • Reduced labour requirements	• Requires a pre-treatment • Results in a concentrate stream requiring disposal • May be subject to reversible and irreversible fouling • High pressure systems can be energy intensive • Requires replacement of membranes every 3 - 5 years • Low pressure systems do not remove NOM
Advanced Oxidation Systems	• DBP precursor destruction • Can remove colour and micropollutants • Can inactivate *Cryptosporidium* (ozone)	• Not as cost effective as other treatment technologies • May require air stripping to quench residual (ozone)
Dissolved Air Flotation	• Successful for NOM, *Giardia* and *Cryptosporidium* oocyst removal • Can be operated at high rates • Can be a pre-treatment to GAC filtration • Can cope with high turbidity	• Results in a sludge requiring disposal • Higher capital costs than sedimentation • Can be difficult to maintain a stable floc blanket in cold conditions

Hydraulic loading rates that are commonly applied to the aforementioned technologies are detailed in Table 2.4.

Table 2.4 Hydraulic loading rates for various treatment systems.

Technology	Hydraulic loading rate	Comment	Reference
Slow sand filter	0.1-0.2 m h^{-1}	Regulations	EPA (1995)
	0.15 m h^{-1}	Drinking water	Haig et al. (2014)
	0.45 m h^{-1}	Pre-treated surface water	Bichai et al. (2014)
Rapid gravity filter	5-7.5 m h^{-1}	Regulations	EPA (1995)
	3.7 m h^{-1}	Clarified drinking water	Hyde et al. (1987)
	5 m h^{-1}	Pre- and post-coagulated water	Han et al. (2009)
Intermittent filter	0.0017-0.0083 m h^{-1}	Water with added cryptosporidium	Logan et al. (2001)
	0.00028-0.0136 m h^{-1}	Wastewater	Healy et al. (2007)
	0.0017-0.0067 m h^{-1}	Wastewater	Leverenz et al. (2009)
Reverse osmosis	$6.25*10^{-6}$ m^3 m^{-2} s^{-1}	Desalination of geothermal waters	Tomaszewska and Bodzek (2013)
	1.37 L min^{-1}	High turbidity storm water	Lin et al. (2012)
	$1.19*10^{-6}$ m^3 m^{-2} s^{-1}	Potable water reuse	Alturki et al. (2010)
Ultrafiltration	$6.17*10^{-5}$ m^3 m^{-2} s^{-1}	Seawater	Tansakul et al. (2011)
	$4.16*10^{-5}$ m^3 m^{-2} s^{-1}	Humic acid solution	Li et al. (2016)
Nanofiltration	$5*10^{-7}$ - $3.25*10^{-6}$ m^3 m^{-2} s^{-1}	Groundwater	Arora and Maheshwari (2011)
	$1*10^{-6}$ - $2.7*10^{-5}$ m^3 m^{-2} s^{-1}	Raw water sources	de la Rubia et al. (2008)
DAF	5-30 m h^{-1}	Drinking water	Edzwald (2010)
	8-12 m h^{-1}	Drinking water	Zabel (1985)
	23 m h^{-1}	Drinking water	Lakghomi et al. (2012)

2.7 Reutilisation of waste products for drinking water treatment

The EU produces 2.3 billion tonnes of waste annually, of which 10% (or 250 million tonnes) includes municipal waste, and 90% includes industrial, commercial, agricultural, and other business related waste (Ruggiero, 2013). In agriculture, wastes are generated at production, post-harvest and processing stages (Parfitt et al., 2010), and amount to 1.3 billion tonnes per year worldwide (FAO, 2011). About 850 million tonnes of construction and demolition (C&D) waste is generated in the EU per year, representing 37% of the total waste generation in the EU (Fischer and Werge, 2009). However, the level of recycling and reuse of C&D waste varies greatly (between less than 10% to over 90%) across the EU. The concept of a ‘zero waste’ industry may not be feasible, and while industries such as the C&D industry have a policy of reduction, reuse, recycle and disposal (Yuan and Shen, 2011), there is a tendency amongst stakeholders to only consider the use of wastes within the same sector (Duran et al., 2006), without considering their use in other sectors. One such avenue for the use of these wastes is in the water treatment sector, particularly as less than half the population of some countries in the developing world have access to clean, potable water (FAO, 2015), and a need has been identified for cost-effective and robust solutions to improve water purification in both the developed and developing world (Shannon et al., 2008). Although the trend of improving drinking water supplies is increasing, in 2015, 663 million people were deprived of good quality drinking water, leaving much scope for improvements (WHO/UNICEF, 2015).

Interventions to water technologies must include sophisticated strategies to combine water and energy savings, while striving for the ultimate goal of a circular economy (Bagatin et al., 2014). Although a ‘zero-waste’ society is not yet achievable, steps in the right direction are necessary with all new developments. Total recycling of used products and an entirely circular economy is not realistic, but it is possible to achieve a sustainable future by attempting to reach this goal (Reh, 2013). The maintenance of environmental and economic benefits is important when investigating material recovery concepts (Dahlbo et al., 2015), and so, disposal or use post-treatment must also be considered to ensure a holistic design approach. It is necessary to ensure new production processes do not create extra environmental impacts, which could undermine those beneficial changes found by utilizing waste products (Mirabella et al., 2014).

Sand filtration is commonly used in drinking water purification. However, it can have shortfalls regarding the removal of certain contaminants (Water_Team, 2012). A multi-layer filter containing a variety of media may have the potential to tackle problematic contaminants. Anthracite and coal are most commonly used in multi-layer filters, but these are costly and unsustainable adsorbents (EPA, 1995). Adsorption is evolving, as it produces satisfactory results, while being cost-efficient and easy to design and operate (Bibi et al., 2015). The exploration of different adsorbents, both manufactured and recycled, is paving the way for a new generation of filters, containing a variety of media from many different sources (Bhatnagar and Sillanpää, 2010). Utilization of waste from sectors such as industry, agriculture and C&D as adsorbents allows for the development of sustainable and effective treatment technologies. The use of waste from certain processes could provide a sustainable alternative for water treatment systems than abstraction of sand.

There is increasing interest in the utilisation of waste materials, and there is a gap in knowledge in terms of the application to water treatment processes, by investigation of adsorption of a variety of contaminants. This section investigates a variety of media from three sectors (industry, agriculture and C&D) that could be used in filters for the removal of contaminants from water.

2.7.1 Industrial by-products and waste

Industrial activities generate products and residues from both production and consumption. As industrial activity continues to increase, so too does the creation of excessive waste. In 2012, 48% of total waste in the EU was disposed of to landfill, and the remainder was either recycled, or used for energy recovery, backfilling or incineration (Eurostat, 2015). The utilisation of industrial by-products and wastes in water treatment is infrequently examined in the literature. The wastes that will be considered in this paper are fly ash and GGBS, and Bayer residue, and chemical characteristics are detailed in Table 2.5. Fly ash was chosen as it comprises 85% of all ash produced in coal combustion products (CCP), with approximately 780 million tonnes produced worldwide (Heidrich et al., 2013). Ground granular blast furnace slag was chosen as it is a product of over 1 billion tonnes of steel produced (Juckes, 2011), and Bayer residue because of the increasing accumulation of the waste (EAA, 2013).

Table 2.5 Media characterisation.

	Fly Ash	**GGBS**	**Bayer Residue**	**Coconut Shell**	**Coffee Waste**	**Rice Husk**	**Crushed Concrete**	**Masonry Waste**
SiO_2	44.5-67%	35%	5-30%					66.52%
Al_2O_3	22.2-30.7%	10%	10-22%					14.2%
Fe_2O_3	1.1-14.4%		20-45%					5.45%
CaO	0.4-4.2%	40%	0-14%					6.06%
BaO	0-0.5%							
MgO	0.3-1.6%	8%						2.35%
Na_2O	0.2-0.9%		2-8%					0.67%
K_2O	0.5-2.9%							2.09%
TiO_2	0.9-1.9%		4-20%					
P_2O_5	0.1-2.7%							
SO_3	0.1-0.5%							0.75%
Carbon %				48.6	57-59	35		
Hydrogen %				6.5	7.1-7.6	4-5		
Oxygen %				44.6	26-23	31-37		
Nitrogen %				0.1	1.2-1.3	0.23-0.32		
Sulphur %				0.1		0.04-0.08		
Ash %						22-29		
Moisture						8-9		
Ca g kg^{-1}							240-551	
Fe g kg^{-1}							17-29	
Al g kg^{-1}							18-30	
P g kg^{-1}							1-13	
Cu mg kg^{-1}							37-87	
Pb mg kg^{-1}							33-87	
Cr mg kg^{-1}							22-115	
Cd mg kg^{-1}							1-20	
Reference	Ward and French (2006)	Ecocem (2015)	EAA (2013)	Daud (2004)	Pujol et al. (2013)	Kumar et al. (2012)	Egemose et al. (2012)	Naceri and Hamina (2009)

2.7.1.1 Fly ash

Fly ash (specifically coal fly ash) is a waste product of the incineration process. It is defined as a non-hazardous mineral combustion waste, with coal fly ash falling under the category of slags and ashes from thermal treatment combustion (Eurostat, 2010). It has a recognised potential use as a raw/construction material in applications such as cement and concrete addition (ESB Moneypoint, 2012), with more than half of the concrete used in the USA containing fly ash (World Coal Association, 2015). The current utilisation rate for fly ash use in the EU is approximately 43%, leaving over 17 million tonnes for disposal or stockpiling (Ecoba, 2015).

Fly ash is produced by the incineration process when coal is burned as a power source, and in incineration of municipal solid wastes, sugar cane bagasse, rice husks and tea dusts. For many years production has exceeded utilisation capabilities, meaning a large proportion is landfilled (Ecoba, 2015). For the purposes of this review, power station fly ash (coal combustion) is of most interest, as it is the largest source of fly ash production (Iyer and Scott 2001). The major components are silica, Al, Fe oxides, C, Ca, Mg, and sulphur in varying amounts, depending on the original source (Iyer and Scott 2001). Chemical characteristics are detailed in Table 2.5. With such a large variety of elements, fly ash has potential for many uses (Figure 2.8), and efforts should be made to avoid landfilling.

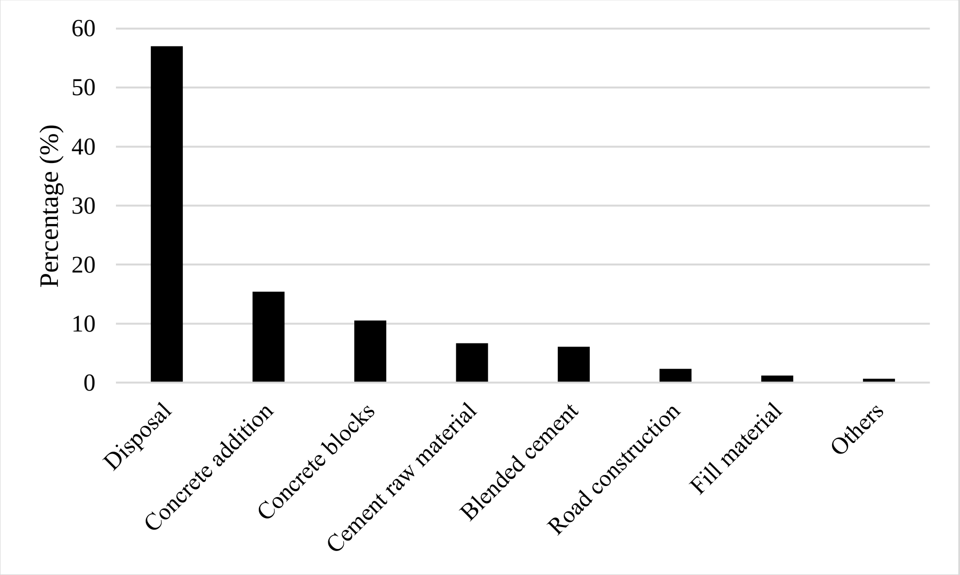

Figure 2.8 Disposal and utilisation of fly ash in the construction industry and underground mining in Europe (EU 15) in 2010 (Ecoba, 2015).

2.7.1.1.1 Current uses

In the construction industry, fly ash is mostly used in concrete addition (35.9% of total use of fly ash in 2010), with other uses including blended cement, road construction and concrete blocks (Ecoba, 2015). Research has been carried out on increasing the amount of fly ash in certain concrete mixtures to increase performance (Mehta, 2002). This must be cautioned however, as fly ash can adsorb concrete surfactants which may have negative effects on the mixture (Ahmed and Hand, 2014). The fine nature and elemental composition of fly ash has led to investigations into the use of fly ash as a fertiliser (Jala and Goyal, 2006) and for soil conditioning, which has demonstrated positive results on a short-term basis (Kalra et al., 1998), though this should only be used where the fly ash will not compromise the soil quality (Pandey and Singh, 2010).

2.7.1.1.2 Potential for use in water treatment

Fly ash has been well recognised for its efficacy as an adsorptive material for various contaminants in aqueous solutions (Ahmaruzzaman, 2010). Table 2.6 gives an overview of the adsorption potential, based on adsorption isotherm modelling, targeting in particular those contaminants of interest in this thesis. Fly ash also has the ability to uptake metals, such as Pb and Cu (Alinnor, 2007), and zinc (Zn) and manganese (Mn) (Nascimento et al., 2009) from aqueous solutions, and its capacity may be improved by the presence of humic acid in water (Wang, et al., 2008a). Metal removal using fly ash can also be enhanced by coating with chitosan (Adamczuk and Kołodyńska, 2015). Lignin removal can be achieved by fly ash (Andersson et al., 2011), as can phenanthrene (An and Huang, 2012). Little research has been carried out on NH_4^+-N adsorption, other than cation exchange capacity (CEC) investigations with synthesised zeolite from fly ash.

Many studies have been carried out to investigate the efficacy of zeolite that is synthesised from fly ash (ZFA), for example to remove heavy metals from wastewater (Querol et al., 2002), P from an aqueous solution (Chen et al., 2006), and for humic acid removal from water (Li et al., 2011). Synthetic zeolites from fly ash have been shown to have a CEC of up to 3 meq g^{-1}, allowing for the uptake of heavy metals and cations such as NH_4^+-N (Querol et al., 2002). Wu et al. (2006) investigated the increase of CEC of ZFA by salt treatment, and simultaneous P and NH_4^+-N removal, which was particularly effective at low concentrations. A mild acid treatment has been shown to have a similar effect on ZFA (Zhang et al., 2007).

The main disadvantage to using fly ash in water treatment is the potential for metal leaching. By its nature, metals are an intrinsic characteristic of fly ash (Chou et al., 2009). However, with the introduction of some precautionary measures, where necessary, this can be mitigated. Measures may include a leaching behaviour test (for example, where systems may contain other adsorptive media), forced extraction, immobilisation of elements, and destruction of persistent pollutants (Wang and Wu 2006).

Acid, heat, and activation all have a positive effect on the adsorption capacity of fly ash (Li et al., 2006). However, for the most sustainable and cost-effective approach, the raw state is generally stated to be most desirable (Alinnor, 2007). Phosphorus and humic acid can also be successfully removed from water (Table 2.6) using fly ash. However, there is little investigation of co-adsorption and contaminant interaction. Wang et al. (2008a) studied the positive effect of humic acid presence on metal adsorption, but to comprehensively assess the potential for the use of fly ash in a sustainable technology, it is necessary to study the raw water contaminants in a combined and natural environment.

2.7.1.2 Ground granulated blast furnace slag

Ground granular blast furnace slag is a waste product of the steel production industry. It is non-hazardous, and is a finely ground powder. Similar to fly ash, GGBS falls under the category of mineral combustion wastes, and is hazardous if it contains metals (Eurostat, 2013). Over a billion tonnes of steel is manufactured per annum, leading to the availability of a large amount of GGBS (Juckes, 2011).

Ground granulated blast furnace slag is produced from blast furnaces used in Fe production. Molten slag is produced when iron-ore, coke and limestone are melted in a blast furnace. Slag floats on the molten iron, and once removed, is granulated, to form GBS or ground to produce GGBS (Siddique and Bennacer, 2012). Ground granulated blast furnace slag typically contains oxides of Ca, silica, Al and Mg in varying proportions (Ecocem, 2012).

Table 2.6Previous studies of fly ash adsorption.

Contaminant	Adsorption Capacity	Comment/Conditions	Isotherm	Reference
Phosphate	63.2 mg g^{-1}	Raw	Langmuir	Li et al. (2006)
	58.9 mg g^{-1}	Heat activated at 700°C	Langmuir	
	78.4 mg g^{-1}	Acid activated with 0.25 M HCl	Langmuir	
	27.4 g g^{-1}	At 40°C, with initial concentration of 100 mg/L	Langmuir	Ugurlu and Salman (1998)
	20. mg g^{-1}	Raw fly ash	Langmuir	Wu et al. (2006)
	35.3 mg g^{-1}	Salt treated zeolite synthesised from fly ash	Langmuir	
	42. mg g^{-1}	Raw fly ash	Langmuir	Chen et al. (2007)
Humic Acid	126.6 mg g^{-1}	zeolite synthesised from (high calcium) fly ash	Langmuir	Li et al. (2011)
	31.6 mg g^{-1}	zeolite synthesised from (low calcium) fly ash	Langmuir	
	36.6 mg g^{-1}	Raw, single pollutant system	Langmuir	Wang et al. (2008a)
	45.5 mg g^{-1}	Raw, all unburned carbon present	Langmuir	Wang and Zhu (2007)
DOC	0.3 mg g^{-1}	Hydrophobic acid fraction of DOC. Fly ash eluted with methanol	Langmuir	Wei et al. (2011)
Copper	29.12 mg g^{-1}	Hydrothermal modified zeolite synthesised from fly ash	Langmuir	Visa (2016)
	36.22 mg g^{-1}	Chitosan coated fly ash	Langmuir	Adamczuk and Kołodyńska (2015)
	152 mg g^{-1}	Fly ash based geopolymer	Langmuir	Al-Harahsheh et al. (2015)

2.7.1.2.1 Current uses

In Europe, almost 18 million tonnes of GGBS is currently used in the cement and concrete industries (Ecocem, 2015). This is the most common use for GGBS. It acts as a direct replacement for cement, and has many advantages including extending the life cycle of concrete, making concrete more durable, and reducing the carbon and energy footprint of concrete production (Ecocem, 2015). Blended cements (GGBS and ordinary Portland cement) have a superior resistance to sulphates and an increased chloride binding capacity (Siddique and Bennacer, 2012).

2.7.1.2.2 Potential for use in water treatment

Ground granulated blast furnace slag has not been previously identified as an adsorptive material, and little research has been carried out in this regard. The chemical composition of GGBS would indicate potential for a strong CEC for cation and metal adsorptions. Further research is necessary to investigate pre-treatments which would allow the adsorption potential of GGBS to be harnessed and utilised.

2.7.1.3 Bayer residue

Bayer residue (also called bauxite residue or red mud) is a primary waste product of the Al production industry. Accumulation of the residue is estimated to be increasing by 110 million tonnes per annum, with 2700 million tonnes already in storage in 2010 (EAA, 2013). Bayer residue is highly alkaline and has a fine particle size, leading to environmental issues around disposal and storage.

Aluminium is most often refined from bauxite ore, which is readily available all over the world. The ore contains high levels of Al oxides, which can be extracted by the Bayer process. This involves heating the bauxite in caustic soda under high temperature and pressure, to form sodium aluminate and an insoluble residue - known as Bayer residue (Deelwal et al., 2014). The sodium aluminate is further treated to form Al hydroxide or oxide. The Bayer residue typically contains Fe oxide, Al oxide, titanium oxide, Ca oxide, silica oxide and sodium oxide (EAA, 2013).

2.7.1.3.1 Current uses

Bayer residue is stored at or close to the alumina manufacturing facility in a bauxite residue storage area or in dry stacking facilities (Nikraz et al., 2007). Bauxite residue storage areas should be carefully controlled, with hydrosphere monitoring to avoid any negative environmental or ecological impacts (EAA, 2013). It is a concerning issue for many nations, with the goal of 20% utilisation of fresh mud set by the Chinese government for the end of 2015 (Liu et al., 2014). Approximately 110 million tonnes of Bayer residue are produced and stored worldwide annually (EAA, 2013), and this is expected to increase to 4 billion tonnes by 2015 (Liu and Naidu, 2014). Therefore, it is the subject of ongoing research to identify potential uses and alternative disposal mechanisms such as soil amelioration, construction and groundworks restoration (EAA, 2013). Work has been carried out on the use of Bayer residue as a construction additive or filling material (Deelwal et al., 2014). Limited research has been carried out on the use of Bayer residue as a coagulant or as an industrial catalyst, showing it may have potential in this area (Wang, et al., 2008b), for example to purify a bio-diesel waste stream (Resende et al., 2013). Work has also been carried out on iron recovery from Bayer residue (Liu and Naidu, 2014).

2.7.1.3.2 Potential for use in water treatment

Previous studies indicate that Bayer residue has potential as an adsorptive material for removal of contaminants from water supplies, and it has been suggested that exhausted material be re-used in the construction sector (Ali and Gupta, 2006). Metal removal from aqueous solution has been examined successfully (Hua et al., 2014), although further work is required to understand the removal techniques and consequences (Brunori et al., 2005). Bayer residue has been shown to be effective in P removal (Table 2.7), and limited studies of NO_3^--N, along with other anion adsorption studies (Bhatnagar et al., 2011), have produced positive results. Gaps exist in the adsorption potential of NH_4^+-N and DOC, although Lopez et al. (1998) observed NH_4^+-N removal from secondary effluent from a wastewater treatment plant. Bayer residue can also achieve more than 90% bromate removal from aqueous solutions (Chen et al., 2016). The positive results indicate that further research should be carried out to assess the removal capabilities of a spectrum of contaminants.

The most relevant disadvantage to using Bayer residue in water treatment processes is reflected in environmental concerns (Liu et al., 2011). Its chemical and mineralogical characteristics require treatment before storage and it is important to ensure it does not further pollute water or leach contaminants. The adsorption potential may outweigh the concerns, and carefully designed systems could mitigate any possible concerns.

2.7.2 Agricultural waste

The agricultural sector is constantly growing, particularly as trade relations strengthen between countries and demographics continue to put pressure on food production systems. Thirty-eight percent of the EU budget is spent on agriculture, with exports steadily rising and currently estimated to have a value of €122 billion (European Commission, 2015b). Globally, trade flow values have increased fivefold in the past 50 years (United Nations, 2015). Twelve percent of the total land area of the world is used for crop production in the agricultural sector (United Nations, 2015). This produces many different types of wastes and by-products. In this thesis, those examined are coconut shell, tea and coffee wastes, and rice husk.

2.7.2.1 Coconut shell

Coconut shell is frequently used as a carbonaceous source for activated carbon, as it results in a strong, dense carbon (Cooney, 1999). Although powdered coconut shell can be used for adsorption, the most common use is as an activated carbon source. This is a successful adsorbent, but the activation process can be expensive, and using the raw material as is would be a more sustainable approach.

Activated carbon is manufactured in a two-step process. First, raw materials go under a carbonization process in an inert environment, and then the carbonized product is activated with oxidising gases (Hu and Srinivasan, 1999). The oxidation process erodes a network of internal channels and pores, while creating a surface of oxides, to increase the surface area and make the material more suitable for adsorption (Cooney, 1999).

Table 2.7 Previous studies of Bayer residue adsorption.

Contaminant	Adsorption Capacity	Comment/Conditions	Isotherm	Reference
Phosphate	113.9 mg g^{-1}	Raw Heat activated at 700°C	Langmuir	Li et al. (2006)
	345.5 mg g^{-1}	Acid activated with 0.25 M HCl	Langmuir	
	161.6 mg g^{-1}		Langmuir	
	K = 0.47	Acid activated with 2M HCl, experiment @ 30°C	Freundlich	Huang et al. (2008)
	K = 0.62	Acid activated with 2M HCl, experiment @ 40°C	Freundlich	
	K = 0.24	Raw, adsorption experiment @ 30°C	Freundlich	
	K = 0.33	Raw, adsorption experiment @ 40°C	Freundlich	
	75.9 mg g^{-1}	Acid activated with 20% HCl	Langmuir	Pradhan et al. (1998)
	58.1 mg g^{-1}	Neutralised and aggregated, 48 h study	Langmuir	Lopez et al. (1998)
Nitrate	365.8 mg g^{-1}	Acid activated with 20% HCl @ 40°C	Langmuir	Cengeloglu et al. (2006)
	117.8 mg g^{-1}	Original red mud	Langmuir	
Ammonium	18 % removal efficiency	Packed column	N/A	Lopez et al. (1998)

K: Freundlich adsorption capacity factor

2.7.2.1.1 Current uses

In developing countries, coconut shells have practical uses such as bowls and utensils, but the most common large-scale use for coconut shell is the production of activated carbon. More than 61 million tonnes of coconuts are grown worldwide annually, most commonly used for drinking, coconut oil, and dessicated coconut (UNCTAD, 2012). This volume of raw material gives much scope for activated carbon production. Coconut shells have also been used in construction, to create coconut shell aggregate concrete; however, this is not commonly used (Gunasekaran et al., 2012).

2.7.2.1.2 Potential for use in water treatment

Table 2.8 presents a selection of previous studies investigating adsorption using coconut shell in terms of relevant contaminants for drinking water treatment. Coconut-based adsorbents are well studied in terms of biosorption for water treatment. Bhatnagar et al. (2010) reviewed a variety of coconut biosorbents for removal of metals, dyes, pollutants, anions and radionuclides from water, concluding that the potential for use is great, although knowledge gaps still exist in terms of real effluent use, regeneration and recovery studies.

Coconut shell has been successfully used in adsorption of metals such as Cu, Pb, cadmium (Cd) and Zn (Sousa et al., 2010), and dye adsorption (Cazetta et al., 2011), various anions such as those mentioned in Table 2.8, and fluoride (Sathish et al., 2007). Nickel can also be adsorbed using coconut shell (Vocciante et al., 2014). Adsorption of dyes can be indicative of an adsorbent's affinity to adsorb various molecular weights of organic matter (Zhang et al., 2007), thus activated carbon from coconut shell has good potential to adsorb NOM. Studies have shown that the presence of NOM in aqueous solutions can inhibit or at least compete with adsorption of other trace organic compounds that are commonly found in drinking water by pore blockage and site competition (Quinlivan et al., 2005).

Evidence suggests that coconut shell-derived activated carbon is useful in terms of water treatment. However, the carbonization and activation process can be expensive and technology-intensive, meaning that it is not as sustainable as other by-products. It is also likely to become saturated and exhausted, requiring a regeneration treatment.

Coconut shell could be combined with another adsorbent to reduce the need for regeneration yet achieve effective and sustainable water treatment.

2.7.2.2 Tea/coffee wastes

Worldwide coffee and tea production is a large industry, with the total coffee production per crop year 2014/15 at 141.7 million 60 kg bags (ICO, 2015) and world tea crop production in 2013 was 5.3 million tonnes (FAOSTAT, 2015). The chemical composition of tea varies depending on the type, but the largest proportion generally comprises polyphenols, as well as sugars, some amino acids, lipids, and some minerals (Harbowy et al., 1997). Similarly, coffee varies depending on the type, but major constituents are fatty acids, hydrocarbons and sterols (Pujol et al., 2013).

2.7.2.2.1 Current uses

Coffee and tea grounds/leaves are most commonly disposed of in compost or in landfill disposal. Coffee grains can be beneficial for vermi-composting, by allowing the kitchen waste to become more stable for earthworm populations (Adi and Noor, 2009). However, if a potential use is identified, it would reduce the need for landfill disposal. Studies have also been carried out to investigate the preparation of activated carbon from these wastes by pyrolysis (Reffas et al., 2010) and acid impregnation for improved adsorption of dyes (Ma and Ouyang, 2013).

2.7.2.2.2 Potential for use in water treatment

Coffee grounds (Safarik et al., 2012) and tea grains have been used successfully in dye adsorption (Nasuha et al., 2010), which can be used to indicate a potential for use in cationic adsorption requirements (Franca et al., 2009). Metal removal has been achieved using both coffee grounds and tea leaf wastes (Djati Utomo and Hunter, 2010). Phenol removal has also been successful with activated carbon prepared from coffee residue (Lamine et al., 2014). Wang et al. (2014) reported a NO_3^--N removal efficiency of almost 52% using green tea extract.

Table 2.8 Previous studies of coconut shell activated carbon adsorption.

Contaminant	Adsorption Capacity	Comment/Conditions	Isotherm	Reference
Ammonium	K = 44.9	Activated carbon from coconut shell, at pH 9	Freundlich	Boopathy et al. (2013)
	K = 1875	5:3 Limestone:GAC mix	Freundlich	Hussain et al. (2007)
Nitrate	33.7 mg g^{-1}	NaOH modified coconut shell powder	Langmuir	de Lima et al. (2012)
	10.3 mg g^{-1}	$ZnCl_2$ activated coir pith (from coconut husk)	Langmuir	Namasivayam and Sangeetha (2008)
	18.6 mg g^{-1}	Activated carbon from coconut shell, at pH 2-4	Langmuir	Ohe et al. (2003)
	55.8 mg g^{-1}	Anion exchanger from coconut shell	Langmuir	Orlando et al. (2002)
	6.2 mg g^{-1}	Anion exchanger from coconut shell	Langmuir	Orlando et al. (2003)
Phosphate	3.0 mg g^{-1}	5:3 Limestone:GAC mix	Langmuir	Hussain et al. (2011)
	200 mg g^{-1}	NaOH modified coconut shell powder	Langmuir	de Lima et al. (2012)
	5.1 mg g^{-1}	$ZnCl_2$ activated coir pith (from coconut husk)	Langmuir	Namasivayam and Sangeetha (2004)
	K = 0.0001	Activated carbon from coconut shell	Frumkin	Agrawal et al. (2011)
Copper	38.97 mg g^{-1}	Activated carbon from coconut shell	Langmuir	Fang et al. (2013)
	7.25 mg g^{-1}	Fixed-bed column of coconut shell	N/A	Acheampong et al. (2013)
	86.01 mg g^{-1}	Activated carbon from coconut shell	Langmuir	Moreno-Piraján et al. (2011)
Aluminium	0.957 mg g^{-1}	Activated carbon from coconut shell		Ghazali et al. (2012)

K: Freundlich adsorption capacity factor

2.7.2.3 Rice husk

Rice husks (hulls) are the outer covering on the grain, separated from rice during milling. In Asia, 700 million tonnes of rice husk are produced annually (Santiaguel, 2013), accounting for 92% of the worldwide rice production (Ricehusk.com, 2015). The chemical composition of rice husk includes cellulose, hemicellulose, lignin, silica, ash, and protein (Krishnani et al., 2008).

2.7.2.3.1 Current uses

Rice husk was generally considered a waste product, but in recent years, it has become a commodity, and has uses such as power production (from biomass gasification) and a raw material for chopstick manufacture (Santiaguel, 2013). It can also be used in horticulture, animal bedding, and as a material in composites (Ricehusk.com, 2015). Thermal treatment of the husk can aid in oil (Angelova et al., 2011) and petroleum adsorption (Kenes et al., 2012).

When rice husk is burnt, it produces an ash, with a high silica content, that can be used in concrete production and insulation products (Singhania, 2004). The ash has also been used in purification methods, such as the preparation of biodiesel from frying oil (Manique et al., 2012). Similarly, oil polluted water can be cleaned using the ash (Vlaev et al., 2011).

2.7.2.3.2 Potential for use in water treatment

From various studies and reviews, it is clear that rice husk is a successful adsorbent (Ahmaruzzaman and Gupta, 2011). Table 2.9 details the previous adsorption studies of the contaminants examined in this review, indicating that rice husk can be used in a treatment technology.

Rice husk has proven to adsorb metals from wastewater successfully, particularly when used as a starting material for activated carbon preparation (Daifullah et al., 2003). A partial alkali digestion of rice husk also improved the metal binding ability, showing a good affinity for eight different heavy metals (Krishnani et al., 2008). Mohan and Sreelakshmi (2008) found that treating rice husk with P increased its affinity for metal adsorption. Other studies confirm the affinity of rice husk for adsorption of metals such as Cd (Ye et al., 2010), nickel (Ni) and Zn (Srivastava et al., 2007), and Pb and mercury (Hg) (Feng et al., 2004), and also for dye adsorption (Kumar et al., 2014). Rice husk ash can also be used as a precursor to activated carbon, which has been successful for dye removal (Liu et al., 2012).

To further assess the potential of using rice husk in a water treatment technology, it is necessary to compare the advantages to its current uses, to ensure it is a viable adsorption source. It is also necessary to assess the cost of having to modify the husk, compared to using a raw, untreated material.

2.7.3 Construction and demolition by-products

Construction and demolition wastes encompass a wide variety of media, from wood, metals and plastics, to textiles and paper, oils and minerals (Eurostat, 2013). Figure 2.9 shows the composition of C&D wastes, for EU member states, excluding Estonia and Finland (European Commission, 2011). Large quantities of C&D waste is produced every year and can account for more than 25% of all waste in the EU (European Commission, 2015c). Although recycling efforts are substantial (greater than 50%), there is still a necessity for further re-use of some of this material (Fischer and Werge, 2009). In 2012 in Europe, 40 million tonnes, of a total 295 million tonnes, of mineral waste from C&D was deposited onto or into land, meaning there is a large quantity of potential mineral waste available (Eurostat, 2015). This will allow for compliance with the EU Waste Framework Directive (2008/98/EC; EC, 2008), which states that recycling efforts must be raised to at least 70% (Fischer and Werge, 2009). To aid in reaching this target, it is necessary to examine the potential for certain C&D wastes for other purposes, such as water and wastewater treatment. The wastes of interest in this review are crushed concrete, masonry waste and wood waste.

Table 2.9 Previous adsorption studies using rice husk.

Contaminant	**Adsorption Capacity**	**Comment/Conditions**	**Isotherm**	**Reference**
Nitrate	55.6 mg g^{-1}	Anionic sorbent prepared with rice husk	Langmuir	Katal et al. (2012)
	74.4 mg g^{-1}	Anion exchanger produced from rice husk	Langmuir	Orlando et al. (2002)
	6.2 mg g^{-1}	Anion exchanger produced from rice husk	Langmuir	Orlando et al. (2003)
	70.2 mg g^{-1}	Activated carbon prepared from rice husk	Langmuir	Zhang et al. (2013)
Phosphate	89.6% removal	Chemically activated rice husk	Not specified	Yadav et al. (2015)
	64.3% removal	Raw rice husk	Not specified	
Ammonium	39.8 mg g^{-1}	Biochar prepared from rice husk	Langmuir	Kizito et al. (2015)
	2.6 mg g^{-1}	Rice husk charcoal	Langmuir	Han et al. (2013)
	1.4 mg g^{-1}	Activated carbon prepared from rice husk	Pseudo-second order	Zhu et al. (2012)
Humic acid	45.5 mg g^{-1}	Activated carbon prepared from rice husk	Langmuir	Daifullah et al. (2004)
	8.2 mg g^{-1}	Modified rice husk ash	Langmuir	Imyim and Prapalimrungsi (2010)
Copper	8.89 mg g^{-1}	NaOH pretreated rice husk	Langmuir	Li et al. (2015)
	12.77 mg g^{-1}	Rice husk		Konga et al. (2015)
	5.01 mg g^{-1}	Rice husk ash	Langmuir	Vieira et al. (2014)

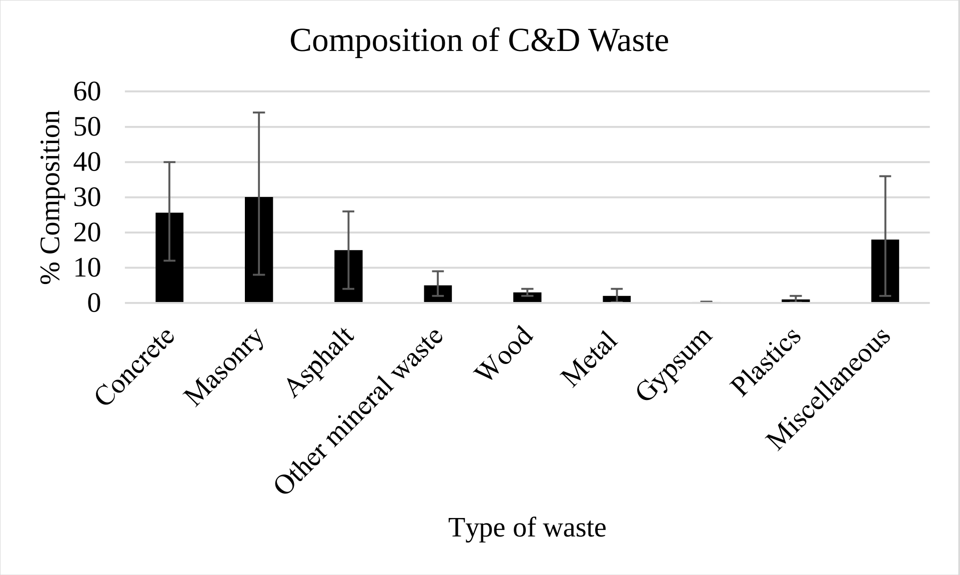

Figure 2.9 Composition of C&D waste from EU member states excluding Estonia and Finland. Adapted from (European Commission, 2011).

2.7.3.1 Crushed concrete

Crushed concrete is a waste product from the C&D industry, resulting from the demolition of buildings and concrete structures. Crushed concrete comprises the largest fraction of C&D waste (Figure 2.9), so finding an alternative use is extremely important. It comprises the standard components of a concrete mixture, aggregates, water, cement and sand. This results in a chemical composition of Ca, Al, and Fe oxides (Egemose et al., 2012).

Production of crushed concrete arises from the need to reduce landfill waste from all industries, including the C&D industry, with crushing meaning it is more suitable for use elsewhere. Debris and rubble from buildings that have been damaged in destructive earthquakes, along with regeneration demolition, and rebuilding roads and runways result in large amounts of waste. The debris is crushed and ground using various techniques dependent on the required use (Topçu and Şengel, 2004).

2.7.3.1.1 Current uses

A certain amount of old concrete from the C&D sector still goes to landfill. Crushed concrete can be reused as a form of aggregate; however, this must be done with caution, as increasing amounts of waste concrete aggregate can decrease density, workability, hardness and compressive strength (Topçu, 1997).

2.7.3.1.2 Potential for use in water treatment

Table 2.10 details previous work on adsorption studies using crushed concrete. Egemose et al. (2012) investigated the use of crushed concrete as a filter material for urban and agricultural runoff. The study found that it was effective in P removal, but observed that caution must be taken to ensure the pH and alkalinity of the effluent is controlled. During a column study to treat secondary effluent wastewater from a municipal wastewater treatment plant, Berg et al. (2005) discovered that although crushed gas concrete (lightweight concrete) was effective at reducing the concentration of P by 80-100%, the DOC was unchanged, meaning crushed concrete may not be effective as a stand-alone filter media, depending on the contaminants in question. Crushed concrete has shown potential for metal adsorption, with successful adsorption of Cu, Zn and Pb (Coleman et al., 2005). There are indications that crushed concrete may be a successful filter media for removal of contaminants from aqueous solutions, but further work would have to be carried out across a broad spectrum of contaminants to fully assess its potential.

Table 2.10 Previous adsorption studies using crushed concrete.

	Adsorption Capacity	**Comment/Conditions**	**Isotherm**	**Reference**
Phosphate	19.6 mg g^{-1}	Initial P concentration of 1000 mg L^{-1}	Not specified	Egemose et al. (2012)
	17.3 mg g^{-1}	Initial P concentration of 100 mg L^{-1}	Langmuir	Oguz et al. (2003)
	70.9 mg g^{-1}	Initial P concentration of 10 mg L^{-1}	Langmuir	Renman and Renman (2012)
	α:4.976 and β:0.0042	Ordinary Portland cement	Frumkin	Agyei et al. (2002)

2.7.3.2 Masonry

Masonry waste comprises a large proportion of the C&D waste generated in the EU (Figure 2.9), approximately 30%, and is classified under the same waste stream as concrete and gypsum-based materials. It refers to a mixed waste comprising bricks, tiles and ceramics, and any other masonry rubble; and can arise from construction of civil infrastructure, or from demolition (European Commission, 1999). The properties of masonry, both physical and chemical, vary depending on the proportions of the components present in any one sample (del Rio Merino et al., 2010). It can also vary depending on location, given that different regions may use different types of bricks. In some countries, such as Pakistan, brick powder is readily available and may have few costs associated with its use (Bibi et al., 2015). In general, it comprises silicate minerals, rich in silicon, Al oxides and hydroxides (Naceri and Hamina, 2009).

2.7.3.2.1 Current uses

Masonry waste from the C&D industry can be reused in the same industry, particularly as aggregate for concrete production, mortars, roof elements, concrete blocks and concrete tiles (del Rio Merino et al., 2010). There have also been studies carried out to investigate the use of masonry waste as a replacement of clinker in cement (Naceri and Hamina, 2009), and as a pozzolonic admixture (Lavat et al., 2009).

2.7.3.2.2 Potential for use in water treatment

Table 2.11 details the studies which have investigated those contaminants of interest in this review. Crushed brick has been used to remove dye from aqueous solutions effectively (Hamdaoui, 2006). Metals, such as Cu (Djeribi and Hamdaoui, 2008) and Hg (Labidi, 2008), have also been removed from aqueous solutions using crushed brick. Brick has also been used for microbiological adsorption, with *Clostridium beijerinckii* found to adsorb onto the surface (Qureshi et al., 2000). Ceramics have also been used in contaminant removal from aqueous solutions. Fluoride has been successfully adsorbed by granular ceramic (Chen et al., 2011), and silica ceramic has been used to remove arsenic from aqueous solution (Salim and Munekage 2009). Brick powder has also been successfully used for both fluoride and arsenic removal (Bibi et al., 2015).

It is clear that there is potential in the use of masonry waste as an adsorbent for water treatment. With the ability to adsorb such a variety of contaminants, the next step would be to assess its potential to adsorb multiple contaminants simultaneously. The biggest disadvantage, however, is the lack of uniformity. Depending on the source, the masonry waste composition could have a huge variance, which will in turn affect the potential for use.

Table 2.11 Previous adsorption studies with masonry waste.

Contaminant	Adsorption Capacity	Comment/Conditions	Isotherm	Reference
Nitrate	14.1 mg g^{-1}	Brick with particle size <710 μm	Langmuir	Selvaraju and Pushpavanam (2009)
Phosphate	18.2 mg g^{-1}	Brick with particle size <710 μm	Langmuir	Selvaraju and Pushpavanam (2009)
	0.9 mg g^{-1}	La(III) loaded granular ceramic	Langmuir	Chen et al. (2012)
Ammonium	112.4 mg g^{-1}	Novel ceramic adsorbent	Langmuir	Zhao et al. (2013)
	35% removal	Broken brick as biofilter	Not specified	Savage and Tyrrel (2005)

2.7.3.3 Wood waste

Although wood waste only accounts for 2% of the EU C&D waste (Figure 2.9), it is a relevant waste to investigate, given that in certain countries this figure may be higher. For example, in Ireland, in 2010, wood accounted for 5% of total C&D waste collected, amounting to 45,000 tonnes (EPA, 2010). Wood waste can arise from discarded treated and untreated wood products, off-cuts, shavings, chip and dust from wood processing and virgin wood mixed in with waste wood (EPA, 2013). The composition of wood varies depending on the source of the timber. It is imperative to encourage the use of wood in a material recovery sense, as currently a significant proportion is used in energy (Dahlbo et al., 2015).

2.7.3.3.1 Current uses

Waste wood has many different uses, including fuel, landscaping, bedding, composite boarding manufacture, landfill cover and composting. However, the use of waste wood as fuel brings environmental concerns, given the likelihood of halogenated organic compounds or heavy metals to be present, following preservation methods (EPA, 2013).

2.7.3.3.2 Potential for use in water treatment

Wood waste, in the form of wood chips, has been successfully used in adsorption of dye from aqueous solutions (Nigam et al., 2000). Sawdust has been successfully used in the same way (Hanafiah et al., 2012). Wood also has good capacities for metal adsorption (Rafatullah et al., 2012). Alternative methods for using wood waste in water treatment would be as a biochar, for nutrient (Wang et al., 2015), perchlorate (Fang et al., 2014), or metal adsorption (Jiang et al., 2015); or as an activated carbon for dye (Ma et al., 2014) and metal adsorption (Lo et al., 2012). Table 2.12 details adsorption studies that have been carried out using relevant contaminants, mainly in the form of biochar adsorption, indicating that there is a possibility of using this material, though further research should be carried out.

It is clear that waste wood does have potential for use in water treatment. However, there will be a lot of variability depending on the original type of wood used. Another issue could be the release of organics into the water. To avoid a release, a pre-treatment could be advised and perhaps the use of a multi-media technology to harness different sorption capacities.

A brief summary of the advantages and disadvantages of each media, along with the raw material availability, is presented in Table 2.13. Where definite amounts are not available, figures for the parent material have been given. This review indicates that there is a large scope for use of media in water treatment, therefore mitigating current environmental issues such as waste disposal and storage, while aiming to improve water treatment services globally. It is important to note that some media can also be successfully regenerated, once the adsorption potential has been reached, meaning that the filter can be used incurring much less cost than a full replacement.

Table 2.12 Previous studies of adsorption using wood waste.

Contaminant	Adsorption Capacity	Comment/Conditions	Isotherm	Reference
Ammonium	5.4 mg g^{-1}	Biochar from maple wood, pH adjusted	Langmuir	Wang et al. (2015b)
	54.8 mg g^{-1}	Biochar from mixed wood, 1400 mg L^{-1} initially	Langmuir	Kizito et al. (2015)
	5.3 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015c)
Nitrate	8.9 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015c)
	43.5 mg g^{-1}	Activated biochar from pine wood	Langmuir	Chintala et al. (2013)
Phosphate	32 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015c)
Copper	2.24 mg g^{-1}	Aspen wood fibers	Langmuir	Huang et al. (2009)
	1.39 mg g^{-1}	Rubber wood shavings	Pseudo-second order	Nordin et al. (2012)
	6.79 mg g^{-1}	Hardwood biochar	Langmuir	Chen et al. (2011)

2.7.4 Post-treatment use of media

It is clear from the review of previous studies that the scope for alternative media use as adsorbents in water treatment is very broad, encompassing many different types of media and contaminants. However, a problem still remains with disposal of the media post-treatment. The recycling of waste does often create larger environmental benefits, particularly than energy recovery methods, but this is not always the case and should be carefully analysed (Dahlbo et al., 2015). Although adsorption can create a purpose for an otherwise discarded material, adsorption is not an infinite solution. To avoid pollution swapping (the production of contaminants that may occur in an effort to reduce a particular contaminant), it is necessary to either regenerate or find a safe disposal mechanism. This will also ensure any contaminants adsorbed onto the media will not pollute land or water.

The use of the media post-treatment depends on the constituents of the water it was used to treat. If the raw water contained heavy metals, it would be necessary to ensure that metals would not pose a threat to the next purpose of the media. In the case of adsorption of organic pollutants, successful regeneration and desorption techniques, such as biological degradation, chemical desorption, oxidation, and thermal desorption, may be used to restore the quality of the media (Zhu et al., 2009). Where nutrients are problematic contaminants, land fertilisation may be a potential area of utilisation post-treatment. This would be doubly beneficial as it would improve the land quality and provide a useful purpose for what is otherwise a waste material.

2.7.4.1 Regeneration

It is recognised that there exists a knowledge gap on large scale regeneration of adsorbents, particularly non-carbonaceous adsorbents (Omorogie et al., 2014). Traditional regeneration techniques include thermal, chemical, and bioregeneration. Emerging regeneration techniques include electrochemical, ultrasound, oxidation, and supercritical fluid methods (Duan et al., 2013). Although many of these techniques have proved effective, it is necessary to implement large-scale regeneration of media, for both economic and environmental benefits (Omorogie et al., 2014).

Table 2.13 A brief summary of various media discussed.

Media	Opportunities	Advantages	Disadvantages
Fly ash	17 M t	Nutrient, metal and humic acid removal Disadvantages may be mitigated by pre-treatment	Potential for metal leaching
GGBS	<18 M t used in Europe	Limited research available	Solidification in water Potential for metal leaching
Bayer residue	>2700 M t	Phosphorus and metal removal	Potential for contaminant leaching
Coconut shell	>60 M t of coconut grown per annum	Metal, dye and anion removal	Expensive carbonization and activation processes required
Tea/Coffee wastes	>5 M t of tea produced per annum	Metal and cation removal Dye removal when pre-treated	Expensive pre-treatments may be required
Rice husk	>700 M t	Metal and dye removal	Expensive pre-treatments may be required
Crushed concrete	25% of all C&D waste	Phosphorus and metal removal	Potential for contaminant leaching from concrete constituents
Masonry	30% of all C&D waste	Nutrient, metal and microbiological removal	Variation in raw material
Wood waste	2% of all C&D waste	Nutrient and metal removal	Variation in raw material Expensive pre-treatments may be required

Regeneration of metal oxides, such as fly ash and Bayer residue, has not been extensively studied. The studies which have been carried out, tend to refer to treated media, such as impregnated fly ash (Yang et al., 2016) or activated carbon prepared from fly ash (Aslam et al., 2015). However, it has been found that where these media have been used to adsorb various metals, it can make the media more stable (Jacukowicz-Sobala et al., 2015). It has also been shown that methods such as thermal desorption can be used to restore the media to its previous conditions (Yang et al., 2016). This can result in the media being used for land reclamation, or in construction methods such as those mentioned in the "current uses" sections above. Fly ash, once exhausted by certain adsorbents, can be used as a filler in paper-making with few side-effects (Saakshy et al., 2015). Although similar studies have not been carried out in relation to GGBS, the chemical composition would suggest similar results. The USEPA have developed a number of tests which can be used to investigate the potential leaching and toxicity of spent sorption material and suitability for use on land (Jacukowicz-Sobala et al., 2015).

Regeneration of coconut shell activated carbon is well researched, with up to five adsorption-regeneration cycles being tested. For adsorption of gaseous sulfur, complete regeneration can be achieved using water vapour (Shi et al., 2015). Microwave regeneration was not as effective when used to regenerate from benzene and toluene adsorption, achieving just 50% removal efficiency after five cycles (Mohammed et al., 2015). Thermal regeneration with 0.1M NaOH was very effective for regeneration from Pb removal, with removal efficiencies of over 90% after cycling (Itodo et al., 2014). Other activated carbons have been regenerated successfully by electrical-assisted acid washing (Weng et al., 2014), supercritical carbon dioxide operating conditions (Carmona et al., 2014) and pyrite-activated sodium persulfate oxidation (Liang and Chen, 2010).

Similar to the other agricultural wastes, several regeneration techniques have proved successful for both tea wastes (Fadhil et al., 2012) and coffee wastes (Plaza et al., 2012). These wastes can be used as a source material for activated carbon and so respond well to regeneration. Although regeneration can still mean the pollutant is present, it becomes concentrated, and may be easier to dispose of (Kyzas, 2012), while the material can be returned to its original state. Alternative disposal mechanisms include manufacturing blended fuel briquettes from tea and coffee wastes, due to high calorific values (Nandal et al., 2014).

Bioregeneration has successfully been used for rice husk regeneration (Aktas and Cecen, 2007), as have chemical techniques. Chemically modified rice husk for Hg adsorption was successfully regenerated using 0.1M HCl, only losing 10% adsorption capacity (Song et al., 2016). Regeneration by NaOH has been successfully used for rice husk that has been used for arsenate (Luo et al., 2016) and Pb adsorption (Masoumi et al., 2016). Rice husk ash, a product of the incineration of rice husk, has many uses including catalyst carriers, fillers in cement, fertilisers, and production of gels and polymers (Kumar et al., 2016). This would be a useful post-treatment use of rice husk, provided that the contaminants would be contained and not leached to the environment.

Construction and demolition wastes are not well researched in terms of regeneration processes. Where an activated carbon was produced from wood waste, regeneration would be most likely successful. For concrete and masonry, depending on the source water contaminants, there is potential for use as aggregate or fill in the construction industry. However, extensive testing would be necessary to ensure no damage would occur to the environment. Regeneration techniques are clearly successful when considering agricultural waste products. However, when considering industrial or C&D waste, regeneration is not well researched and may not be as successful.

2.7.4.2 Economic and environmental outlook

When considering regeneration techniques, it is important to recognise the economic and environmental costs of regeneration techniques. Where acid regeneration is used, it can be corrosive and difficult to store. Thermal regeneration techniques can require complex instrumentation and large capital expenditure (Aslam et al., 2015). Regeneration can also produce a high concentrate waste stream, which can bring about further issues of waste management (Igunnu and Chen, 2012). Therefore, it is important to analyse filter media holistically, including potential regeneration and costs, to ensure the most sustainable approach is taken.

It is important in this instance, to ensure that the use of the media in water treatment does not devalue the original product. Desorption techniques may be used to restore the product, although may create another issue regarding waste creation as the pollutant will now be concentrated. In some instances, the original product may become more stable, and may still be useful for its current uses. In other cases, for example when used for nutrient capture, the media may then be used as a fertiliser. The ultimate use of the media will depend on the raw water being treated, and how that impacts on the media. However, it is clear that this is an area worth researching with clear gaps in knowledge evident.

The notion of a 'circular economy' requires products, materials, and services to be maintained within the economy for as long as possible, and is a major step towards a zero-waste society (European Commission, 2015d). Although the utilisation of these products does not result in an infinitely long term solution, and further disposal mechanisms must be investigated, it does result in a more sustainable use for waste products. Evidently, in certain circumstances, regeneration of adsorption material is a possibility, although there is a large scope for further research in this area. The European Commission have identified waste management as a critical aspect of the circular economy, and recognises the need to involve public authorities, businesses, and investors (European Commission, 2015d). In order to fully engage these entities, it is important to have a viable solution to a difficult-to-solve problem. If the media can be sufficiently exploited to treat water in a sustainable fashion, those entities will have an invested interest in aiming to develop the technologies to their full potential. There is a recognised lack of studies considering industrial symbiosis, logistics and large-scale operation (Mirabella et al., 2014), and it is clear from the review that there is a large scope for development in this area. In this instance, the combination of research and industry, along with public authorities, could work together to fully develop a sustainable method of removing contaminants from water, while avoiding the creation of waste, and therefore leading towards a circular economy.

2.8 Justification for methodology chosen

Following a comprehensive literature review, it is clear that there is a requirement for a sustainable, adaptable technology for effective water treatment. A sensible approach is to modify traditional treatment methods such as filtration, to optimise its sustainability and adaptability. Another common issue is the accumulation of waste from industry, agriculture, and C&D sectors. Much of this waste is in the form of a material that can either be used in its raw state, or activated, as a filter media. Although there have been many studies conducted on the adsorptive potential of alternative media, few media have been examined for the removal of contaminants from abstraction water for WTPs at both laboratory-scale and pilot-scale.

For the current study, it was decided to approach the design by first selecting a variety of media. Some of those chosen included known adsorbents, such as GAC and zeolite. Industrial and C&D waste materials were chosen due to local availability. Bayer residue is a waste product of Rusal Aughinish Alumina, and is stored in lagoons in Co. Limerick, in mid-west Ireland. Fly ash and bottom ash are produced by ESB Ireland (the Electricity supply board), in the coal-fired power plant located in Moneypoint, Co. Clare, in south-west Ireland. Pyritic fill was removed from the foundations of houses in Co. Dublin, where it was expanding and causing cracking of walls.

The contaminants chosen included organic C, NO_3^--N, NH_4^+-N, PO_4^{3-}-P, Cu and Al, based on listed exceedances by the EPA in Ireland (EPA, 2012a). A wide range of contaminants were chosen to gain maximum knowledge of each media's potential for water treatment in relation to these contaminants of particular interest.

Following this, it was decided to examine a selection of the media in laboratory-scale filters, hydraulically loaded with water containing C, NO_3^--N, NH_4^+-N, and Al. The concentrations chosen were based on Irish exceedances reported in recent years, and encompassed metals, nutrients, and NOM. Media placement within the columns was based on adsorption characteristics of the media. Two hydraulic loading regimes were chosen: slow (continuous) loading, as it has proved successful in the past for drinking water treatment, and intermittent loading, a novel loading regime for drinking water treatment. Both regimes use less energy than rapid gravity filters, and may be more suitable for a smaller WTP. The filters were operated for 90 days, at which point clogging was observed across all filters.

Given that clogging had occurred, a redesign was required before pilot-scale construction began. Pyritic fill had not been included in the laboratory-scale filters, and was introduced when fly ash and zeolite had been deemed unsuitable. Two novel designs were examined at pilot-scale. SUVA and DOC analyses were chosen as the primary indicators of performance, given success in previous studies and also its accessibility by using common laboratory instruments. SUVA has been shown to be more accurate than organic carbon analysis alone. Two loading regimes were investigated and the filters were operated for 240 days.

2.9 Summary

In this chapter, the background of the research was presented. An introduction to global water sources was presented, alongside legislation and regulations pertaining to Ireland, the European Union and the United States of America.

Common contaminants were identified, and advantages and disadvantages of alternative treatment technologies were briefly discussed. This was followed by an in-depth analysis of waste materials with adsorption potential for water treatment, their current uses, and potential regeneration or final uses. Some of the key gaps in knowledge identified were:

- Emerging contaminants such as DBPs are causing problems for authorities, but traditional contaminants also remain to be an issue. There is a lack of simple solutions to tackle both types of contaminants.
- Many of the current state-of-the-art technologies for DBP removal focus on the DBPs post-formation. There is a need to focus on the precursors to limit formation in the distribution network.
- Many filtration systems continue to use sand, where other locally sourced media may be available and potentially more successful.
- There has been little research to date on clogging of drinking water filters or the clogging of potential adsorption media.
- There is a need for industries to be more cautious with material disposal and use, water treatment could bridge this gap by allowing for the use of industrial waste materials as filter media.

- Although adsorption is a common method of analysing potential for use, there is a lack of follow-through in testing these media at laboratory-scale and pilot-scale, which would result in a more accurate forecast of the reliability of the filter.
- Adsorption could be used to design bespoke filters, by targeting the present contaminants with specific layers within the filter.

In the following chapter, the bench-scale adsorption experiment is described, with detailed analysis including effects of time, temperature and pH.

3 Use of industrial waste-products and natural media to adsorb nutrients, metals and organic carbon from drinking water

3.1 Overview

The aim of this chapter was to quantify the efficacy of various novel media, which could potentially be used in water filtration systems, operated under different temperatures and pH, to remove nutrients (NO_3^--N, PO_4^{3-}-P, NH_4^+-N), DOC (as a precursor to DBPs) and metals (Al, Cu) from water. The media investigated were coarse sand (the study control), zeolite, GAC, pyritic fill, Bayer residue, bottom ash, fly ash, and GBS.

The study has been published in Science of the Total Environment (Grace, M.A., Healy, M.G., Clifford, E., 2015. Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water. Science of the Total Environment 518-519: 491–497. doi:10.1016/j.scitotenv.2015.02.075).

3.2 Introduction

Conventional WTPs comprise screening, coagulation/flocculation, sedimentation, filtration and disinfection processes (EPA, 1995). A key aspect of this design is contaminant removal, which may encompass physical, biological and chemical processes. The design of a filter focuses predominantly on physical and chemical removal techniques, namely, straining and adsorption.

Adsorption is a surface phenomenon, and can be defined as the process whereby substances in solution (adsorbate) are accumulated on a suitable interface (adsorbant) (Metcalf and Eddy, 2003). Temperature, kinetics, pH, and the nature of the adsorbate and adsorbant can affect adsorption (Ali and Gupta, 2006). Adsorption isotherms, such as those developed by Langmuir, Freundlich, Elovich and others (Ali and Gupta 2006; Foo and Hameed 2010), may be used to model adsorption.

This chapter optimises the design of filters by examining the efficacy of seven media (fly ash, bottom ash, Bayer residue, GBS, pyritic fill, GAC and zeolite), to adsorb NO_3^--N, NH_4^+-N, DOC, Al, Cu and P. Each medium and contaminant was modelled to a

Langmuir, Freundlich or Tempkin adsorption isotherm, and the impact of pH and temperature (ranging from 10°C to 29°C) on their performance was quantified.

This chapter aims to classify media in terms of adsorption potential for use in drinking water treatment processes, by determining the most effective media across a wide range of contaminants.

3.3 Materials and Methods

3.3.1 Media characterisation

The composition of the media, as well as their effective sizes (d_{10}), as determined using BS 1377-2:1990 (BSI 1990) is shown in Table 3.1. The sources of the media are given in the footnote below the table. Coarse sand was sourced from a quarry specialising in water filter media. Zeolite contains naturally occurring clinoptilolite, which is a known ion exchanger (Hendricks, 2011). Granular activated carbon is formed by the pyrolysis of a carbonaceous substance, followed by a controlled oxidation stage to activate the carbon (Cooney, 1999). Bayer residue is a waste product of the Al manufacturing process and is stored in large lagoons, resulting in storage and potential environmental problems (Brunori et al., 2005). Bottom ash and fly ash are waste products of incineration. Pyritic fill is a waste product of the construction industry. Granular blast furnace slag is a waste product of the steel manufacturing industry, and is mainly used as a cement substitute in a reduced carbon footprint concrete mix. The media characterisation in Table 3.1 was carried out by Brookside Laboratories Inc, USA. Metals were analysed using Mehlich-3 soil test extractant (Mehlich, 1984), and the total exchange capacity was analysed using TEC by summation (Ross, 1995).

3.3.2 Adsorption isotherms

One gram of each media, with particle sizes as tabulated in Table 3.1, was placed in separate 50 mL capacity containers (at n=3), and was overlain by 25 mL of deionised water made up to concentrations of 0, 5, 10, 20, 30, 50, 60 and 100 mg L^{-1} of either NO_3^--N, NH_4^+-N, PO_4^{3-}-P, or TOC; 0, 10, 20, 30, 100, 500 and 1000 mg L^{-1} of Cu; and 0, 0.3, 0.4, 0.5, 0.8 and 1 mg L^{-1} of Al. Nitrate, NH_4^+-N and PO_4^{3-}-P were made up using KNO_3, NH_4Cl and K_2PO_4 reagent-grade powders, respectively (APHA, 1995).

Table 3.1 Physical and chemical characterisation of media.

Media	**Coarse Sand**	**Zeolite**	**Pyritic Fill**	**Bayer Residue**	**Fly ash**	**GBS**	**Bottom Ash**	**GAC**
Chemical (%)								
Al (%)							0.42	
Ca (%)	-	-	-	-	-	-	-	9.85
Fe (%)							1.6	
K (%)	4.27	-	0.58	0.45	0.12	0.75	0.04	77.73
Al (mg kg^{-1})	87	263	163	8388	1223	2083		49
Cd (mg kg^{-1})		-	-	-	-	-	0.28	-
Co (mg kg^{-1})		-	-	-	-	-	0.43	-
Cr (mg kg^{-1})		-	-	-	-	-	14.3	-
Cu (mg kg^{-1})	4.65	1.18	9.29	4.17	4.35	0.25	8.1	0.55
Fe (mg kg^{-1})	39	23	687	59	189	90		14
Mg (mg kg^{-1})	22.57	12.8	6.04	0.18	13.59	20.38	2120	3.78
Mn (mg kg^{-1})	3.00	15.00	64.00	1.00	22.0	95.	92	2.00
Mo (mg kg^{-1})		-	-	-	-	-	0.63	-
Na (mg kg^{-1})	15.00	655.0	48.00	18280	175.	174	859	219.
Ni (mg kg^{-1})		-	-	-	-	-	9.9	-
P (mg kg^{-1})	4	3	3	10	1044	4	171	87
Pb (mg kg^{-1})		-	-	-	-	-	3.9	-
V (mg kg^{-1})		-	-	-	-	-	13.7	-
Zn (mg kg^{-1})	1.37	1.64	13.80	0.4	4.43	0.49	19.7	0.4
Iodine No (mg gm^{-1})		-	-	-	-	-	-	1100
Moisture (%)		-	-	-	-	-	-	5
Ash (%)		-	-	-	-	-	-	4
Effective size (mm)	1.31	1.02	0.34	0.06	0.06	0.36	0.64	0.58
Total exchange capacity (meq 100 g^{-1})	0.96	22.13	80.76	108.8	54.19	80.42		12.99

Dissolved organic carbon was made up using laboratory-grade humic acid, adapted from the method described in Abdul et al. (1990). Solutions of Cu and Al were sourced from Hach Lange (Germany). Each sample mixture was placed on a reciprocal shaker for 24 h at 250 rpm. At t=24 h, the supernatant water in each container was filtered through 0.45 µm filters and analysed for the nutrient or metal of interest. The initial and final concentrations of NO_3^--N, NH_4^+-N, PO_4^{3-}-P and Al were analysed using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Dissolved organic carbon was analysed using a TOC analyser (BioTector Analytical Systems Ltd) and Cu was analysed using a spectrophotometer (Hach Lange, Germany). To ascertain whether any of the media released metals, the 0 mg L^{-1} samples were split and sent for metal analysis by ICP-MS. The suite of metals included Al, barium, Ca, Cd, Mg, potassium (K), Cr, Fe, Hg, Mn, Ni, Pb, boron, Cu and sodium.

The data were modelled either by Langmuir, Freundlich or Temkin adsorption isotherms. The Langmuir isotherm assumes monolayer adsorption sites with equal energies, and that adsorption is reversible (Metcalf and Eddy, 2003). The form of the Langmuir isotherm is (McBride, 2000):

$$q_i = q_{max}\left(\frac{k_A C_e}{1+k_A C_e}\right) \qquad \textit{Eqn 1}$$

where q_i is the quantity of contaminant adsorbed per gram of media (g g^{-1}), C_e is the equilibrium contaminant concentration in the pore water (g m^{-3}), k_A (m^3 g^{-1}) is a measure of the affinity of the contaminant for the media, and q_{MAX} (g g^{-1}) is the maximum amount of contaminant that can be adsorbed onto the media.

Unlike the Langmuir isotherm, the Freundlich isotherm assumes a heterogeneous surface and a non-uniform distribution of heat of adsorption (Widiastuti et al., 2011):

$$q = K_F C_e^{1/n} \qquad \textit{Eqn 2}$$

where K_F is the Freundlich capacity factor, $1/n$ is the intensity parameter, and C_e and q are as in Eqn 1.

The Temkin isotherm is slightly different from the other adsorption isotherms in that it considers the adsorbate-adsorbate interactions, and assumes that due to these, the heat of adsorption of molecules decreases linearly with coverage (Vijayaraghavan et al., 2006):

$$q_e = B_1 ln(K_t C_e) \qquad \textit{Eqn 3}$$

where C_e and q are as above, K_t is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, and the constant B_1 is related to the heat of adsorption. B_1 is defined as $\frac{RT}{b}$, where R is the gas constant (0.008134 kJ (mol

K^{-1}), T is the absolute temperature (degrees K) and b is the constant related to the heat of sorption (J mol^{-1}).

3.3.3 Kinetics of adsorption

The rate at which adsorption occurred was measured using kinetic studies. In these studies, the samples were prepared as in Section 3.3.2, placed on the reciprocating shaker for 24 h, and 2.5 mL samples were taken at t=1, 4, 8, 12 and 24 h. Analysis of the data accounted for the volume withdrawn at each sampling interval, and the mass adsorbed over time was calculated.

3.3.4 Effect of pH on adsorption

The effect of pH on adsorption was examined by adjusting the pH of each sample before shaking on the reciprocal shaker. The pH was adjusted to approximately 4 by the addition of 1 mol L^{-1} HCl to the supernatant-spiked water. The unadjusted pH was between 6 and 11. The samples were then shaken for 24 h at room temperature and the appropriate adsorption isotherm was fitted to the data. The pH-adjusted samples were analysed with the Langmuir or Freundlich isotherms, depending on best fit.

3.3.5 Effect of temperature on adsorption

To study the effect of temperature on adsorption, experiments similar to those above were carried out at three temperatures, 10°C, 19°C, and 29°C. The samples were prepared as in Section 3.3.2 and placed on the reciprocating shaker in stabilized temperature conditions for 24 h. The data were fitted to an appropriate isotherm model and using the Langmuir constant (k_A), free energy change, or adsorption energy, was calculated using the thermodynamic formula (Khan and Singh, 1987; Liu, 2009; Widiastuti et al., 2011):

$$\Delta G^{\circ} = -RTlnK \qquad Eqn\ 4$$

where ΔG° is the adsorption energy (kJ mol^{-1}), R is the ideal gas constant (0.008314 kJ mol^{-1} K^{-1}), T is the temperature (degrees Kelvin), and K is the Langmuir equilibrium constant. It is known that the equilibrium constant of adsorption depends on the isotherm model selected, and constants determined by different methods are not comparable (Liu, 2009). As *K* is the Langmuir constant, only data fitting to the Langmuir isotherm were compared.

3.4 Results and Discussion

3.4.1 Adsorption isotherms

Many of the industrial by-products examined had good potential as adsorption media for nutrients and metals (Table 3.2). Fly ash performed well, particularly with regard to DOC, PO_4^{3-}-P, NH_4^+-N and Cu. The presence of surface oxides on fly ash may adsorb organic compounds, such as DOC (Cooney 1999). Fly ash also had a high total exchange capacity, which promotes NH_4^+-N and metal adsorption (Rengaraj et al. 2004; Widiastuti et al. 2011). Phosphorus adsorption is likely to occur with the presence of binding elements such as Ca, Fe and Al on fly ash (Table 3.1). These results are consistent with previous work (Ali and Gupta 2006; Li et al. 2006). However, fly ash desorbed Al, resulting in a concentration of 0.255 Al mg L^{-1} after shaking with deionised water for 24 h, in the 0 mg L^{-1} sample. Adsorption capacities of Cu on fly ash of up to 18.8 mg g^{-1} have also been observed (Visa, 2012). Raw data and adsorption isotherm plots can be found in Appendix B.

Table 3.2 Adsorption constants for Langmuir and Freundlich adsorption isotherms at 19°C.

Contaminant	**Media**	**Isotherm**	**R^2**	**Q_{max} (μg g^{-1})**	**1/n**	**K (μg^{1-N} g^{-1} ml^N)**	**B_1 (J mol^{-1})**	**K_t (L mol^{-1})**
DOC	Coarse Sand	N/A (Desorption)						
	Zeolite	Langmuir	0.71	37				
	Fly Ash	Freundlich	0.73		1.17	0.262		
	Bottom Ash	Langmuir	0.54	48				
	GAC	Langmuir	0.42	327				
	GBS	Freundlich	0.86		1.56	0.101		
	Pyritic Fill	Freundlich	0.85		1.66	0.152		
	Bayer Residue	Freundlich	0.83		0.68	0.019		
Nitrate	Coarse Sand	Freundlich	0.86		0.76	0.002		
	Zeolite	N/A (Desorption)						
	Fly Ash	N/A (Desorption)						
	Bottom Ash	N/A (Desorption)						

	GAC	Tempkin	0.68				0.26	0.31
	GBS	Langmuir	0.66	45				
	Pyritic Fill	Freundlich	0.9		2.57	0.009		
	Bayer Residue	Freundlich	0.71		1.95	0.00003		
Ammonium	Coarse Sand	Langmuir	0.83	44				
	Zeolite	Langmuir	0.81	1044				
	Fly Ash	Freundlich	0.82		0.79	0.0129		
	Bottom Ash	Freundlich	0.92		0.49	0.0037		
	GAC	Freundlich	0.86		1.25	0.0003		
	GBS	Freundlich	0.81		1.00	0.0029		
	Pyritic Fill	Freundlich	0.87		0.86	0.0040		
	Bayer Residue	Langmuir	0.83	57				
Aluminium	Coarse Sand	Langmuir	0.85	0.66				
	Zeolite	Langmuir	0.74	1.20				
	Fly Ash	N/A (Desorption)						
	Bottom Ash	Langmuir	0.81	0.18				
	GAC	Langmuir	0.63	3.68				
	GBS	N/A (Desorption)						
	Pyritic Fill	Langmuir	0.76	1.4				
	Bayer Residue	N/A (Desorption)						
Phosphate	Coarse Sand	Freundlich	0.51		0.34	0.0118		
	Zeolite	Langmuir	0.68	13				
	Fly Ash	Langmuir	0.99	6480				
	Bottom Ash	Freundlich	0.74		0.54	0.0038		
	GAC	Langmuir	0.82	41				
	GBS	Langmuir	0.99	3610				
	Pyritic Fill	Langmuir	0.97	878				
	Bayer Residue	Langmuir	0.97	204				
Copper	Coarse Sand	Langmuir	0.88	20.6				
	Zeolite	Langmuir	0.9	771				
	Fly Ash	Langmuir	0.89	1381.6				
	Bottom Ash	Langmuir	0.92	79.3				
	GAC	Langmuir	0.87	22.8				
	GBS	Langmuir	0.83	2259.9				
	Pyritic Fill	Langmuir	0.91	1357.5				
	Bayer Residue	Langmuir	0.79	1201.7				

Bayer residue was effective in terms of nutrient and Cu adsorption. This was expected due to the cation exchange and metals present (Table 3.1). These results were consistent with Lopez et al. (1998), who measured Cu adsorption of the same order as the current study. However, desorption of Al and Fe were observed in the current study, with concentrations of Al and Fe in the supernatant water after 24 h of shaking of 4 mg Al L^{-1} and 2.3 mg Fe L^{-1}, respectively.

Granular blast furnace slag is not currently studied in terms of nutrient or metal adsorption, as its sole use is in cement production. However, based on the analysis in Table 3.1, the high CEC and the metals present would indicate that this medium does have adsorption potential. However, its tendency to solidify when saturated with water may be a limiting factor in its use for water treatment. It was also observed that GBS desorbed Al after shaking for 24 h, and the supernatent had a final concentration of 3.6 mg L^{-1}.

Bottom ash did not appear to be as effective as the other industrial by-products in nutrient or metal adsorption. However, pyritic fill performed well across all six contaminants (Table 3.2), but did not rank highest in the removal of any contaminant. The composition of pyritic fill may be predominantly mudstone or sandstone, depending on the location in which it is quarried, so its adsorption capacity is potentially variable. However, mineral pyrite has been recognised as an adsorbant, particularly regarding P, and adsorption capacities of up to1.6 mg PO_4^{3-}-P g^{-1} have been measured (Chen et al., 2014). It is known that P binding occurs in the presence of Ca, Al and Fe oxides (Egemose et al., 2012), which explains the results of the pyritic fill adsorption studies.

The performance of zeolite in NH_4^+-N removal, at 1.04 mg g^{-1}, was lower than that observed with Australian zeolite (Widiastuti et al., 2011). This could be attributed to the difference in location of the mined zeolite. Ortho-phosphate adsorption was poor and shaking with NO_3^--N resulted in desorption, meaning anion adsorption was poor. However, metal adsorption by zeolite was very effective, in terms of both Cu and Al, and was due to the ion exchanging capacity of zeolite (Hendricks, 2011).

Granular activated carbon adsorbed all three nutrients, but did not perform as well as some industrial waste-products examined in this chapter. This was due to the relative lack of metal oxides available for nutrient interaction. Adsorption of DOC was particularly strong, and it performed well for both metals analysed. Coarse sand was more effective than GAC in nutrient adsorption, and while it had good metal removal, it was not as effective as GAC. Aside from the metal desorption stated above, the ICP-MS analysis did not identify desorption of any other metals.

3.4.2 Kinetics of adsorption

Figure 3.1 shows the kinetic results for the contaminants and media tested. This was carried out at 19°C. All the media adsorbed 60% of the NH_4^+-N within 8 h of contact. Nitrate, Al and P adsorption followed the same trend. Copper adsorption was slightly different than other contaminants, in that for zeolite, pyritic fill, GBS, Bayer residue and fly ash, almost all adsorption had taken place after 4 h. Dissolved organic carbon adsorption by fly ash occurred almost immediately, with 96% of adsorption occurring within 1 h. There was a decrease in the rate of adsorption for all media after 8 h. This was most likely due to a combination of adsorption sites becoming unavailable or contaminant concentration being too low. This was to be expected, as initially, the concentration of the adsorbate is high, and all sites are vacant (Widiastuti et al., 2011)

3.4.3 Effect of pH on adsorption

Table 3.3 shows the effect reducing pH, to approximately 4, had on the adsorption of each contaminant for each media. This was carried out at 19°C. For DOC adsorption, bottom ash (without pH modification) was modelled by Langmuir isotherm. However, the data were modelled to Freundlich when the pH was adjusted. This was based on the fit of the regression coefficient. Coarse sand desorbed DOC at unadjusted pH, but some adsorption activity was observed when the pH was adjusted to 4. For the other media (zeolite, fly ash, GAC, GBS, pyritic fill and Bayer residue), pH adjustment allowed for increased adsorption of DOC. This was to be expected as the DOC comprised mainly humic acid, and acidic species are known to adsorb more effectively at lower pH (Cooney, 1999). However, the results indicate that the benefits of adjusting the pH would likely not be a cost-effective intervention in improving adsorption kinetics.

Nitrate did not model well to any of the above isotherms following pH adjustment. Where modelling was successful, the differences between the unadjusted and adjusted K values from the Freundlich isotherm were small.

In general, NH_4^+-N adsorption did not improve with pH adjustment, and fine sand did not adsorb NH_4^+-N when the pH of the solution was adjusted. Zeolite modelled well to Langmuir isotherm following pH adjustment, and demonstrated improved adsorption characteristics, reflecting observations in literature (Widiastuti et al., 2011).

pH adjustment had a tendency to improve Al adsorption except in the case of GAC, where the adsorption capacity was halved with pH adjustment. It was noted that pH adjustment allowed Bayer residue to slightly adsorb Al (1 µg g^{-1}) - Al desorbed at an unadjusted pH. pH adjustment did not improve PO_4^{3-}-P removal. Previous studies have noted a positive relationship between pH and retention capacity for P with rates of adsorption increasing with pH (Egemose et al., 2012). Copper adsorption proved to be more effective at a unadjusted pH, reflecting other studies, where it has been found that adsorption can increase as much as 85% when the pH is increased from 2.5 to 8 (Chen et al., 1996).

3.4.4 Effect of temperature on adsorption

Table 3.4 summarises the results of the thermodynamic study. The data analyses were limited due to the use of the Langmuir adsorption isotherm to calculate the equilibrium constant used in Eqn 4. Therefore, data not modelled to Langmuir across more than one temperature range were excluded from the table for clarity. The negative values of the adsorption energy ($\Delta G°$) indicate that the adsorption process was of a spontaneous nature, and heat energy was released, for each set of reactions modelled (Widiastuti et al., 2011). Adsorption by coarse sand is more energetically favourable at lower temperatures for both NH_4^+-N and Cu, as indicated by decreasing values at lower temperatures.

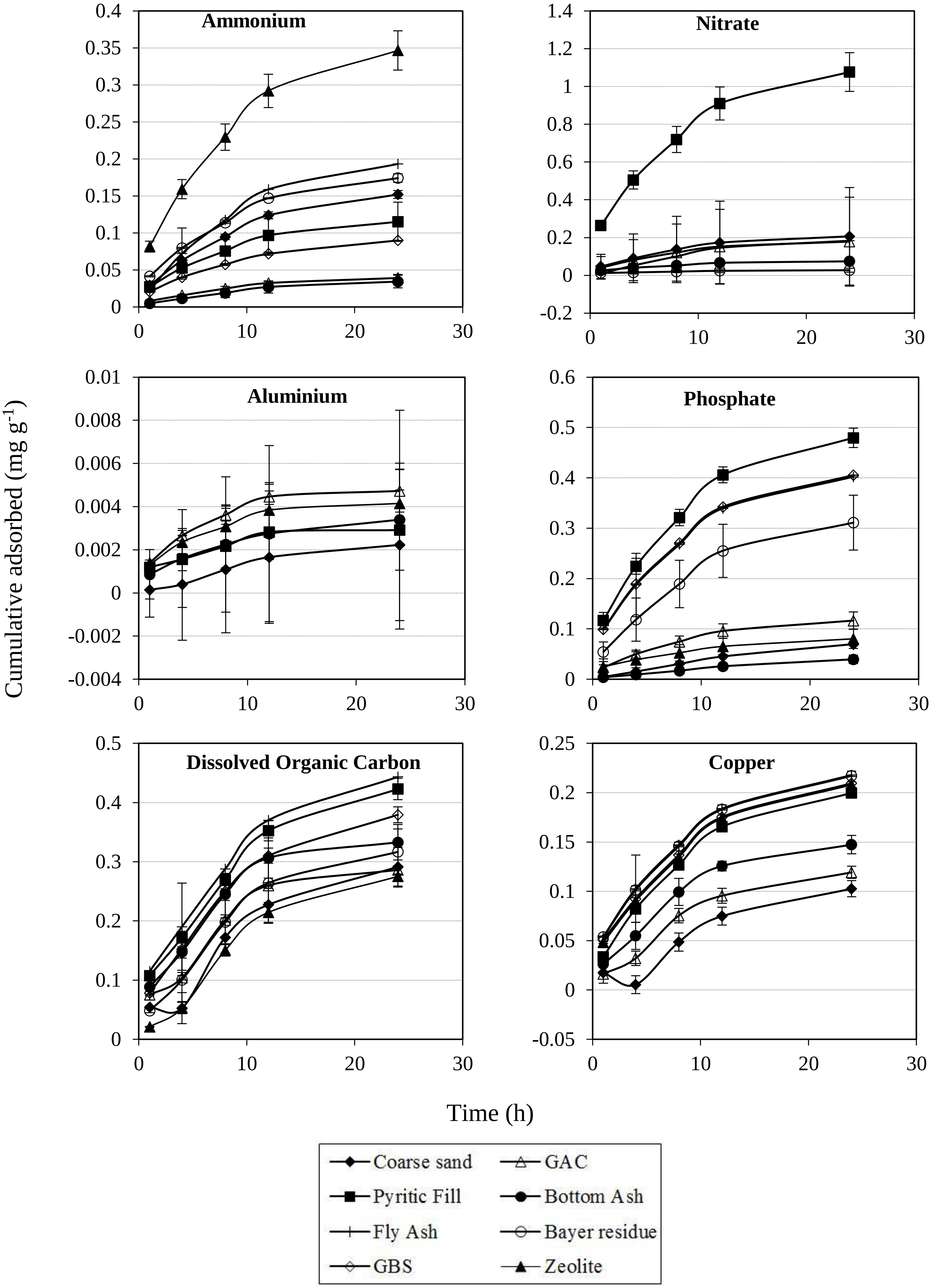

Figure 3.1 Kinetic results over a 24 h period at 19°C.

Adsorption by zeolite was more energetically favourable with increasing temperature for PO_4^{3-}-P, similar to earlier studies investigating zeolite adsorption of nutrients (Widiastuti et al., 2011). It has been noted previously that Cu adsorption is not radically affected by temperature (Gündoğan et al., 2004). However, the results of the current study indicate that Cu adsorption is more favourable at a lower temperature – a positive result for a filtration unit that would most likely be located outdoors. Adsorption by GAC tended to be more energetically favourable at lower temperatures (Cooney, 1999). For pyritic fill, the lower temperatures were also more effective for Al and Cu adsorption.

3.4.5 Impact of adsorption isotherm studies on filter design

Based on the adsorption isotherms developed in this chapter, media may be used in filters to target specific problematic contaminants that may be present in abstraction water. These media could potentially be layered to create an effective, sustainable and multifunctional treatment system, using alternative media, without, as demonstrated in this chapter, the need for adjustment of the pH of the water prior to filtration. A layered configuration would also allow the utilisation of adsorption properties from each of the media, while having the ability to control any potential metal leaching. The kinetics study indicates that as long as the average hydraulic retention time within a filter exceeds 8 h, effective water treatment will occur.

Some of the media investigated currently poses problems with disposal and/or storage. The potential use of these media in the water sector may result in a more sustainable option for what are otherwise considered to be waste materials. The wide variety of materials explored in this chapter could enable designers use locally sourced material depending on the availability in the area.

Table 3.3 Isotherm constant comparisons for unadjusted isotherm tests (pH 6-11) and pH adjusted (pH 3.5-4).

Contaminant	**Media**	**Langmuir**		**Freundlich**	
		Q_{max} (µg g^{-1}) adjusted	**Q_{max} (µg g^{-1}) unadjusted**	**K adjusted**	**K unadjusted**
DOC	Zeolite	0.141	0.037		
	Fly Ash			2.9	0.26
	GAC	0.298	0.327		
	GBS			0.075	0.101
	Pyritic Fill			0.178	0.152
	Bayer Residue			0.132	0.019
Nitrate	Pyritic Fill			0.094	0.009
	Bayer Residue			0.032	$3.41*10^{-5}$
Ammonium	Sand	0.054	0.044		
	Fly Ash	0.0002	0.0129		
	GBS	0.0003	0.0029		
	Pyritic Fill	0.0003	0.004		
Aluminium	Sand	0.0031	0.0006		
	Zeolite	0.0025	0.0012		
	Bottom Ash	0.0010	0.0001		
	GAC	0.0018	0.0036		
	Pyritic Fill	0.0013	0.0014		
Phosphate	Zeolite	0.05	0.01		
	GAC	0.04	0.04		
	GBS	0.21	3.61		
	Bayer Residue	0.17	0.20		
Copper	Sand	0.020	0.020		
	Zeolite	0.020	0.771		
	Bottom Ash	0.010	0.079		
	GAC	0.019	0.022		

Table 3.4 Thermodynamic data analysis at 10°C, 19°C and 29°C.

Media	Contaminant	ΔG (kJ mol^{-1}) @ 10°C	ΔG (kJ mol^{-1}) @ 19°C	ΔG (kJ mol^{-1}) @ 29°C
Coarse Sand	Ammonium	-36.00	-21.78	
	Copper	-37.04	-32.54	
Zeolite	Phosphate	-23.59	-25.94	
	Copper	-33.72	-27.12	
Fly Ash	Copper	-35.41	-18.76	
GAC	Aluminium	-29.69	-30.82	-30.77
	Phosphate	-32.32	-21.71	-26.18
	Copper	-33.11	-18.79	
Pyritic Fill	Aluminium		-36.62	-41.67
	Phosphate	-36.00	-15.31	
	Copper	-33.44	-18.66	-39.45
Bayer Residue	Ammonium	-17.87	-23.34	-11.75
	Phosphate	-22.65	-17.94	-20.88
	Copper		-18.15	-29.01

3.5 Conclusions

- Fly ash and Bayer residue have good adsorption potential for DOC, nutrients and Cu.
- Granular blast furnace slag and pyritic fill have good adsorption potential for DOC, nutrients and metals (which has been unreported to date). Granular activated carbon and zeolite, known ion exchangers and adsorptive media, were successful in the adsorption of each contaminant investigated in this study.
- Improved adsorption occurs at lower pH for DOC. However, for other water parameters, depending on the media, pH adjustment is not necessary for optimal adsorption. In this study, there was no instance in which pH adjustment was necessary for adsorption; therefore adjusting pH is unlikely to be a cost-

effective intervention to improve adsorption kinetics. Optimal adsorption of Cu and PO_4^{3-}-P occurred without modifying the pH.

- Kinetic adsorption studies showed that at least 60% of adsorption (where adsorption occurred) had taken place after 8 h. This may be useful in designing a filter using these media, as the retention time can be adjusted to achieve the required adsorption.

3.6 Summary

This chapter has determined the media with most adsorption potential for treating a variety of drinking water contaminants. Chapter 4 details a laboratory-based filter experiment designed to investigate how these media will perform in conjunction with each other, under a simulated water treatment scenario. It also examines the potential for clogging within the filter.

4 Performance and surface clogging in intermittently loaded and slow filters containing novel media

4.1 Overview

The aim of this chapter was to test alternative media, in terms of performance and clogging mechanisms, and compare these to sand filters. The filters were operated under two different loading regimes (continuous and intermittently loaded), and comprised stratified layers comprising combinations of Bayer residue, zeolite, fly ash, granular activated carbon, or sand, dosed with a variety of contaminants (DOC, Al, NH_4^+-N, and NO_3^--N).

This study has been published in the Journal of Environmental Management (Grace, M.A, Healy, M.G., Clifford, E., 2016. Performance and surface clogging in intermittently loaded and slow sand filters containing novel media. Journal of Environmental Management 180: 102-110. doi:10.1016/j.envman.2016.05.018).

4.2 Introduction

Sand filters are commonly used in water treatment to remove contaminants by physical, chemical and biological mechanisms (EPA, 1995), but they may not be effective in the removal of specific contaminants, such as ECs, or DBPs, such as DOC (Chuang et al., 2011; EPA, 2015a; Gang et al., 2003). Consequently, there has been much research into the use of alternative media, particularly industrial by-products and waste products, or coated media, for use in filters for the treatment of targeted contaminants (Bhatnagar and Sillanpää, 2010; Fu and Wang, 2011; Rahman et al., 2013). Although these media have been examined extensively at bench-scale level, their efficacy has been infrequently examined in laboratory, pilot or large-scale filters (Bailey et al., 1999; Bhatnagar et al., 2011). This is a major knowledge gap, as a layered configuration in a water filter may allow the utilisation of adsorption properties from each of the media, and may have the ability to control any potential metal leaching. Moreover, the use of waste materials in a filtration unit is potentially an effective and sustainable means of water treatment. While the viability of these media for use in filters depends on their efficacy in the removal of contaminants, it equally depends on their capacity to treat water without clogging.

This chapter focuses on the use of two industrial by-products, Bayer residue and fly ash, and a natural medium, zeolite, combined with GAC and sand, in layered filter configurations. Bayer residue is a waste product of the Al production industry, and is often stored in bauxite residue storage areas close to the production site (EAA, 2013). Fly ash, a by-product of incineration, is most commonly used in the manufacture of concrete (Mehta, 2002). Natural zeolites are known adsorbents of contaminants in water and wastewater treatment (Wang and Peng 2010). Each of these has been used previously for adsorption of contaminants, and previously reported maximum adsorption capacities are summarised in Table 4.1.

Table 4.1 Previous studies on the use of media for adsorption.

Media	**Contaminant**	**Adsorption Capacity (mg g^{-1})**	**Comment**	**Reference**
Bayer Residue	Phosphorus	1.1	Initial Concentrations between 0.1 and 1mg L^{-1}	Huang et al. 2008
		345.5	Activated Bayer residue	Li et al. 2006
		0.204	Raw Bayer Residue	Chapter 3
	Nitrate	115.3	Raw Bayer residue	Cengeloglu et al. 2006
		363.2	Activated bayer residue	Cengeloglu et al. 2006
	Al	0.064		Komnitsas et al. 2004
Fly Ash	Phosphorus	75.4	Activated fly ash	Li et al. 2006
		42.6	Raw fly ash	Vohla et al. 2011
		6.5	Raw fly ash	Chapter 3
	Flouride	20.3		Bhatnagar et al. 2011
	Copper	2.36		Gupta and Ali 2000
		1.38	Raw fly ash	Chapter 3
	Zinc	2.54		Gupta and Ali 2000

Zeolites	Ammonium	2.13		Widiastuti et al. 2011
		1.04	Raw zeolite	Chapter 3
	Lead	9.97		Nguyen et al. 2015
	Copper	8.53		Nguyen et al. 2015
		0.78	Raw zeolite	Chapter 3
	Zinc	5.83		Nguyen et al. 2015

While the performance of slow and intermittently loaded filters is important in the selection of suitable filter media, the hydraulic function and permeability are also crucial parameters that need to be considered.

Therefore, the aim of this chapter was to (i) determine the mechanisms of clogging of the filters and (ii) assess the performance of intermittently and constantly loaded filters, each containing the novel filter media and operated for a period of 90 days, in the removal of contaminants (DOC, Al, NH_4^+-N, and NO_3^--N) of water.

4.3 Materials and Methods

4.3.1 Filter construction

Three filter configurations, each replicated at n=3, were examined with constantly loaded and intermittently loaded operational regimes, giving a total of 18 filters (Figure 4.1). The first configuration *('Config 1')* was a three-layer stratified filter (each layer had a depth of 0.33 m) containing (downwards from the filter surface) Bayer residue, zeolite and coarse sand. The second configuration ('*Config 2'*) was a four-layer filter, with equal layers of 0.25 m media, containing (downwards from the filter surface) flyash, GAC, zeolite and coarse sand. The d_{10} of each medium is given in Table 4.2. The third configuration ('Control') was a 1-m deep single layer sand filter with an d_{10} of 0.18 mm and uniformity coefficient of 2.19 (EPA, 1995).

The filter configurations were chosen based on adsorption results obtained in Chapter 3, where NH_4^+-N removal was focused at the surface of the filter, and Al, DOC, and NO_3^--N further down through the media. The configurations took cognisance of the

K_s of each media, which was measured prior to the experiment. Each filter had a free-board depth of 0.5 m above the filter surface. Physical and chemical characteristics of the media are detailed in Table 4.2.

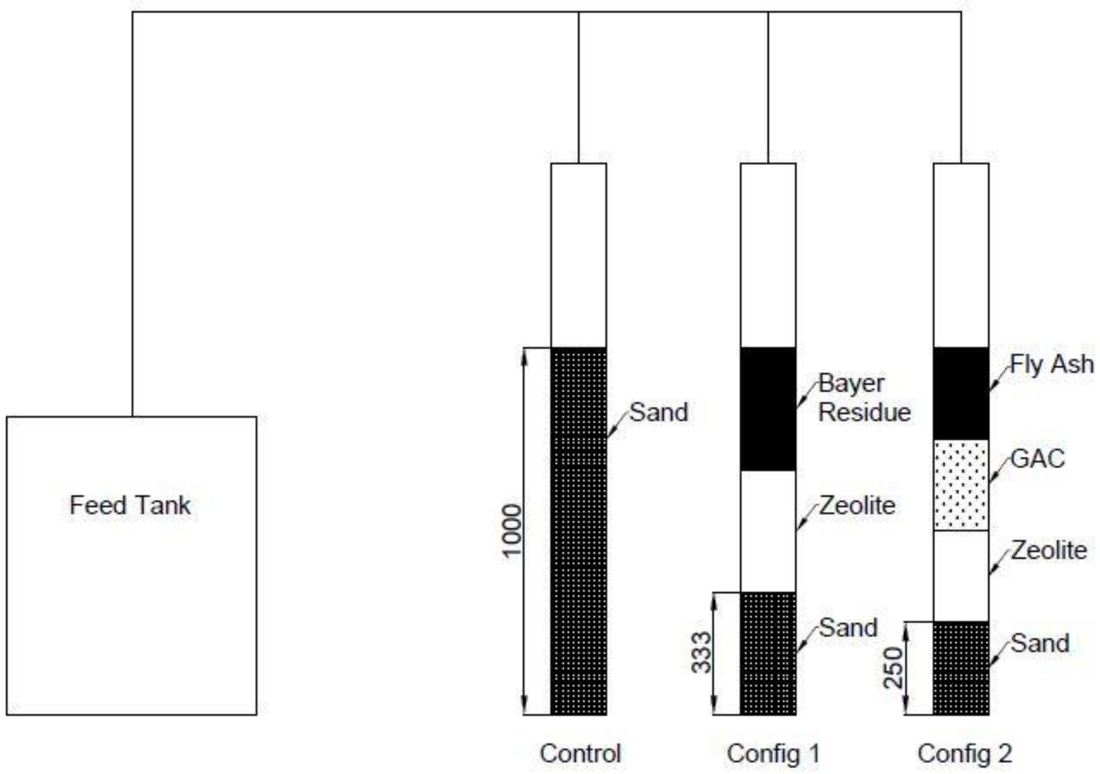

Figure 4.1 Filter configurations.

4.3.2 Filter operation

The intermittently loaded filters were subjected to an initial loading rate (day 1 of experiment) of 0.1 m h^{-1} following the Irish EPA guidelines for slow sand filters (intermittent filters are not currently used for large-scale drinking water treatment) (EPA, 1995). The intermittent filters were dosed for 10 min every 2 h using a peristaltic pump (7528-10, Masterflex L/S Variable-Speed Drive). A head of water of 0.5 m was maintained above the constantly loaded filters.

Table 4.2 Characterisation of media.

Media	Sand[a]	Zeolite[b]	Bayer Residue[c]	Fly ash[d]	GAC[e]
Chemical					
Ca (%)*	-	-	-	-	9.85
K (%)*	-	-	-	-	77.73
Al (mg kg^{-1})*	87	263	8388	1223	49
Cu (mg kg^{-1})*	4.65	1.18	4.17	4.35	0.55
Fe (mg kg^{-1})*	39	23	59	189	14
Mg (mg kg^{-1})*	22.57	12.8	0.18	13.59	3.78
Mn (mg kg^{-1})*	3	15	1	22	2
Na (mg kg^{-1})*	15	655	18280	175	219
P (mg kg^{-1})*	4	3	10	1044	87
Zn (mg kg^{-1})*	1.37	1.64	0.4	4.43	0.4
Total exchange capacity (meq 100 g^{-1})*	0.96	22.13	108.8	0.06	0.58
Organic Matter (%)*	0.1	0.1	5.7	0.22	72.3
Effective size, d_{10} (mm)	1.31	1.02	0.06	0.06	0.58

*Analysis by Brookside Laboratories

The water feed, which was the same for both intermittent and slow loading regimes, comprised tap water dosed with NH_4^+-N (synthesised using laboratory-grade NH_4Cl to a concentration of 5 mg L^{-1}), NO_3^--N (synthesised using laboratory-grade KNO_3 to a concentration of 20 mg L^{-1}), Al (synthesised using laboratory-grade aluminium powder to a concentration of 2 mg L^{-1}), and DOC (synthesised using laboratory-grade humic acid to a concentration of 10 mg L^{-1}). These concentrations were based on maximum exceedances reported by the Irish EPA (Water_Team, 2012). The humic acid was prepared using a method adapted from Abdul et al. (1990), to remove as much of the non-water soluble fraction as possible. This involved mixing the humic acid with deionised water for 25 min and then centrifuging at 1000 RCF for 30 min before filtering through 0.45 µm filter paper. Using humic acid as the DOC source resulted in influent suspended solids (SS) of approximately 200 mg L^{-1}, greater than would be present in a standard groundwater or surface water source, allowing an investigation of clogging occurrence at a high mass loading rate. The two loading regimes were operated in parallel for 90 days, and samples were taken from the influent and the base biweekly.

4.3.3 Statistical analysis

Statistical analysis was carried out using SPSS 22 software (IBM, 2014). The data were checked for normal distribution using the Shapiro-Wilk test. The Kruskal-Wallis test for non-parametric data was used, where the null hypothesis is that the distribution, and the medians of the test fields are the same across groups.

4.3.4 Hydraulic conductivity

The variety of media used in this study meant that both the constant head test (appropriate for media with a K_s of between 10^{-2} and 10^{-5} m s^{-1} (British Standard Institution, 1990a) and the falling head test (appropriate for media with a $K_s \leq 10^{-5}$ m s^{-1}, ASTM 2007) were required to analyse the K_s of the filters. Samples of the virgin media were tested initially for K_s. At the end of the 90 day trial, samples of media were collected at incremental depths to analyse K_s variation with depth. The sample collection in each filter was terminated when the K_s measured at a given depth returned to that of the virgin sample.

For the constant head test, two undisturbed media cores, 0.05 m in diameter, were taken at 0.02 m incremental depths from the filter surface. Water was kept at a constant head over the top of the sample, using an overflow valve to maintain the head of water. The sample was retained in an open-ended vessel to allow the water to flow freely through the sample. The hydraulic gradient was defined as (Rodgers et al., 2004):

$$\frac{dH}{dZ} = 1 + \frac{z}{l} \qquad \textit{Eqn 5}$$

where dH/dZ is the hydraulic gradient, z is the head of water, and l is the height of the sample. The hydraulic gradient was calculated using Darcy's law (Craig, 2004):

$$\frac{Q}{A} = K_s\left(\frac{dH}{dZ}\right) \qquad \textit{Eqn 6}$$

where Q is the volume of water flowing per unit time ($m^3\ s^{-1}$), A is the cross-sectional area (m^2), K_s is the saturated hydraulic conductivity (m s^{-1}), and dH/dZ is the hydraulic gradient (m m^{-1}).

The falling head test was carried out at incremental depths of 0.05 m from the surface (the difference in incremental depths between constant and falling head tests was due to limitations with the laboratory apparatus). The samples were saturated for 24 h before being placed in an overflow vessel, which was clamped in an apparatus that allowed a free flow through the base. The reservoir water was de-aired and the manometer was filled. The test was then carried out by allowing the de-aired water in the manometer to flow through the sample. The time taken for the meniscus to fall between two measurements on the manometer was recorded, and the K_s was calculated using (ASTM, 2007):

$$K_s = 2.3\frac{A_2}{A_1}\frac{L}{T}log\left(\frac{h_1}{h_2}\right) \qquad Eqn\ 7$$

where K_s is the saturated hydraulic conductivity (m s^{-1}), A_2 is the cross-sectional area of the manometer (m^2), A_1 is the cross sectional area of the sample (m^2), L is the height of the sample (m), T is the time taken for the water level to fall (s), h_1 is the height of the water in manometer at t = 0 (m), and h_2 is the height of the water in the manometer at t = T (m).

4.3.5 Chemical composition

Media samples were taken at incremental depths of 0.02 m from the surface. Organic matter analysis was carried out by LOI, as described in Schulte and Hopkins (1996). Metal analysis was carried out using the Mehlich soil extractant method (Mehlich, 1984). Total exchange capacity was carried out using the method described in Ross (1995). Ammonium was analysed using the 1 N KCl method (Dahnke, 1990) and NO_3^--N was analysed using the saturated paste extract method (Gavlak et al., 2003). The media characteristics were determined using BS 1377:2 (British Standard Institution, 1990b).

4.4 Results and Discussion

4.4.1 Filter performance

The performance of each filter configuration is summarised in Table 4.3. Turbidity removal was effective among all configurations, although it did not reduce to below the MAC of 1.0 NTU (SI No 278 of 2007). However, the initial turbidity of the synthetic water was much higher than would be expected in raw water prior to treatment. Dissolved organic carbon removal was most effective in *Config 2*, where higher percentage removals were exhibited in both loading regimes, in comparison to the other configurations. These removals were also higher than those found in conventional WTPs, which can be expected to remove 10-50% of DOC (Kim and Kang, 2008). Effective DOC removal is important, given that DOC is a pre-cursor to many DBPs, and has been identified as a major problem in Irish drinking water treatment plants (EPA, 2015a).

Aluminium removal was greater than 94% in all filters, and there was no significant difference in the performance of *Config 1* and *2* (p=0.114). In all cases, the filters were able to reduce the concentration of Al to below the MAC of 200 µg Al L^{-1} (SI No 278 of 2007). Aluminium removal could attributed to ion exchange, a common practice for Al removal from aqueous solutions (Pesavento et al., 1998). This is particularly likely in the case of Bayer residue which exhibits a high TEC (Table 4.2). Aluminium adsorption may also have been enhanced by molecular interaction with humic acid present in the water feed (Elfarissi et al., 1998; Tombácz et al., 2000).

All filters were capable of NH_4^+-N removal, with significantly higher removal of NH_4^+-N occurring in *Config 1* and *2*, versus the Control, when operated under intermittent loading (p=0.01). The trend of NO_3^--N production, coupled with high NH_4^+-N present in the influent supply suggested that nitrification was occurring within the filters. Raw removal data, along with time series removal plots can be found in Appendix C.

4.4.2 Visual observation

After 90 days of operation, clogging was observed across all filter configurations (Figure 4.2). The clogging layer was most likely caused by a build-up of organic matter, due to the loading of humic acid with high suspended solids, and biomass accumulation (Mauclaire et al., 2004). Despite the filters not being seeded with biomass, the occurrence of nitrification indicates that a biomass layer was present. This was evident in both *Config 1* and *2*, where a gel-like layer was visible on the surface of each column operated in either loading regime. The Control was slightly different, in that a colour change was evident at the uppermost layer, but the larger particle size meant the gel-like layer was less obvious. This was verified by the organic matter analysis (Section 4.4.4) on all three configurations, where the organic matter content decreased with depth from the surface in the filter. SEM images can be found in Appendix C.

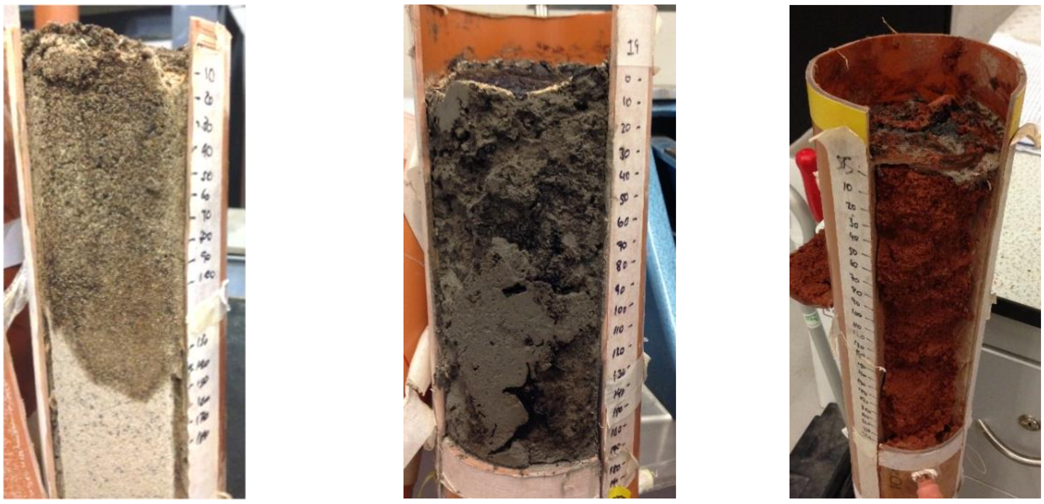

Figure 4.2 Clogging layers evident in sand, fly ash, and Bayer residue.

4.4.3 Hydraulic conductivity

The K_s results are displayed in Figure 4.3. The results are normalised against the K_s of the virgin media, where K is the hydraulic conductivity of the clogged media and K_v is the K_s of the virgin media. There was some variation in the K_s of the Control filters, which could be due to the arrangement of the coarse and fine sand during column construction, followed by migration of the fines. There is also evidence of scatter in Config 1. This may be due to the nature of the Bayer residue (which has a mud-like texture) and voids within the layer of media that were evident upon deconstruction. However, a general trend of increasing conductivity with depth below the surface was observed.

Table 4.3 Filter performance after 90 days of operation with standard deviation.

		Continuous Loading			**Intermittent Loading**		
		Control	**Config 1**	**Config 2**	**Control**	**Config 1**	**Config 2**
Average hydraulic loading rate[a] (L m^{-2} d^{-1})		1424 ± 48	600 ± 268	577 ± 12	676 ± 30	592 ± 228	655 ± 208
Influent (mg L^{-1})	**DOC**	5.7 ± 2.2	5.7 ± 2.2	5.7 ± 2.2	6 ± 1.7	6 ± 1.7	6 ± 1.7
	Al	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2
	NH_4^+-N	5.9 ± 2	5.9 ± 2	5.9 ± 2	5.8 ± 1.3	5.8 ± 1.3	5.8 ± 1.3
	NO_3^--N	19.9 ± 3.2	19.9 ± 3.2	19.9 ± 3.2	18.3 ± 4.1	18.3 ± 4.1	18.3 ± 4.1
Turbidity (NTU)	**Influent**	19 ± 7	19 ± 7	19 ± 7	19 ± 4	19 ± 4	19 ± 4
	Effluent	6 ± 1	4 ± 2	2 ± 1	6 ± 1	5 ± 3	4 ± 3
% Change	**DOC**	16.7 ± 3.3	34.9 ± 10.9	71.5 ± 4.8	24.3 ± 2.5	34.4 ± 4.8	63.3 ± 10
	Al	93.6 ± 3.0	93.5 ± 3.2	97.6 ± 0.2	94 ± 0.8	94.7 ± 4.4	96.4 ± 2.9
	NH_4^+-N	56.5 ± 1.9	75.9 ± 10.9	88.5 ± 1.9	60.2 ± 3	84.7 ± 2.1	84.8 ± 2.8
	NO_3^--N	-29.8 ± 10.3	-28.1 ± 5.4	12 ± 1.6	-30.6 ± 13.9	-44.3 ± 5.4	-16.3 ± 19.3
Avg mass removal (g m^{-3} d^{-1})	**DOC**	1.6 ± 0.25	1.3 ± 0.36	2.4 ± 0.15	1.0 ± 0.08	1.2 ± 0.13	2.4 ± 0.38
	Al	2.6 ± 0.06	0.9 ± 0.02	0.9 ± 0.003	1.0 ± 0.01	0.9 ± 0.04	1.0 ± 0.03
	NH_4^+-N	4.6 ± 0.45	2.7 ± 0.33	3.0 ± 0.09	2.4 ± 0.19	2.9 ± 0.07	3.2 ± 0.09
	NO_3^--N	-7.9 ± 5.73	-3.3 ± 0.73	1.8 ± 0.12	-3.5 ± 1.82	-4.4 ± 0.51	-1.7 ± 2.23

[a] Average hydraulic loading rate was calculated from the initial and final hydraulic loading rates, to best describe the columns as clogging occurred.

The extent of clogging in the Control filters differed depending on the operational regime (Figure 4.3). In the constantly loaded filters the clogging layer extended, to approximately 0.3 m below the top surface of the filter, whereas the K_s of the intermittent filters returned to that of the virgin media between 0.15 and 0.2 m below the top surface of the media. This was evident by both a colour change of the sand and the hydraulic conductivity results. This was greater than the clogging depth reported by Zhao et al. (2009), who observed a decreasing K_s near the filter surface of an organically-loaded, continuously fed, laboratory-scale, vertical flow constructed wetland, operated for 2 months, and concluded clogging occurred in the top 0.15 m layer. The clogging characteristics, as observed visually, of *Config 1* and *Config 2*, i.e. the formation of a gel-like layer on the surface of the media, did not differ much between the two loading regimes. This is most likely due to the nature of the media; both fly ash and Bayer residue having a small particle size (Table 4.2) meant that the clogging layer formed more quickly on the surface of the media (Hand et al., 2008; Thullner, 2010).

4.4.4 Organic matter composition

Figure 4.4 displays the organic matter composition (percentage organic matter per dry weight) of samples taken throughout the clogging layer. In each configuration and each loading rate, more organic matter was measured on the surface of the filter than at further depths. This is consistent with the hydraulic conductivity and observation results, which report a layer of organic matter at the surface, leading to the clogging of the filters. The Bayer residue in *Config 1* had higher initial concentrations of organic matter present, which appeared to leach down as water passed through the filter, demonstrated by the percentage decreasing below that of the virgin media with depth from the surface.

4.4.5 Performance outlook

The performance results indicate that Bayer residue and fly ash are the two most feasible media for use in water filters, based on contaminant removal. However, these two media were also prone to clogging. To carry these media forward to a pilot-scale study, a redesign of the filter configuration is required, to assess whether clogging is as likely to occur if these media were not at the uppermost layer of the filter. In some locations, the removal of DOC may be more important than the footprint of the filter, in which case these media may indeed be the most successful. The adsorption capacity of both media is undoubtedly powerful, as shown in the filter performance in this study, and is well documented in literature (Cengeloglu et al. 2006; Li et al. 2006; Kurniawan et al. 2006; Bhatnagar and Sillanpää 2010). However, for some treatment plants, where there is a need for units with a small footprint, the permeability of the media may be most important. Cost may also be a criterion in filter selection, as media costs can differ extensively from location to location. For example, in countries with reserves of natural zeolite it may be low cost material, whereas countries relying on production of synthetic zeolites may find it to be an expensive resource and it may not be feasible for use (Misaelides, 2011). It is also important to note the risks that may be present when dealing with industrial by-products such as Bayer residue and fly ash, for example, the potential for metal leaching from the media. In order to harness the adsorption potential, yet prevent any leaching, a stratified filter must be carefully designed.

Across all configurations and both loading regimes, the build-up of organic matter was the main clogging mechanism, shown by observation, hydraulic conductivity analysis, and chemical characterisation of the percentage organic matter present. Based on performance alone, *Config 2* was the most effective filter configuration, and continuous loading was most effective regarding DOC removal. However, the fine particles of fly ash meant that clogging was a significant problem, meaning that this option is not viable for long-term use. *Config 1* was consistent across both loading regimes and the clogging layer did not extend as deeply as in *Config 2*. This means it would be more cost effective for replenishment. The Control performed best in the constantly loaded regime, although the clogging layer extended 0.1 m deeper in this regime than in the intermittently loaded regime. This would suggest that the current method of removing 0.15 - 0.3 m of sand, in 20 or 30 stages, is, in fact, a conservative estimate of the extent of clogging, and that intermittently loaded filters would require less sand removal than constantly loaded filters.

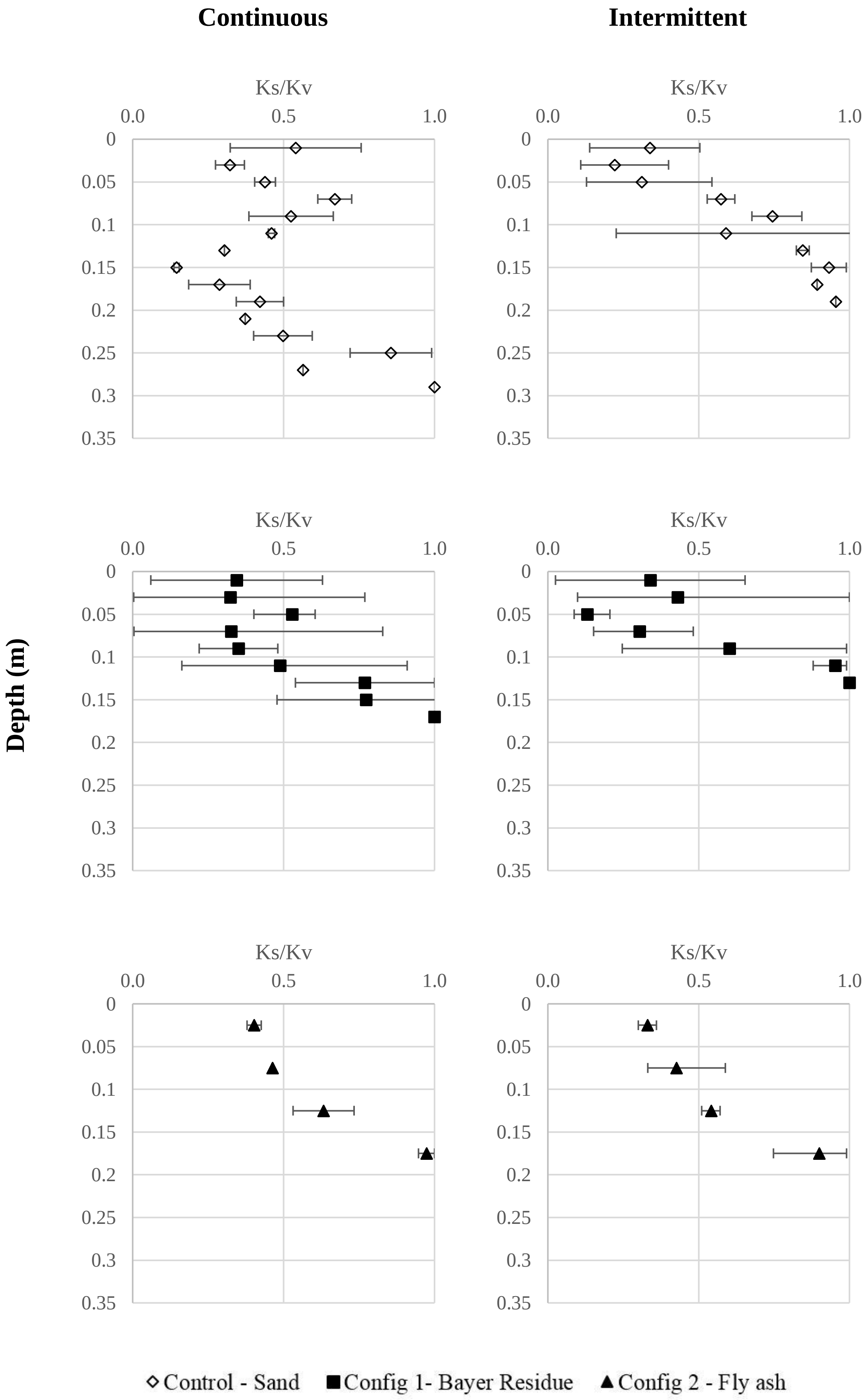

Figure 4.3 Relative hydraulic conductivity variation in the uppermost layer with maximum and minimum values.

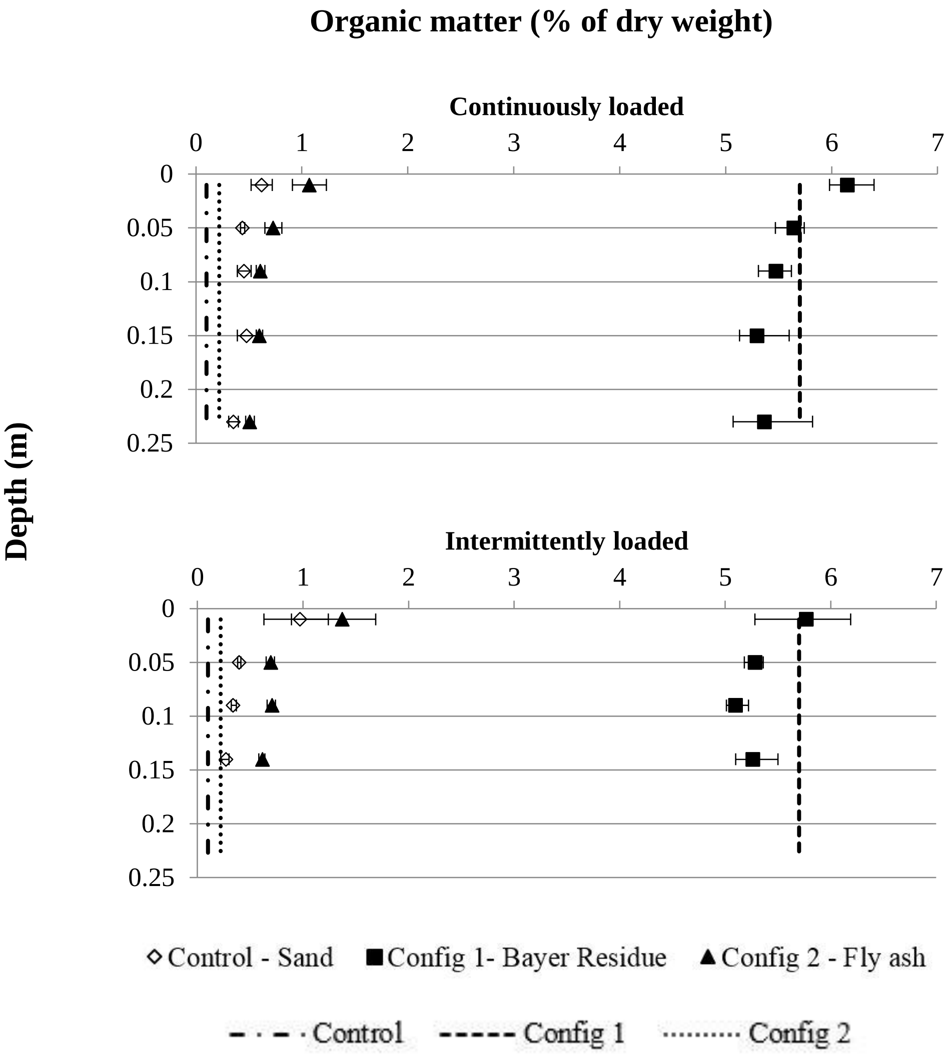

Figure 4.4 Organic matter percentages of dry weight of media (with max and min) per depth in each configuration, with initial concentrations shown as vertical lines.

4.5 Conclusions

The current model of a sand filter for water treatment is effective for certain contaminants. However, with urbanisation, population growth and industrial development, there is constant pressure on current water resources and infrastructure to meet the demand for supply and treatment quality. With variations from place to place in contaminants and source water quality, a more effective approach may be to focus on location-specific designs. The use of novel media could allow this, as well as targeting contaminants that fail to be removed by traditional sand filters. For a thorough approach to media selection, it is important to look at performance potential, but it is also vital to understand the clogging mechanisms. To date, there has been little prior research on clogging of drinking water filters. This chapter focused on clogging of novel media, while maintaining efficient water treatment.

A layer-by-layer deconstruction of the filters showed that the main clogging mechanism in all cases was a build-up of organic matter on the surface of the media. Although *'Config 2'* (fly ash, GAC, zeolite and sand) was effective in DOC removal, this configuration was more likely to clog than the Control (sand), and therefore requires a larger area for filtration. The constantly loaded sand filters were found to have clogged to a deeper depth below the surface than those that were intermittently loaded. The current method of re-sanding the slow sand filter (wherein 20 or 30 scrapings are carried out, removing 0.010 - 0.015 m each time) may be conservative, as the clogging layer did not extend below 0.3 m, despite a high suspended solids concentration in the influent. Further research should investigate the potential of using these media in an alternative configuration to harness the positive adsorption of the media, while reducing the potential for clogging.

4.6 Summary

This chapter concluded that although effective water treatment was achieved using various novel media in stratified filters, clogging occurred, which rendered the configurations examined impractical. Based on laboratory results of Chapters 3 and 4, Chapter 5 examines the performance of a redesigned filter operated at the location of an operational water treatment plant, using lake water as the source water.

5 Performance of novel media in stratified filters to remove organic carbon from lake water

5.1 Overview

The aim of this chapter was to design, operate and monitor the performance of filters, operated in intermittent and continuously loaded regimes at pilot-scale. The filters comprised media chosen to optimise DOC removal and to prevent surface clogging. Two configurations were chosen, one containing equal layers of sand, Bayer residue and pyritic fill, and the other containing sand, GAC and pyritic fill. The filter configurations were based on results from Chapters 3 and 4, and were operated at pilot-scale in a WTP.

5.2 Introduction

The majority of WTPs use ground water or surface water, which can contain fluctuating amounts of TOC, as their source. Organic carbon enters water bodies by leaching from land, particularly from peatlands, and concentrations in source water can fluctuate depending on temperature, land use, rainfall and depth to water table (Grand-Clement et al., 2014). Organic carbon in a WTP can increase the amount of disinfection required, act as a precursor to DBPs, and be responsible for membrane fouling and corrosion (Matilainen et al., 2010; Velten et al., 2011). The presence of DBPs in drinking water has numerous suggested ill-effects on human health including bladder cancer, genetic mutations, and foetal abnormalities (Grellier et al., 2015; Richardson et al., 2007).

Many treatment technologies, such as dissolved air flotation, membrane filtration, ultra-filtration, and oxidation (Matilainen et al., 2010), have been designed to focus on the removal of organic carbon or DBPs. Although these technologies can prove successful under some operational conditions, many have high capital and maintenance costs (for example, membrane filtration can be prone to fouling under high suspended solids and turbidity conditions (Tian et al., 2013)). A relatively low cost alternative in WTPs is the use of traditional sand filters, but they are not as successful in DOC removal as other technologies (Kim and Kang 2008; Teksoy et al. 2008).

This chapter focuses on the removal of DOC by novel filters, which could be retrospectively fitted to any conventional water treatment facility. The filters comprised stratified layers of a variety of media, including sand, Bayer residue, GAC, and pyritic fill. The filters were operated under two loading regimes, continuous and intermittent, at loading rates similar to recognised design standards.

This chapter aims to identify a filter configuration, using results from previous chapters, to successfully treat water, using a standard drinking water source.

5.3 Materials and Methods

5.3.1 The study site and context

The WTP examined in this chapter has a lake water source (Figure 5.1) which contains TOC and has existing practices in place for mitigating DBP formation. It currently uses ozonation, followed by GAC filtration to reduce the chlorine consumption of treated water, by removing biodegradable organics (Bourbigot et al., 1986), thereby reducing the likelihood of DBP formation.

Figure 5.1 Water treatment plant (and pilot-scale study) location (Microsoft, 2016).

5.3.2 Filter construction

Two novel filter configurations, each constructed in triplicate (i.e. n=3 for each configuration), were operated under intermittent and constant loading regimes (Figure 5.2 and Figure 5.3). Intermittently loaded filters were investigated, as they are commonly used in wastewater treatment, and may be more applicable for instances requiring less water or for household point-of-use systems (Sobsey et al., 2008).

Table 5.1 Media characteristics.

Media	**Coarse Sand**	**Pyritic Fill**	**Bayer Residue**	**GAC**
Chemical (%)				
Al (%)				
Ca (%)	-	-	-	9.85
Fe (%)				
K (%)	4.27	0.58	0.45	77.73
Al (mg kg^{-1})	87	163	8388	49
Cd (mg kg^{-1})		-	-	-
Co (mg kg^{-1})		-	-	-
Cr (mg kg^{-1})		-	-	-
Cu (mg kg^{-1})	4.65	9.29	4.17	0.55
Fe (mg kg^{-1})	39	687	59	14
Mg (mg kg^{-1})	22.57	6.04	0.18	3.78
Mn (mg kg^{-1})	3.00	64.00	1.00	2.00
Mo (mg kg^{-1})		-	-	-
Na (mg kg^{-1})	15.00	48.00	18280	219.
Ni (mg kg^{-1})		-	-	-
P (mg kg^{-1})	4	3	10	87
Pb (mg kg^{-1})		-	-	-
V (mg kg^{-1})		-	-	-
Zn (mg kg^{-1})	1.37	13.80	0.4	0.4
Effective size (mm)	1.31	0.34	0.06	0.58
Total exchange capacity (meq 100 g^{-1})	0.96	80.76	108.8	12.99

Figure 5.2 Six continuous and six intermittently loaded columns in place at the pilot-scale study location.

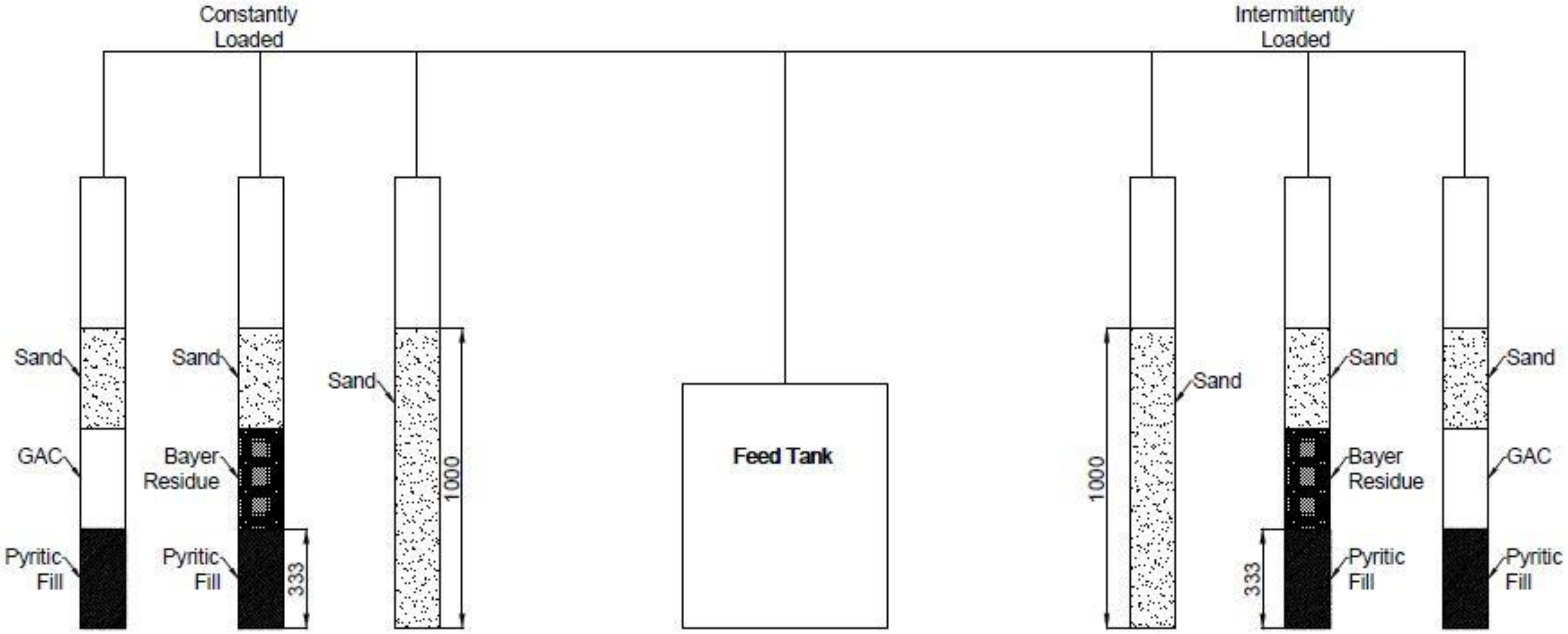

Figure 5.3 Schematic of filter set-up.

Both configurations were 1 m deep and each comprised three 0.33 m deep layers. '*Design A'* contained (from the surface downwards) layers of sand, Bayer residue, and pyritic fill. *'Design B'* contained (from the surface downwards) layers of sand, GAC, and pyritic fill in equal layers. These media were chosen based on bench- and laboratory-scale testing. Both sets of filters were instrumented with sample ports at the media interfaces. The aim of the sample port analysis was to investigate where the majority of the removal was occurring, with a view to further improving the design. After 100 days of operation, 1 m deep sand filters (Control) were constructed, which were operated under both loading regimes (n=3 in each regime). This enabled comparison between the performances of the novel filters against conventional sand filters. The sand had an d_{10} of 0.18 mm and a uniformity coefficient of 2.19, as per Irish EPA guidelines (EPA, 1995). The constantly loaded filters had a freeboard depth of 0.7 m above the surface of the media. Media characteristics are presented in Table 5.1. The study ran for a total of 240 days from June to February, and during that time the air temperature ranged from 1.3°C to 20.9°C (Met Éireann, 2016).

5.3.3 Filter operation

Each set of filters was loaded with untreated lake water (the average water composition over the duration of the study is detailed in Table 5.4). A holding tank was filled daily using a surface-mounted continuous duty pump (Antares, model no 140608777) and water was then pumped onto each filter according to its loading regime. The constantly loaded filters were kept under a constant head of 0.5 m of water. This was controlled by the installation of overflow lines. The constantly loaded filters were loaded with a multichannel peristaltic pump (7528-10, Masterflex L/S Variable-Speed Drive). The intermittent filters were timer-controlled, and were dosed for 2 min every 2 h using a submersible pump (4011708104033, Eheim Compact 1000 L h^{-1}). Each set of filters had a hydraulic loading rate (HLR) of 0.1 m h^{-1}, as recommended by the Irish EPA for slow sand filtration for water treatment (EPA, 1995).

5.3.4 Water contaminant analysis

Water samples were taken on a weekly or bi-weekly basis from the base of each filter and the raw water source and every three or four weeks from sample ports. The pH of each sample was recorded (Eutech pH 700 meter), and the samples were filtered through 0.45 µm filter paper (11406-47-ACR). Ortho-phosphorous, NO_3^--N, NO_2^--N, NH_4^+-N, and alkalinity were analysed using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Dissolved organic carbon, dissolved inorganic carbon (DIC), total phosphorus (TP) and total nitrogen (TN) were analysed using a TOC analyser (BioTector Analytical Systems Ltd). UVA_{254} absorbance was measured using a UV-Visible spectrophotometer (Cary 50, Agilent Technologies), using a quartz sample cell with a path length of 10 mm. Metal analysis was carried out on water samples over the first 63 days of operation, using ICP-MS, in order to ensure there was no heavy metal leaching from the media into the effluent water. Samples could only be taken from sample ports in the continuously loaded filters, as sufficient volume could not be extracted from the intermittently loaded columns for DOC analysis. Empty bed contact times were calculated approximately based on average flow through rates and media volumes, and then used to express bed volume removals.

Dissolved organic carbon and UVA_{254} were used to calculate SUVA, to further assess the quality of treatment. The SUVA was calculated by (Edzwald, 1993):

$$SUVA(L\,mg^{-1}m^{-1}) = \frac{UVA_{254}}{DOC} \times 100 \qquad \textit{Eqn 8}$$

where UVA_{254} was measured in cm^{-1}, and DOC was measured in mg L^{-1}. Table 5.2 gives the necessary information for correct interpretation of the formula (EPA, 2012b).

Table 5.2 Explanation of SUVA values (USEPA, 2012).

SUVA ($L\ mg^{-1}\ m^{-1}$)	**Content**	**UV Absorbance**	**Chlorine Demand**	**THM Formation Potential**
<2	High fraction of hydrophilic non-humic matter	Low	Low	Low
2-4	Mix of hydrophobic and hydrophilic non-humic matter	Medium	Medium	Medium
>4	Humic, highly aromatic hydrophobic matter	High	High	High

5.3.5 Quantification of clogging in filters

At the end of the study, the filters were destructively sampled. This involved a hydraulic conductivity investigation, important for determining the hydraulic function of the filters (Urbonas, 1999), as well as a detailed chemical analysis of the filter media both pre- and post-filtration, to determine what had been absorbed and how the filter media were affected by long term operation.

5.3.5.1 Hydraulic conductivity tests

Saturated hydraulic conductivity (K_s; m s^{-1}) testing was carried out on the surface layer of each filter, to check for any potential clogging of the surface layer. This involved taking 0.05 m diameter cores from each filter, in 0.05 m layers from the filter surface, until the hydraulic conductivity returned to that of the virgin media. A constant head test was used to measure the K_s (British Standard Institution, 1990b), which was calculated using Darcy's Law (Craig, 2004):

$$\frac{Q}{A} = K\left(\frac{dH}{dZ}\right) \qquad \textit{Eqn 9}$$

where Q is the flow rate ($m^3\ s^{-1}$), A is the cross sectional area (m^2), and dH/dZ is the hydraulic gradient ($m\ m^{-1}$).

5.3.5.2 Organic matter testing

Media samples were taken at the top and bottom of each layer, and analysed for organic matter using LOI (British Standard Institution, 1990c). The LOI at each depth analysed was expressed as a percentage of the LOI of virgin media.

5.3.6 Statistical analysis

Statistical analysis was carried out using mass removal data, on SPSS 22 software (IBM, 2014). Each design was analysed to ensure the replicates were true, before carrying out statistical analysis. Data were checked for normality using the Shapiro-Wilk test, and comparisons between designs were made using ANOVA and the Mann-Whitney tests (using a confidence interval of 0.05 for significance). Each column in *Design A*, in the intermittently loaded regime, was decommissioned after 60 days, as the flow through each column became too slow to be deemed worthwhile continuing. Therefore, for comparisons between *Designs A* and *B* in the constantly loaded flow regime only, data from Day 60 onwards were used. For comparisons between *Designs A* and *B* and the sand filters (Control), only data from Day 100 (the time at which the sand filters were constructed) were used.

5.4 Results and Discussion

5.4.1 Influent characteristics

Influent characteristics of the source water are presented in Figure 5.4 (with reference to ambient temperature and rainfall). The DOC concentrations in the lake water varied significantly over the course of the study, with the highest concentration occurring at day 239 after a series of rainfall events in January/February (Figure 5.4). Trends of DOC are known to change seasonally (Sutherland et al., 2015), and previous studies have reported decreases in Autumn and Spring (Eimers et al., 2008), and increases in November and May (Brooks et al., 2015). Evidently, the concentration of DOC is dependent on many variables, making it more difficult to design a treatment system that can work efficiently across a large concentration range. The average range in the influent water in the current study was 9.9 mg L^{-1} (from a minimum of 6.9 a maximum of 13.7 mg L^{-1}), over a period of 240 days.

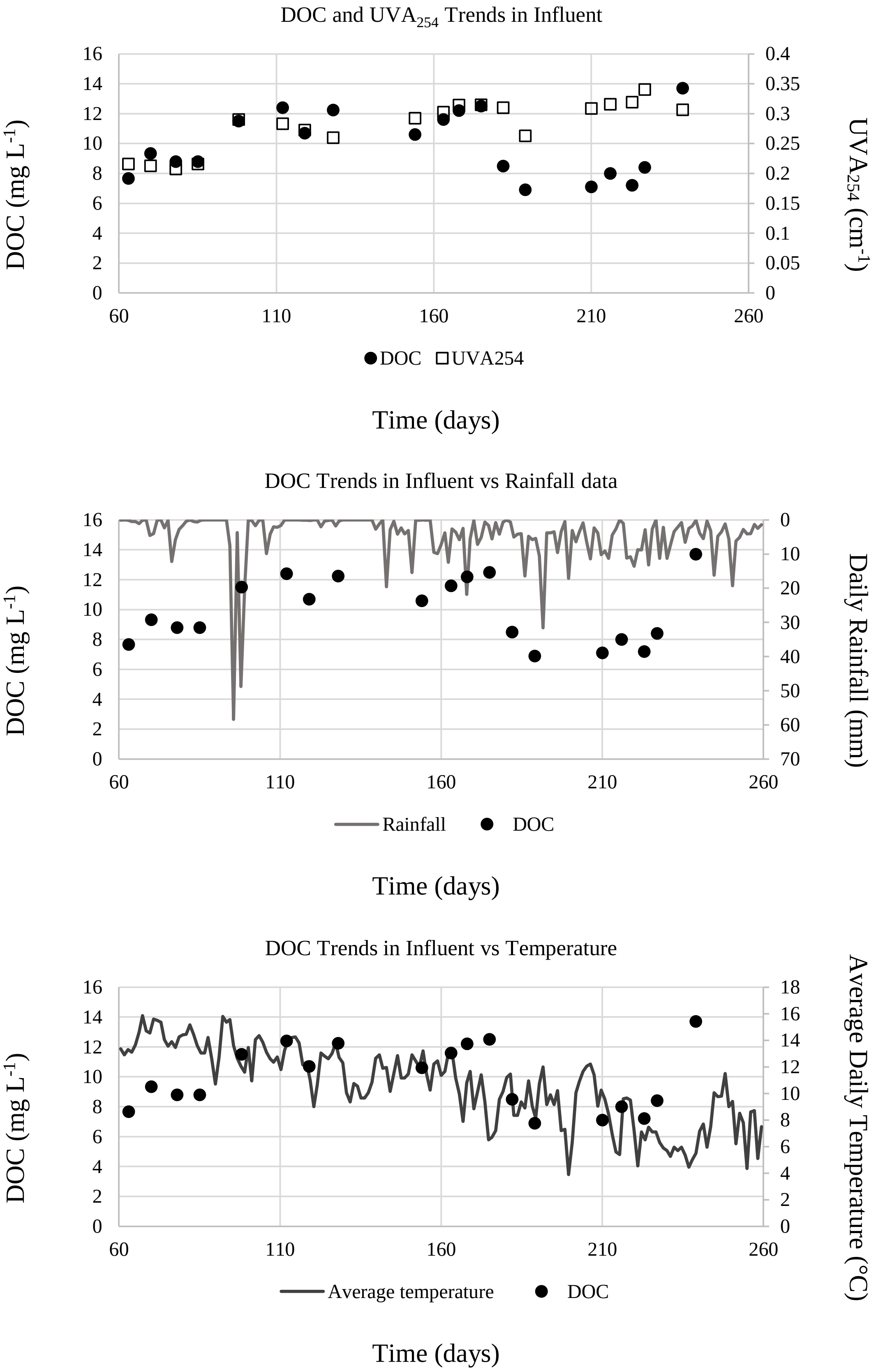

Figure 5.4 DOC concentrations and UVA254 (top) in the influent water, rainfall (middle), and daily average temperature (bottom) (weather data from www.met.ie).

5.4.2 Filter performance

Table 5.4 describes the overall performance of each filter design, under both loading regimes. The concentrations of nutrients in the influent lake water were negligible, making it difficult to draw specific conclusions regarding the performance of the filters. Dissolved organic carbon decreased and DIC increased from influent to effluent, in each of the filter configurations. The absorbance of UV light at 254 nm and the SUVA decreased in both of the filter configurations, but increased in the control filters. Alkalinity and pH increased slightly as the water travelled through the filters, in all cases, which may be attributed to leaching from media. Raw data for this study can be found in Appendix D.

5.4.2.1 Dissolved organic carbon removal

Both filter configurations achieved DOC removal (Table 5.5 and Figure 5.5), and their performance exceeded that of the Controls. When the filters were loaded continuously, *Designs A* and *B* achieved average removals of 27 and 40%, respectively. When operated with an intermittently loaded regime, average removal rates of 31% were achieved in *Design B*. In comparison, DOC removals from the control filters ranged between 4% and 8% in each loading regime. DOC removals per bed volume are displayed in Appendix D (Figure D1), using an estimated empty bed contact time.

Mass removals of DOC are presented in Figure 5.6 and Table 5.3. *Design B* had significantly better DOC mass removals than *Design A* (p=0.001) and the Controls in both operational regimes (p=0.001 and p=0, for intermittent and continuous loading respectively). The loading regime did not have a significant impact on the mass removal rates in *Design B*, which averaged at 8.8 and 7.6 g m^{-2} d^{-1} (where m^2 refers to plan area) for the continuous and intermittently loaded filters, respectively (p=0.86). There was no significant difference between the mass removal rates of the Controls under either continuous or intermittent loading regimes (p=0.349).

Table 5.3 Mass loadings and removals.

	Continuous			**Intermittent**	
	Design A	**Design B**	**Control**	**Design B**	**Control**
Average mass loading (g m^{-2} d^{-1})	20.2±1.3	21.8±0.5	23.8±1.3	22.5±0.6	21.6±0.9
Average mass removal (g m^{-2} d^{-1})	5.2±2.8	8.8±3.6	2.3±1.9	7.6±2.3	1.2±2.6

Table 5.4 Filter performance data tabulated (±standard deviation) over 180 days of the study (from day 60-240). Design A (intermittent loading) was decommissioned after 60 d of operation.

			Loading rate ($L\ m^{-2}\ d^{-1}$)	**DOC ($mg\ L^{-1}$)**	**DIC ($mg\ L^{-1}$)**	**UVA_{254} (cm^{-1})**	**SUVA ($L\ mg^{-1}\ m^{-1}$)**	**PO_4^{3-}-P ($mg\ L^{-1}$)**	**NH_4^+-N ($mg\ L^{-1}$)**	**NO_3^--N ($mg\ L^{-1}$)**	**NO_2^--N ($mg\ L^{-1}$)**	**Alkalinity ($mg\ L^{-1}$)**	**pH**
Influent				9.9±2	7.7±1.3	0.281±0.06	2.9±0.8	0.06±0.05	0.06±0.04	0.03±0.05	0.00	30.6±9.4	7.9±0.3
Effluent Concentrations	Continuous Loading	Design A	2037±131	7.2±0.2	11.2±1	0.175±0.02	2.6±0.3	0.08±0.01	0.01±0.04	0.07±0.04	0	40.9±5.3	8.8±0.4
		Design B	2199±52	5.9±0.7	11.5±0.7	0.137±0.03	2.4±0.2	0.07±0.01	0.06±0.01	0.03±0.01	0	40.8±0.7	8.4±0.1
		Control	2407±128	9.1±0.6	8.5±0.5	0.291±0.01	3.4±0.3	0.06±0.01	0.05±0.01	0.02±0.01	0	36.5±1.2	8.3±0
	Intermittent Loading	Design B	2270±60	6.6±0.7	12.7±0.9	0.156±0.02	2.4±0.4	0.07±0.01	0.04±0.00	0.05±0.00	0	46.2±2.9	8.3±0.1
		Control	2179±86	9.6±0.3	8.4±0.3	0.293±0.01	3.3±0.1	0.09±0.02	0.05±0.01	0.02±0.00	0	35.4±0.2	8.4±0.1
Percentage Changes	Continuous Loading	Design A		26.8±2.6	-44.8±13	36.9±8.2	12.8±9	-53.3±28	-40.1±15	-26.4±49	-	-37.5±21	
		Design B		40.1±7.4	-50.3±10	52.8±9.3	21.4±7	-37.5±29	-33.1±12	20.8±19	-	-36.1±2	
		Control		8.5±3.1	-17.4±5	3.8±2	-6.4±5	-21.2±10	-12.5±14	-50.2±4	-	-8.8±2	
	Intermittent Loading	Design B		31.2±8.7	-67.3±8.4	47.5±7.5	22.7±16	-47.4±28	-9.2±26	-78.1±82	-	-57.6±13	
		Control		4.2±3.8	-13.4±3	2.3±3	-5.9±3	-85.6±43	-16.4±18	-32.5±11	-	-7.4±1	

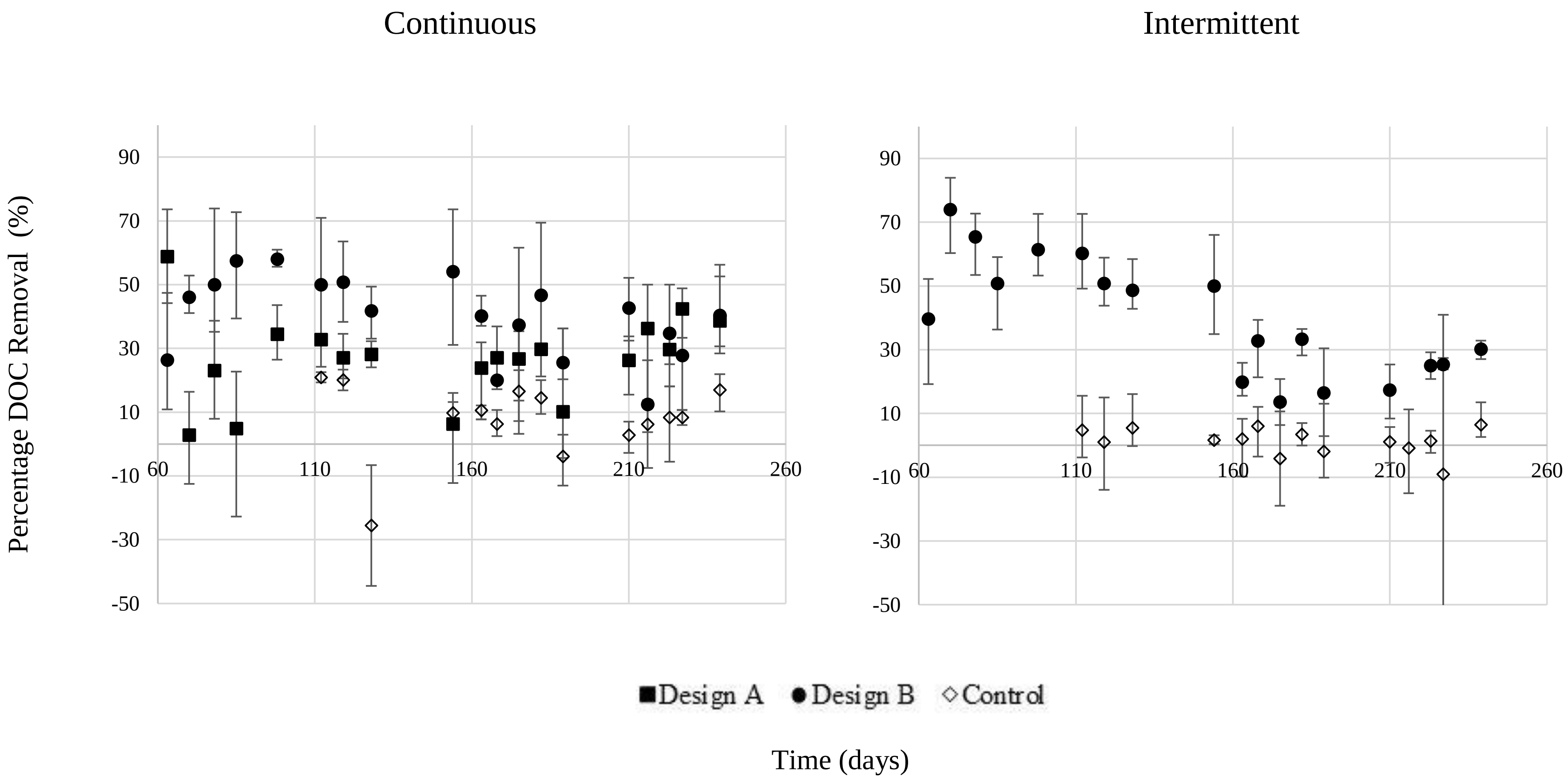

Figure 5.5 Percentage DOC removals of all filter types.

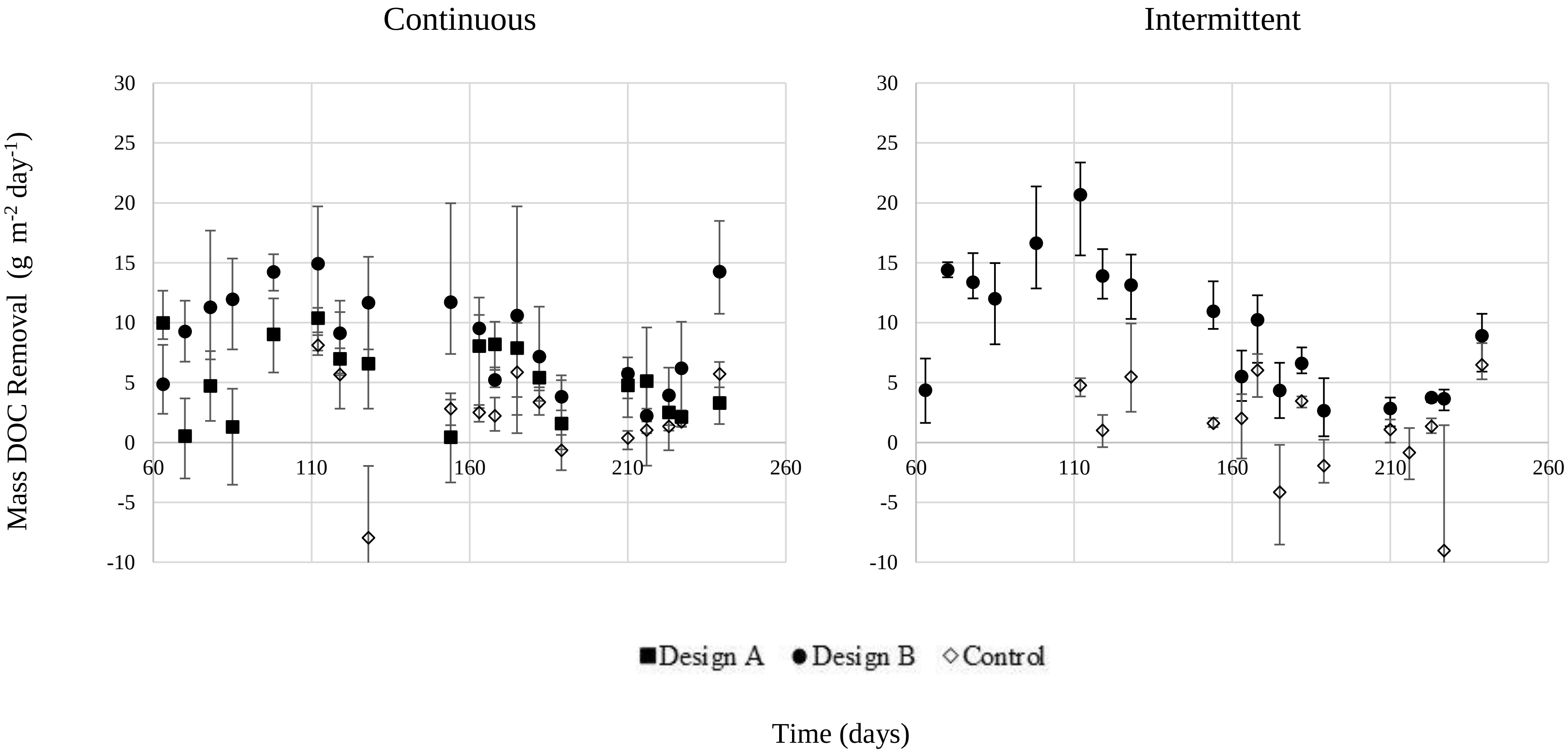

Figure 5.6 Mass removal of DOC from all filter types for the duration of the experiment.

Dissolved organic carbon removal was expected in each of the novel configurations, based on adsorption data from Chapter 3, and in particular in *Design B*, based on previous studies using GAC for carbon removal (Gibert et al., 2013; Velten et al., 2007). The removals were similar to those achieved by Kim and Kang (2008), who measured DOC removal of 49% for the first 3 months of operation, 30% for the following 3 months, and 21% thereafter. Similar removal rates were achieved by Tansakul et al. (2011), who used powdered activated carbon (PAC) as a pre-treatment to ultrafiltration, although when the dosage of PAC was doubled and quadrupled, removal efficiencies increased to 70%. However, ultrafiltration can be prone to fouling quickly.

An increase in DIC in the effluent was observed throughout the experiment for all filters. For GAC filtration, it is understood that the removal mechanism for DOC begins with the physio-chemical adsorptive mechanisms, but after a certain period, the stronger mechanism is microbial activity, which feed on DOC (Boon et al., 2011; Velten et al., 2007). Dissolved inorganic carbon can be characteristic of microbial degradation, where carbon dioxide mineralisation has occurred, and also where DOC has photo-oxidised to DIC (Granéli et al., 1996; Hansell et al., 2004).

5.4.2.2 SUVA analysis

The SUVA analysis is presented in *Figure 5.7*. In almost all instances, the effluent SUVA was less than the influent. The highest reduction occurred in *Design B*, both in the continuous and the intermittently loaded filters, where the average concentrations reduced from 2.9 to 2.4 L mg^{-1} m^{-1} (Table 5.4). The loading regime did not have a significant impact on SUVA reduction ($p=0.9$). *Design A*, operated in the continuous loading regime, also achieved an average SUVA reduction to 2.6 L mg^{-1} m^{-1}.

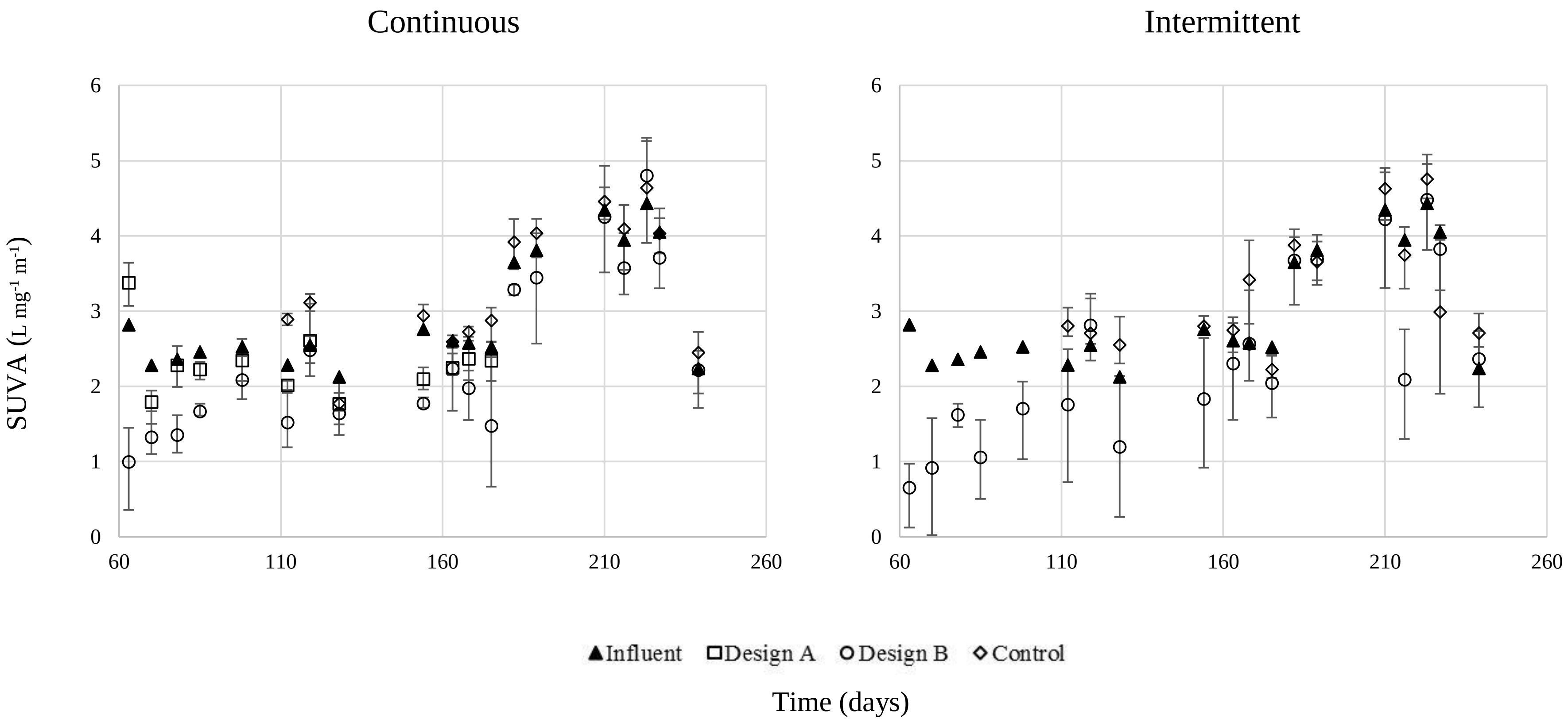

Figure 5.7 SUVA values from influent and effluents.

Results from a WTP in Greece reported a SUVA reduction of 2.22 to 1.26 L mg^{-1} m^{-1} (Papageorgiou et al., 2016), from the beginning of the treatment plant until the end, using pre-ozonation, sand filters, ozonation and GAC filters. This indicates that in a full-scale treatment works, the novel designs presented in this study could be very effective. Papageorgiou et al. (2016) also noted an increase in SUVA following sand filtration, again reflective in the results of the current study.

5.4.2.3 Sample port analysis

The results of the sample port analysis, for the full duration of the study, are presented in Figure 5.8 and Table 5.5. For both *Designs A* and *B*, the top sand layer had some removal of DOC. The sand was included in order to mitigate any potential clogging issue, and to strain the larger particles, if present, from the influent. In *Design A*, the removal of DOC by Bayer residue varied considerably throughout the duration of the experiment, and appeared to desorb DOC at times. This could potentially be mitigated by a redesign, or by combining the medium with another to harness the adsorption potential that is present. For other contaminants, a pre-treatment, or activation, of Bayer residue has proved successful (Huang et al., 2008; Li et al., 2006), which could also be put in place. In *Design B*, GAC had good removal of DOC from the influent. This was consistent with results from Chapter 3 and other studies (Kennedy and Summers, 2015; Kim and Kang, 2008; Lin et al., 2010). However, GAC can exhaust quickly and can be costly, and may not be the most attractive option for use on its own (Corwin and Summers 2010). In both *Designs A* and *B*, pyritic fill also demonstrated some DOC removal. Pyritic fill is not commonly used in treatment of water or wastewater, and to date, there has been little investigation into its use as an adsorbent. From the port analysis study, it is clear that GAC has the greatest potential for DOC removal, followed by sand and pyritic fill.

Table 5.5 Mass removals of DOC per layer of continuously loaded filters.

	Design A			**Design B**		
	Mass removal per filter layer (g m^{-2} d^{-1})					
Day	Sand	Bayer Residue	Pyritic Fill	Sand Layer	GAC Layer	Pyritic Fill
15	9.0±5.5	-10.3±3.0	20.8±9.4	6.4±0.3	7.0±4.4	5.5±7.2
21	0.5±0.2	-6.2±8.8	7.1±5.1	2.5±3.0	19.1±1.2	7.4±3.0
29	7.5±2.6	0.3±2.0	0.4±0.6	10.8±0.3	14.1±7.6	-0.5±4.1
34	0.6±1.0	-0.3±3.2	0.7±1.2	3.1±5.0	5.4±8.1	1.2±3.0
42	6.1±1.5	4.9±6.6	-0.4±6.1	6.9±0.4	13.0±6.9	-0.9±2.0
63	1.2±5.6	9.7±4.1	2.3±6.2	5.5±5.2	4.7±9.5	-3.5±7.8
85	2.4±1.0	3.1±2.2	-3.2±3.4	5.4±2.2	5.6±7.7	2.7±2.2
112	9.8±0.5	5.5±4.9	-3.0±4.1	15.1±14.8	15.7±11.3	-10.9±9.2
163	11.7±1.8	-4.0±5.7	-0.94±9.51	6.9±4.9	-0.3±5.2	5.2±3.3
182	5.6±1.7	-1.9±2.1	1.2±2.8	2.5±1.6	3.5±5.0	1.9±0.9
210	6.6±9.2	4.2±1.7	-4.6±6.2	2.0±3.0	1.2±0.1	3.5±1.7
239	1.2±1.1	3.3±2.3	-1.4±0.8	5.0±2.3	12.5±2.9	5.0±3.0
Average	3.7	0.7	1.6	3.7	8.5	1.4
St. Dev.	5.5	5.6	6.7	6.2	6.2	5.0

5.4.3 Metal analysis

Metal analysis of effluent samples is presented in Table 5.6. *Design A* leached Al and Fe into the water over the first 63 days of operation. Iron concentrations in the effluent returned to an acceptable level after 21 days, and although the amount of Al leached into the effluent water reduced over time, it was still above the threshold for safe drinking water (0.2 mg L^{-1}) (SI No 278 of 2007). The presence of metals in *Design A* was due to the Bayer residue. This is a by-product of the Al production industry, and also contains high levels of Fe (EAA, 2013). Although the presence of metals was concerning, an ion exchanger or polish filter could be added to the treatment system to mitigate the potential for metal leaching. It would also be possible to wash the filter out before use to clear any leaching metals. *Design B* did not leach any metals of concern, other than metals found in the influent.

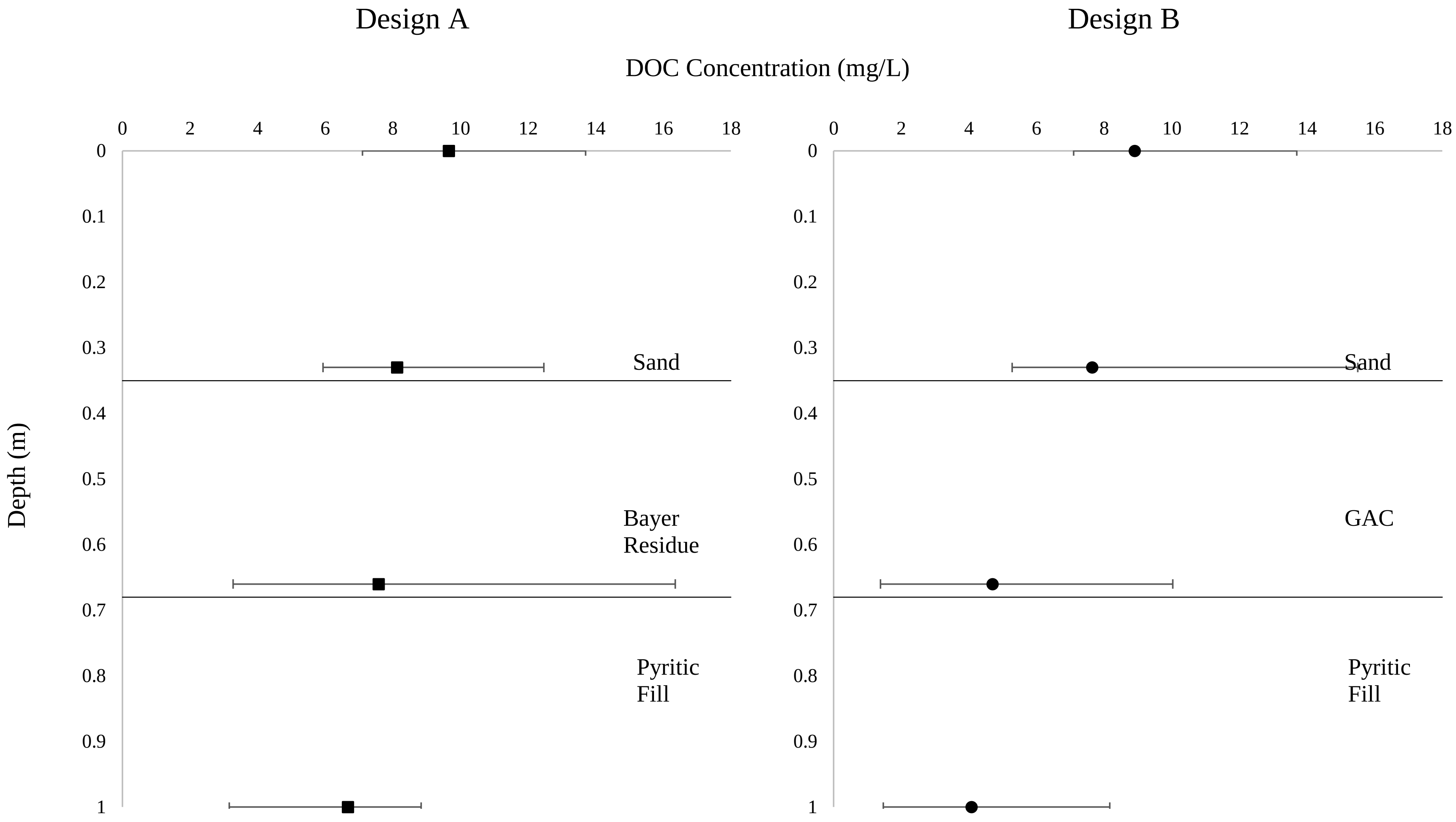

Figure 5.8 DOC analysis from sample ports in continuously loaded filters.

Table 5.6 Effluent metal analysis.

	MAC	**Influent**			**Continuous Design A Average**			**Continuous Design B Average**			**Intermittent Design B Average**		
Time from start of operation (d)		21	34	63	21	34	63	21	34	63	21	34	63
Aluminium (µg/L)	200	100	23	63	587±266	337±170	330±30	160±95	33±16	54±17	110±17	45±11	29±13
Antimony (µg/L)	5	0.3	0.1	0.1	1±1	1±1	1±1	1±0	0±0	0±0	0.4±0.2	0±0	1±0
Arsenic (µg/L)	10	1	0.2	0.7	2±1	2±0	2±0	1±0	1±1	1±0	1±0	0±0	1±0
Barium (µg/L)		63.8	14	76	76±15	19±4	92±69	40±7	30±2	58±5	37.9±16	27±13	83±15
Boron (mg L)	1	0.5	0.2	0.02	1±0	0±0	0±0	1±0	0±0	0±0	0.5±0	0±0	0±0
Cadmium (µg/L)	5	0.4	0.1	0.1	0±0	0±0	0±0	0±0	0±0	0±0	0.4±0.1	0±0	0±0
Calcium (mg/L)		17.6	20	26	150±133	108±150	108±140	32±13	24±4	26±3	213±312	14±12	36±3
Chromium (µg/L)	50	3.8	1	5.6	4±1	7±9	3±2	3±0	1±0	1±0	13±17.3	4±3	1±0
Cobalt (µg/L)		3	1	1	3±0	1±1	2±2	3±0	1±0	1±0	3±0	1±0	1±0
Copper (mg/L)	2	0.015	0.012	0.005	0±0	0±0	0±0	0±0	0±0	0±0	0.04±0.02	0±0	0±0
Iron (µg/L)	200	60	20	110	390±411	20±0	62.5±30.5	437±497	20±0	52±29	130±82	20±0	29±16
Lead (µg/L)	10	0.9	0.3	0.3	1±1	0±0	1±0	2±1	0±0	3±3	2.4±1.6	0±0	0±0
Magnesium (mg/L)		3.7	3.9	3.7	3±2	4±3	5±3	3±2	4±0	4±0	3.2±1.4	4±0	7±2
Manganese (µg/L)	50	22	4.4	42	76±44	54±83	259±348	46±33	1±0	46±2	40.7±37	2±1	42±5
Mercury (µg/L)	1	0.87	2.55	0.13	0±0	3±1	0±0	1±2	2±0	0±0	0.1±0.06	2±1	0±0
Molybdenum (µg/L)		3	1	16	30±19	33±48	51±77	4±1	2±1	2±1	6.2±5.4	1±0	3±2
Nickel (µg/L)	20	4.3	5.2	18.6	9±4	11±8	34±34	6±4	2±0	7±5	17.2±20	4±2	5±2
Sodium (mg/L)	200	31.6	31.2	33.9	73±19	66±37	83±71	34±5	31±1	33±0	40.9±15	31±0	35±1
Zinc (µg/L)		48	56	21	42±17	22±16	86±57	76±57	44±29	61±28	101.3±103	24±13	34±21
Silver (µg/L)		10	1	1	10±0	1±0	1±0	10±0	1±0	1±0	10±0	1±0	1±0

5.4.4 Filter deconstruction

Filter deconstruction was carried out after the filters had been decommissioned. In all cases, little to no clogging was observed (Table 5.7), indicating that the hydraulic function of the filters was preserved throughout the loading period.

During deconstruction, samples were analysed for organic matter content to determine where the majority of the TOC was removed (Figure 5.9). In the case of *Design A*, most of the organic matter remained at the surface (sand) layer, which could be due to both organic matter removal by physical filtration and biofilm build-up. The continuously loaded filters had a larger build-up than the intermittently loaded filters, indicating that the loading regime influenced this. *Design B* had the largest accumulation of organic matter in the second layer, composed of GAC. This was to be as expected, given that *Design B* was more successful in DOC removal, and that microbial layer was likely to be present on the GAC samples (Boon et al., 2011). There was little accumulation of organic matter in the pyritic fill layers. In the control filters, there was limited organic matter accumulation, which was due to the lack of DOC removal. Any accumulation that was present, existed on the surface layer, which was most likely due to straining and/or a biofilm build-up. This layer was evident on all filters.

Table 5.7 Relative hydraulic conductivity analysis of the uppermost layer of each filter. K_s is the saturated hydraulic conductivity of the media, K_v is the saturated hydraulic conductivity of the virgin media.

	Continuous			**Intermittent**	
Depth below surface (mm)	Design A (K_s/K_v)	Design B (K_s/K_v)	Control (K_s/K_v)	Design B (K_s/K_v)	Control (K_s/K_v)
0-50	1	0.8±0.2	1	1	1
50-100	1	1	1	1	1
100-150		1			

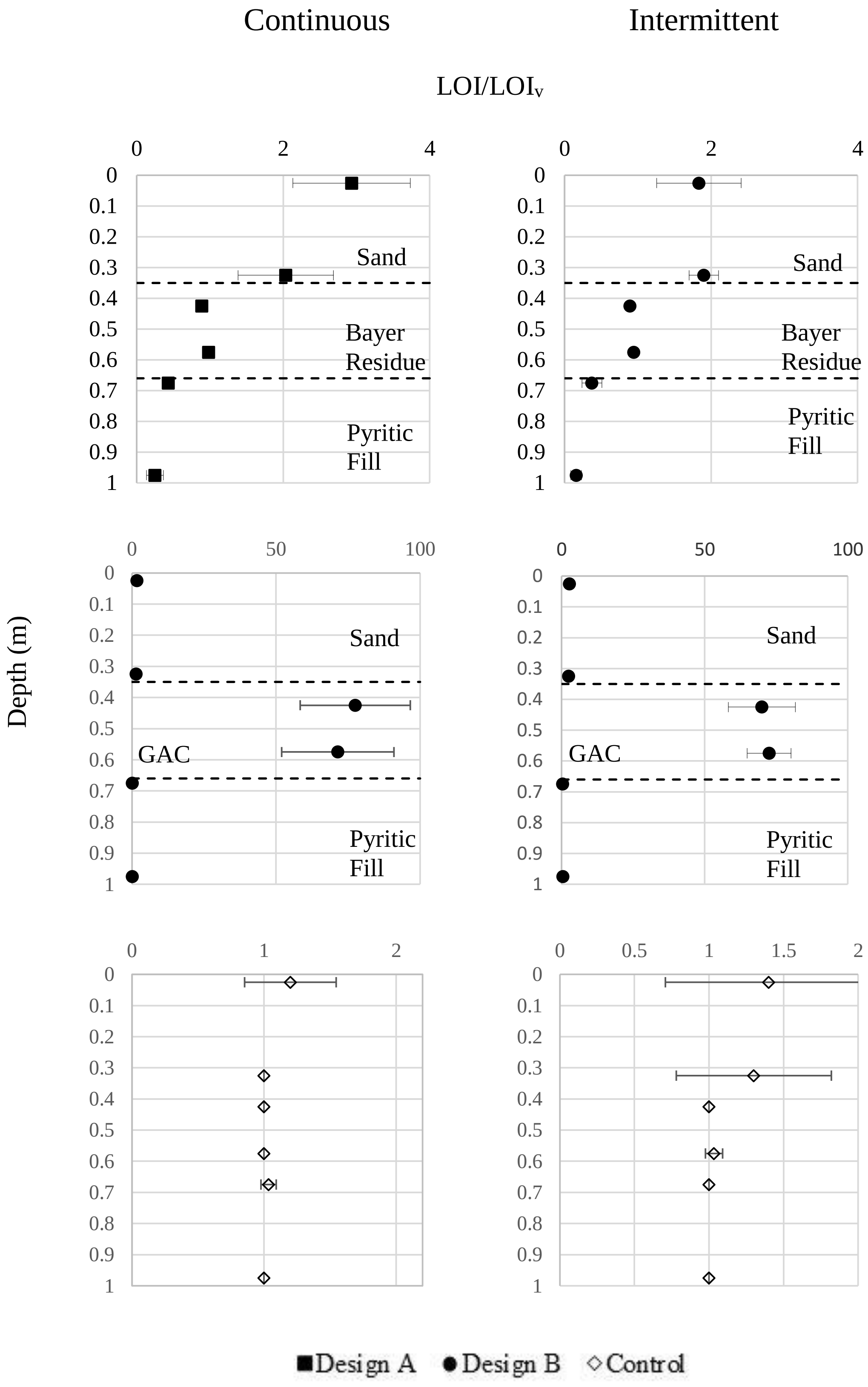

Figure 5.9 Loss on ignition (LOI) of the media as a percentage of the LOI of virgin media. Design A (top), Design B (middle), and control filters (bottom).

5.5 Conclusions

Effective DOC removal at water treatment plants is essential in order to prevent the formation of DBPs. Sand filters are not effective at reducing DOC to a sufficient level, as demonstrated by the control filters. *Design A* (sand, Bayer residue and pyritic fill) was reasonably effective at removing DOC under a continuous loading regime. Metal analysis indicated that there could be potential leaching from Bayer residue, resulting in the design being ruled out for potable water treatment.

Design B, comprising sand, granular activated carbon, and pyritic fill, was most effective. After a study period of 240 days, an average of 40% DOC removal was achieved, with no significant difference between the continuous and intermittent loading regimes. There was no metal leaching from this design. In practice, a continuous loading regime is more desirable as it requires less monitoring and can be more efficient than running a pump on on/off cycles. *Design B* also achieved good SUVA reduction, from 2.9 to 2.4 L mg^{-1} m^{-1}. These results are comparable to other alternative technologies being investigated.

Further investigations should involve increasing loading rates to assess if the filters can be used for higher throughput, to investigate the filters under a rapid gravity system, and to assess where best to place the filters in the treatment process. The filters could be used in place of the conventional sand filters, but could also be used to reduce DOC concentrations, where concentrations are particularly high, to a point where other technologies will be successful.

This chapter concludes that a combination of media, including waste products, can be used for DOC removal, which is more effective than current sand filter designs. The resulting design is sustainable and efficient, and effectively removes SUVA from surface water, reducing the potential for formation of DBPs.

6 Conclusions and Recommendations

6.1 Overview

Existing and newly developed technologies to safely treat and disinfect water are effective, but in many cases, require high capital investment, can be subject to fouling, and require maintenance. More traditional treatment systems such as slow and intermittent filtration, which use adsorption mechanisms to retain potentially harmful contaminants, may be more effective than disinfection. Moreover, waste products and locally sourced material, when used in filters, could provide sustainable solutions for contaminant removal in water treatment plants (WTPs).

In this study, two novel filtration technologies were designed and operated at laboratory- and pilot-scale: a filter containing sand, granular activated carbon (GAC), and pyritic fill; and a filter containing sand, Bayer residue, and pyritic fill. Contaminants investigated included nutrients, metals, and organic matter (with-a-view to removing the precursors to the formation of disinfection by-products (DBPs)). The study examined a variety of media, including waste products (such as Bayer residue, fly ash, and pyritic fill) and known adsorbents (such as sand and GAC).

6.2 Conclusions

The main conclusions are as follows:

- Locally sourced and waste materials, when strategically placed in filters, may be used to retain precursors to DPBs that may occur in WTPs, and can be more effective than traditional sand filters. Such filters require relatively low maintenance and are easy to operate. Care must be taken regarding permeability of the material, ensuring that efficacy is not compromised by using a low-permeability media which may clog quickly. The use of these waste media in water filtration may reduce their environmental impact by prolonging their life cycle.
- In this study, a filter comprising sand, GAC, and pyritic fill, was the most effective of the novel filter configurations examined. After 240 days of operation, average dissolved organic carbon (DOC) removal was 40%, no

metals were leached, and specific ultra-violet absorption (SUVA) was reduced to an average value of 2.4 L mg^{-1} m^{-1}, a value at which the potential for trihalomethane formation is low. Water treatment plants commonly use sand filters, which, as demonstrated in this study, are not as effective in reducing DOC and SUVA.

- For water sources with particularly high DOC concentrations, filters of a similar configuration to those examined in the current study, may be used in conjunction with another technology to reduce the loading of DOC on a WTP. For example, filters could be used to reduce the loading of DOC onto membrane filters, therefore extending the life of the membrane.
- Great care needs to be taken when selecting the media and its configuration in the filters, as leaching of metals or other potentially harmful contaminants that may be present in the media, may occur during operation. For example, this study found that filters containing Bayer residue leached metals. It is recommended that water is passed through the filter before commissioning and metals are monitored until effluent levels have reduced to below the MAC.
- In this study, the media and its configuration determined the likelihood of clogging of the filters. However, when clogging occurred, organic matter extended deeper into the uppermost sand layer in constantly loaded sand filters than those that were intermittently loaded. Although the filters containing fly ash, GAC, zeolite and sand, were effective in DOC removal, clogging reduced their permeability to a greater extent than for the sand filters.
- Adsorption isotherms are a quick and inexpensive method of assessing the suitability of various media for use in filters. These bench-scale tests allow the maximum adsorption capacities to be determined, in addition to quantification of any potential contamination risks arising from the use of specific media.
- Industrial and construction waste products, such as fly ash, Bayer residue, and pyritic fill, can be effectively used to remove nutrients and metals from aqueous solutions, and may be more effective than sand.
- In this study, there was no instance in which pH adjustment was necessary for adsorption; therefore, adjusting pH is unlikely to be a cost-effective intervention to improve adsorption kinetics. In many cases, optimal adsorption occurred at the unadjusted pH.

6.3 Recommendations for future work

- Further investigations should involve increasing hydraulic loading rates to assess if the size of the filters may be optimised. This would make the technology more accessible for use in large WTPs.
- Regeneration of the filters should also be investigated to achieve maximum use of the media. This may extend the lifespan of the filters.
- The study showed that SUVA reduction may be achieved using the filters. Coagulation and sedimentation could be implemented before the filters to maximise organic matter removal. Organic matter removal before disinfection not only lowers the demand for disinfection, but will aid in preventing any further DBP formation from occurring along the pipe network.
- Given that the cost of waste materials is geographically dependent, it is necessary to address the issue on a site by site basis. Cost analysis should also investigate potential pre-treatments available as this may improve the lifetime and the efficiency of the material.
- While the use of waste materials addresses the “circular economy” concept, it is important to ensure the original product is not devalued in the process, for example, by adsorption of metals. Prior to use in filters, a life-cycle assessment should be conducted to ensure that the media are not compromised, and that the overall solution is environmentally and carbon friendly.

6.4 Wider Implications

Effective water treatment is a global concern, and with it, the occurrence of disinfection by-products. The development and research into technologies to safely treat and disinfect water is constantly evolving. However, many of the newly designed technologies are costly and/or require expert maintenance. Alongside this, the disposal of waste materials continues to cause problems for local authorities and governments, with pressure from the European Union to rely less and less on landfilling. This study suggests that by combining the use of waste materials and effective water treatment, both issues can be tackled simultaneously. The use of locally sourced materials may mean that bespoke filters can be designed for specific contaminants, while reducing the overall cost of the filter construction.

Retrofitting a bespoke filter to a conventional WTP is not a complex process, as it may be installed in place of a sand filter to tackle contaminants that were previously untreated. This, in turn, can reduce the need for further treatment and/or excessive disinfection, and would make the treatment process more effective. In particular, the removal of organic carbon during the initial treatment process is key to ensuring a successful disinfection strategy that reduces the likelihood of DBP formation.

There is also the potential to use filters, such as the one described above, in a polishing step in a treatment system that already contains a rapid gravity sand filter. The additional adsorber step would allow for an improved treatment system, without needing frequent regeneration and replacement. Placing the adsorber/polishing filter after the rapid gravity filter would mean that there would be a reduced sediment load, and clogging would be less likely to occur. In this instance, treatment would then be focused on the dissolved contaminants.

Costings are an important aspect to consider when designing a new technology. When waste materials are an intrinsic element, geographical location can have a big impact. For this reason, it is necessary to assess each situation individually. Pre-treatment methods may also increase the cost of the material. However, it also has the potential to improve and extend the effectiveness of the material. A full cost benefit analysis must be carefully carried out to ensure that the best possible use is being made of the material.

When considering the use of waste materials, it is important to recognise the potential implications of using such materials. These materials have the potential to contaminate water and care should be taken that adsorption of contaminants from the water does not transform the waste into a hazardous material. However, targeted use of such materials could not only successfully treat water, but also provide an alternative outlet for materials that may otherwise add to an ever-growing waste problem. Achievement of a circular economy is an ultimate goal, and although this is not likely to be attained in the near future, technologies that find a use for waste materials is undoubtedly a step in the right direction.

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Appendix A

A1: Science of the Total Environment

Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water

Maebh A. Grace, Mark G. Healy*, Eoghan Clifford

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Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water

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HIGHLIGHTS

- The use of waste media in the water sector results in a robust, sustainable option.
- Fly ash and Bayer residue successfully adsorb TOC, nutrients and Cu.
- Granular blast furnace slag and pyritic fill have good adsorption potential.
- pH adjustment is not necessary for optimal adsorption of contaminants.
- Kinetic studies show that at least 60% of adsorption had taken place after 8 h.

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ABSTRACT

Filtration technology is well established in the water sector but is limited by inability to remove targeted contaminants, found in surface and groundwater, which can be damaging to human health. This study optimises the design of filters by examining the efficacy of seven media (fly ash, bottom ash, Bayer residue, granular blast furnace slag (GBS), pyritic fill, granular activated carbon (GAC) and zeolite), to adsorb nitrate, ammonium, total organic carbon (TOC), aluminium, copper (Cu) and phosphorus. Each medium and contaminant was modelled to a Langmuir, Freundlich or Temkin adsorption isotherm, and the impact of pH and temperature (ranging from 10 °C to 29 °C) on their performance was quantified. As retention time within water filters is important in contaminant removal, kinetic studies were carried out to observe the adsorption behaviour over a 24 h period. Fly ash and Bayer residue had good TOC, nutrient and Cu adsorption capacity. Granular blast furnace slag and pyritic fill, previously un-investigated in water treatment, showed adsorption potential for all contaminants. In general, pH or temperature adjustment was not necessary to achieve effective adsorption. Kinetic studies showed that at least 60% of adsorption had occurred after 8 h for all media. These media show potential for use in a multifunctional water treatment unit for the targeted treatment of specific contaminants.

1. Introduction

The demand for clean water is increasing due to population growth, urbanisation, climate change and the development of technologies such as biofuels and hydropower (Bazilian et al., 2011; Olsson, 2013). Many conventional water treatment processes rely heavily on chemicals and energy, along with capital and expertise (Shannon et al., 2008). In the developing world, there is a requirement for basic water treatment facilities that are effective but do not require chemical and energy-intensive technologies. The development of decontamination technologies or the modification of existing, established technologies with sustainable, low-cost materials is essential to promote good human health, protect the environment and reduce water scarcity (Shannon et al., 2008).

The World Health Organisation (WHO) (WHO, 2011) has identified nitrate (NO_3^-) as one of the key chemicals that can cause widespread health effects following short-term exposure, and, in Ireland the maximum allowable concentration (MAC) in drinking waters is 10 mg NO_3^--N L^{-1} (S.I. No 278 of 2007). Ammonium (NH_4^+) is also a parameter of concern, particularly where further nitrification could occur within the water supply system, leading to a suppressed pH and dissolved oxygen (DO) concentration (Wilczak et al., 1996), and increased NO_3^- concentrations in the water supply (Lipponen et al., 2002). In Ireland, for example, the MAC is 0.3 mg NH_4^+-N L^{-1} (S.I. No 278 of 2007). Irish legislation is derived from European Communities (Drinking Water) (No. 2) Regulations 2007, meaning that these values are applicable not only in Ireland but across Europe, and in most cases compare to US regulations (USEPA, 2009). Total organic carbon (TOC) is a measure of the organic carbon content of the water. Irish legislation does not state a MAC, but requires action if an abnormal change is noted (S.I. No 278 of 2007). The presence of TOC

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indicates a potential for disinfection by-product (DBP) formation once chlorination has occurred (Gopal et al., 2007). High concentrations of TOC, particularly of the humic acid form, in water will react with chlorine (Cl) to form disinfection by-products, frequently referred to as 'emerging contaminants' (EC) (WHO, 2011; Gibert et al., 2013). Disinfection by-products can take different formations depending on the molecules available; the most common being total trihalomethanes (TTHM) (Gang et al., 2003), which above a concentration of 100 μg L^{-1} may be harmful to human health (Minear and Amy, 1996; S.I. No 278 of 2007). Removal of organic matter is seen as the most effective way to prevent trihalomethane (THM) formation. Therefore, it is necessary to limit the potential of formation of DBP by removing TOC at source (Minear and Amy, 1996).

Aluminium (Al) can also be an important indication operational efficiency in a water treatment plant (WTP), as, for example, its presence can be caused by poor pH control (EPA, 2010). For example, if pH is not sufficiently controlled, coagulation may not be effective, resulting in Al traces in drinking water where aluminium sulphate is used as a coagulant. It is also a naturally occurring metal, and due to the perceived association between it and dementia, is an important contaminant to control (Calderon, 2000). The MAC is 0.2 mg Al L^{-1} (S.I. No 278 of 2007). The presence of copper (Cu) in drinking water results primarily from interior copper plumbing. However, highly aggressive or acidic raw waters may result in increased Cu concentrations. Removal of Cu is also important for good human health, as it is known to result in gastric irritation (WHO, 2011). The MAC of Cu varies from 1.3 mg L^{-1} in the USA (USEPA, 2009) to 2 mg L^{-1} in Ireland (S.I. No 278 of 2007). Phosphorus (P) is a nutrient required in food production and can enter drinking water sources through surface runoff and (in certain soil types) subsurface drainage from agricultural lands (Cordell et al., 2009). Low phosphate-phosphorus (PO_4^{3-}-P) concentration in water supplies is important to restrict microbial growth in distribution systems (Miettinen et al., 1997). To achieve successful decontamination of raw water supplies, it is essential to reduce the concentration of each contaminant to below the specified MAC.

Conventional WTPs comprise screening, coagulation/flocculation, sedimentation, filtration and disinfection processes (EPA, 1995). A key aspect of this design is contaminant removal, which may encompass physical, biological and chemical processes. The design of a filter focuses predominantly on physical removal techniques, namely, straining and adsorption.

Sand is most commonly used in filters, but dual and mixed media filter configurations, introduced in the 1960s, encourage the use of anthracite, coal and garnet (Hendricks, 2011). However, sand is a finite resource and may not be effective for the adsorption of some EC. Red mud has been used to remove NO_3^- (Cengeloglu et al., 2006). Red mud, crushed concrete and fly ash have also P adsorption capacities of between 2.49 and 19.6 g kg^{-1} (Li et al., 2006; Egemose et al., 2012). Synthetic zeolites have been used to remove Cu (Peña et al., 2000) and natural zeolites have been used to remove NH_4^+ (Widiastuti et al., 2011). However, little research has been conducted into the ability of novel media to remove/adsorb multiple parameters and EC. Therefore, there is a need to investigate the efficacy of alternative, sustainable resources which may be potentially better able to remove EC from water.

Adsorption is a surface phenomenon, and can be defined as the process whereby substances in solution (adsorbate) are accumulated on a suitable interface (adsorbent) (Metcalf and Eddy, 2003). Temperature, kinetics, pH, and the nature of the adsorbate and adsorbent can affect adsorption (Ali and Gupta, 2006). Adsorption isotherms, such as those developed by Langmuir, Freundlich, Elovich and others (Ali and Gupta, 2006; Foo and Hameed, 2010), may be used to model adsorption. However, it has been shown that the maximum adsorption capacity, as calculated by the Langmuir model, does not always correlate with removal in a complex reaction system (Arias et al., 2001). Nonetheless, in literature it is applied in over 95% of liquid-phase adsorption systems (Foo and Hameed, 2010).

The aim of this study was to quantify the efficacy of various novel media, which could potentially be used in water filtration systems, operated under different temperatures and pH, to remove nutrients (NO_3^--N, PO_4^{3-}-P, NH_4^+-N), TOC (as a precursor to EC) and metals (Al, Cu) from water. The media investigated were coarse sand (the study control), zeolite, granular activated carbon (GAC), pyritic fill, Bayer residue, bottom ash, fly ash, and granular blast furnace slag (GBS).

2. Materials and methods

2.1. Media characterisation

The composition of the media, as well as their effective sizes (d_{10}), as determined using BS 1377-2:1990 (BSI, 1990) is shown in Table 1. Coarse sand was sourced from a quarry specialising in water filter media. Zeolite contains naturally occurring clinoptilolite, which is a known ion exchanger (Hendricks, 2011). Granular activated carbon is formed by the pyrolysis of a carbonaceous substance, followed by a controlled oxidation stage to activate the carbon (Cooney, 1999). Bayer residue is a waste product of the Al manufacturing process and is stored in large lagoons, resulting in storage and potential environmental problems (Brunori et al., 2005). Bottom ash and fly ash are by-products of incineration. Pyritic fill is a waste product of the construction industry. Granular blast furnace slag is a by-product of the steel manufacturing industry, and is mainly used as a cement substitute in a reduced carbon footprint concrete mix.

The media characterisation in Table 1 was carried out by Brookside Laboratories Inc, USA. Metals were analysed using Mehlich-3 soil test extractant (Mehlich, 1984), and the total exchange capacity was analysed using TEC by summation (Ross, 1995).

2.2. Adsorption isotherms

One gramme of each media, with particle sizes as tabulated in Table 1, was placed in separate 50 mL capacity containers (at $n = 3$), and was overlain by 25 mL of deionised water made up to concentrations of 0, 5, 10, 20, 30, 50, 60 and 100 mg L^{-1} of either NO_3^--N, NH_4^+-N, PO_4^{3-}-P, or TOC; 0, 10, 20, 30, 100, 500 and 1000 mg L^{-1} of Cu; and 0, 0.3, 0.4, 0.5, 0.8 and 1 mg L^{-1} of Al. Nitrate, NH_4^+-N and PO_4^{3-}-P were made up using KNO_3, NH_4Cl and K_2PO_4 reagent-grade powders, respectively (APHA, 1995). Total organic carbon was made up using laboratory-grade humic acid, adapted from the method described in Abdul et al. (1990). Solutions of Cu and Al were sourced from a supplier (Hach Lange, Germany). Each sample mixture was placed on a reciprocal shaker for 24 h at 250 rpm. At $t = 24$ h, the supernatant water in each container was filtered through 0.45 μm filters and analysed for the nutrient or metal of interest. The initial and final concentrations of NO_3^--N, NH_4^+-N, PO_4^{3-}-P and Al were analysed using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Total organic carbon was analysed using a TOC analyser (BioTector Analytical Systems Ltd) and Cu was analysed using a spectrophotometer (Hach Lange, Germany). To ascertain whether any of the media released metals, the 0 mg L^{-1} samples were split and sent for metal analysis by ICP-MS. The suite of metals included Al, barium, calcium (Ca), cadmium, magnesium, potassium, chromium, iron (Fe), mercury, manganese, nickel, lead, boron, copper and sodium.

The data were modelled either by Langmuir, Freundlich or Temkin adsorption isotherms. The Langmuir isotherm assumes monolayer adsorption sites with equal energies, and that adsorption is reversible (Metcalf and Eddy, 2003). The form of the Langmuir isotherm is (McBride, 2000):

$$q_i = q_{max}\left(\frac{k_A C_e}{1 + k_A C_e}\right) \tag{1}$$

where q_i is the quantity of contaminant adsorbed per gramme of media (g g^{-1}), C_e is the equilibrium contaminant concentration in the pore water (g m^{-3}), k_A (m^3 g^{-1}) is a measure of the affinity of the contaminant

Table 1
Physical and chemical characterisation of media.

Media	Coarse sand[a]	Zeolite[b]	Pyritic fill[c]	Bayer residue[d]	Fly ash[e]	GBS[f]	Bottom ash[e]	GAC[g]
Chemical (%)								
SiO_2	97.72	65–72	74 ± 10	8.9	60.37	35	–	–
Fe_2O_3	1.26	0.8–1.9	2.9 ± 1.5	43.8	8.27	–	–	–
Al_2O_3	0.21	10.0–12	7.6 ± 0.9	15.04	20.53	10	–	–
K_2O	0.05	2.3–3.5	1.05 ± 0.15	–	1.89	–	–	–
L.O.I[h]	0.36	9.0–12	–	9.5	–	–	–	–
CaO	–	2.5–3.7	5.4 ± 5.1	6.6	2.26	40	–	–
MgO	–	0.9–1.2	0.6 ± 0.14	0.09	1.95	8	–	–
Na_2O	–	0.3–0.65	0.3 ± 0.15	5.32	0.65	–	–	–
TiO_2	–	0–0.1	0.3 ± 0.03	9.2	1	–	–	–
MnO	–	0–0.08	0.05 ± 0.05	–	–	–	–	–
SO_4	–	–	7.6 ± 5.7	0.41	2.15	–	–	–
P_2O_5	–	–	–	0.36	0.22	–	–	–
Un-determined		–	–	–	0.71	–	–	–
Al (%)							0.42	
Ca (%)	62.5	22.68	79.12	25.22	84.98	77.13	0.4	9.85
Fe (%)							1.6	
K (%)	4.27	48.94	0.58	0.45	0.12	0.75	0.04	77.73
Al (mg kg^{-1})	87	263	163	8388	1223	2083		49
Cd (mg kg^{-1})		–	–	–	–	–	0.28	–
Co (mg kg^{-1})		–	–	–	–	–	0.43	–
Cr (mg kg^{-1})		–	–	–	–	–	14.3	–
Cu (mg kg^{-1})	4.65	1.18	9.29	4.17	4.35	0.25	8.1	0.55
Fe (mg kg^{-1})	39	23	687	59	189	90		14
Mg (mg kg^{-1})	22.57	12.8	6.04	0.18	13.59	20.38	2120	3.78
Mn (mg kg^{-1})	3.00	15.00	64.00	1.00	22.00	95.00	92	2.00
Mo (mg kg^{-1})		–	–	–	–	–	0.63	–
Na (mg kg^{-1})	15.00	655.00	48.00	18,280	175.00	174	859	219.00
Ni (mg kg^{-1})		–	–	–	–	–	9.9	–
P (mg kg^{-1})	4	3	3	10	1044	4	171	87
Pb (mg kg^{-1})		–	–	–	–	–	3.9	–
V (mg kg^{-1})		–	–	–	–	–	13.7	–
Zn (mg kg^{-1})	1.37	1.64	13.80	0.4	4.43	0.49	19.7	0.4
Iodine no (mg gm^{-1})		–	–	–	–	–	–	1100
Moisture (%)		–	–	–	–	–	–	5
Ash (%)		–	–	–	–	–	–	4
Effective size (mm)	1.31	1.02	0.34	0.06	0.06	0.36	0.64	0.58
Total exchange capacity (meq 100 g^{-1})	0.96	22.13	80.76	108.8	54.19	80.42		12.99

[a] Irwin's Quality Aggregates.
[b] Zeolite Ireland Ltd.
[c] Sandberg LLP.
[d] Rusal Aughinish.
[e] ESB Energy International Moneypoint.
[f] Ecocem Ireland Ltd.
[g] Indo German Carbons Ltd.
[h] Loss on ignition.

for the media, and q_{max} (g g^{-1}) is the maximum amount of contaminant that can be adsorbed onto the media.

Unlike the Langmuir isotherm, the Freundlich isotherm assumes a heterogeneous surface and a non-uniform distribution of heat of adsorption (Widiastuti et al., 2011):

$$q = K_F C_e^{1/n} \tag{2}$$

where K_F is the Freundlich capacity factor, $1/n$ is the intensity parameter, and C_e and q are as in Eq. (1).

The Temkin isotherm is slightly different from the other adsorption isotherms in that it considers the adsorbate–adsorbate interactions, and assumes that due to these, the heat of adsorption of molecules decreases linearly with coverage (Vijayaraghavan et al., 2006):

$$q_e = B_1 \ln(K_t C_e) \tag{3}$$

where C_e and q are as above, K_t is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, and the constant B_1 is related to the heat of adsorption. B_1 is defined as $\frac{RT}{b}$, where R is the gas constant (0.008134 kJ $(mol\ K)^{-1}$), T is the absolute temperature (degrees K) and b is the constant related to the heat of sorption (J mol^{-1}).

2.3. Kinetics of adsorption

The rate at which adsorption occurred was measured using kinetic studies. In these studies, the samples were prepared as in Section 2.2, placed on the reciprocating shaker for 24 h, and 2.5 mL samples were taken at t = 1, 4, 8, 12 and 24 h. Analysis of the data accounted for the volume withdrawn at each sampling interval, and the mass adsorbed over time was calculated.

2.4. Effect of pH on adsorption

The effect of pH on adsorption was examined by adjusting the pH of each sample before shaking on the reciprocal shaker. The pH was adjusted to approximately 4 by the addition of 1 mol L^{-1} HCl to the supernatant-spiked water. The unadjusted pH was between 6 and 11. The samples were then shaken for 24 h at room temperature and the appropriate adsorption isotherm was fitted to the data. The pH-adjusted samples were analysed with the Langmuir or Freundlich isotherms, depending on best fit.

2.5. Effect of temperature on adsorption

To study the effect of temperature on adsorption, experiments similar to those above were carried out at three temperatures, 10 °C, 19 °C, and 29 °C. The samples were prepared as in Section 2.2 and placed on the reciprocating shaker in stabilized temperature conditions for 24 h. The data were fitted to an appropriate isotherm model and using the Langmuir constant (k_A), free energy change, or adsorption energy, was calculated using the thermodynamic formula (Khan and Singh, 1987; Liu, 2009; Widiastuti et al., 2011):

$$\Delta G^\circ = -RT \ln K \tag{4}$$

where ΔG° is the adsorption energy (kJ mol^{-1}), R is the ideal gas constant (0.008314 kJ mol^{-1} K^{-1}), T is the temperature (degrees Kelvin), and K is the Langmuir equilibrium constant. It is known that the equilibrium constant of adsorption depends on the isotherm model selected, and constants determined by different methods are not comparable (Liu, 2009). For this reason, only data fitting to the Langmuir isotherm were compared.

3. Results and discussion

3.1. Adsorption isotherms

Many of the industrial by-products examined had good potential as adsorption media for nutrients and metals (Table 2). Fly ash performed well, particularly with regard to TOC, PO_4^{3-}-P, NH_4^+-N and Cu. The presence of surface oxides on fly ash may adsorb organic compounds, such as TOC (Cooney, 1999). Fly ash also had a high total exchange capacity, which promotes NH_4^+-N and metal adsorption (Rengaraj et al., 2004; Widiastuti et al., 2011). Phosphorus adsorption is indicative with the presence of binding elements such as Ca, Fe and Al on fly ash (Table 1). These results are consistent with previous work (Ali and Gupta, 2006; Li et al., 2006). However, fly ash desorbed Al, resulting in a concentration of 0.255 Al mg L^{-1} after shaking with deionised water for 24 h. Adsorption capacities of Cu of up to 18.8 mg g^{-1} have also been observed (Visa, 2012).

Bayer residue was effective in terms of nutrient and Cu adsorption. This was expected due to the cation exchange and metals present (Table 1). These results were consistent with Lopez et al. (1998), who measured Cu adsorption of the same order as the current study.

Table 2
Adsorption constants for Langmuir and Freundlich adsorption isotherms at 19 °C.

Contaminant	Media	Isotherm	R^2	Q_{max} (μg g^{-1})	1/n	K	B_1	K_t
TOC	Coarse sand	Desorption						
	Zeolite	Langmuir	0.71	37				
	Fly ash	Freundlich	0.73		1.17	0.262		
	Bottom ash	Langmuir	0.54	48				
	GAC	Langmuir	0.42	327				
	GBS	Freundlich	0.86		1.56	0.101		
	Pyritic fill	Freundlich	0.85		1.66	0.152		
	Bayer residue	Freundlich	0.83		0.68	0.019		
Nitrate	Coarse sand	Freundlich	0.86		0.76	0.002		
	Zeolite	Desorption						
	Fly ash	Desorption						
	Bottom ash	Desorption						
	GAC	Temkin	0.68				0.26	0.31
	GBS	Langmuir	0.66	45				
	Pyritic fill	Freundlich	0.9		2.57	0.009		
	Bayer residue	Freundlich	0.71		1.95	0.00003		
Ammonium	Coarse sand	Langmuir	0.83	44				
	Zeolite	Langmuir	0.81	1044				
	Fly ash	Freundlich	0.82		0.79	0.0129		
	Bottom ash	Freundlich	0.92		0.49	0.0037		
	GAC	Freundlich	0.86		1.25	0.0003		
	GBS	Freundlich	0.81		1.00	0.0029		
	Pyritic fill	Freundlich	0.87		0.86	0.0040		
	Bayer residue	Langmuir	0.83	57				
Aluminium	Coarse sand	Langmuir	0.85	0.66				
	Zeolite	Langmuir	0.74	1.20				
	Fly ash	Desorption						
	Bottom ash	Langmuir	0.81	0.18				
	GAC	Langmuir	0.63	3.68				
	GBS	Desorption						
	Pyritic fill	Langmuir	0.76	1.4				
	Bayer residue	Desorption						
Phosphate	Coarse sand	Freundlich	0.51		0.34	0.0118		
	Zeolite	Langmuir	0.68	13				
	Fly ash	Langmuir	0.99	6480				
	Bottom ash	Freundlich	0.74		0.54	0.0038		
	GAC	Langmuir	0.82	41				
	GBS	Langmuir	0.99	3610				
	Pyritic fill	Langmuir	0.97	878				
	Bayer residue	Langmuir	0.97	204				
Copper	Coarse sand	Langmuir	0.88	20.6				
	Zeolite	Langmuir	0.9	771				
	Fly ash	Langmuir	0.89	1381.6				
	Bottom ash	Langmuir	0.92	79.3				
	GAC	Langmuir	0.87	22.8				
	GBS	Langmuir	0.83	2259.9				
	Pyritic fill	Langmuir	0.91	1357.5				
	Bayer residue	Langmuir	0.79	1201.7				

However, desorption of Al and Fe were observed in the current study, with concentrations of Al and Fe in the supernatant water after 24 h of shaking of 4 mg Al L^{-1} and 2.3 mg Fe L^{-1}, respectively.

Granular blast furnace slag is not currently studied in terms of nutrient or metal adsorption, as its sole use is in cement production. However, based on the analysis in Table 1, the high cation exchange capacity and the metals present would indicate that this medium does have adsorption potential. However, its tendency to solidify when saturated with water may be a limiting factor in its use for water treatment. It was also observed that GBS desorbed Al after shaking for 24 h, and had a final concentration of 3.6 mg L^{-1}.

Bottom ash did not appear to be as effective as the other industrial by-products in nutrient or metal adsorption. However, pyritic fill performed well across all six contaminants (Table 2), but did not rank highest in the removal of any contaminant. The composition of pyritic fill may be predominantly mudstone or sandstone, depending on the location in which it is quarried, so its adsorption capacity is potentially variable. However, mineral pyrite has been recognised as an adsorbent, particularly regarding P, and adsorption capacities of up to 1.6 mg PO_4^{3-}-P g^{-1} have been measured (Chen et al., 2015). It is known that P binding occurs in the presence of Ca, Al and Fe oxides (Egemose et al., 2012), which explains the results of the pyritic fill adsorption studies.

The performance of zeolite in NH_4^+-N removal, at 1.04 mg g^{-1}, was lower than that observed with Australian zeolite (Widiastuti et al., 2011). This could be attributed to the difference in location of the mined zeolite. Ortho-phosphate adsorption was poor and shaking with NO_3^--N resulted in desorption, meaning anion adsorption was poor. However, metal adsorption by zeolite was very effective, in terms of both Cu and Al, and was due to the ion exchanging capacity of zeolite (Hendricks, 2011).

Granular activated carbon adsorbed all three nutrients, but did not perform as well as some industrial by-products examined in this study. This was due to the lesser amount of metal oxides available for nutrient interaction. Adsorption of TOC was particularly strong, and it performed well for both metals analysed. Coarse sand was more effective than GAC in nutrient adsorption, and while it had good metal removal, it was not as effective as GAC. Aside from the metal desorption stated above, the ICP-MS analysis did not identify desorption of any other metals.

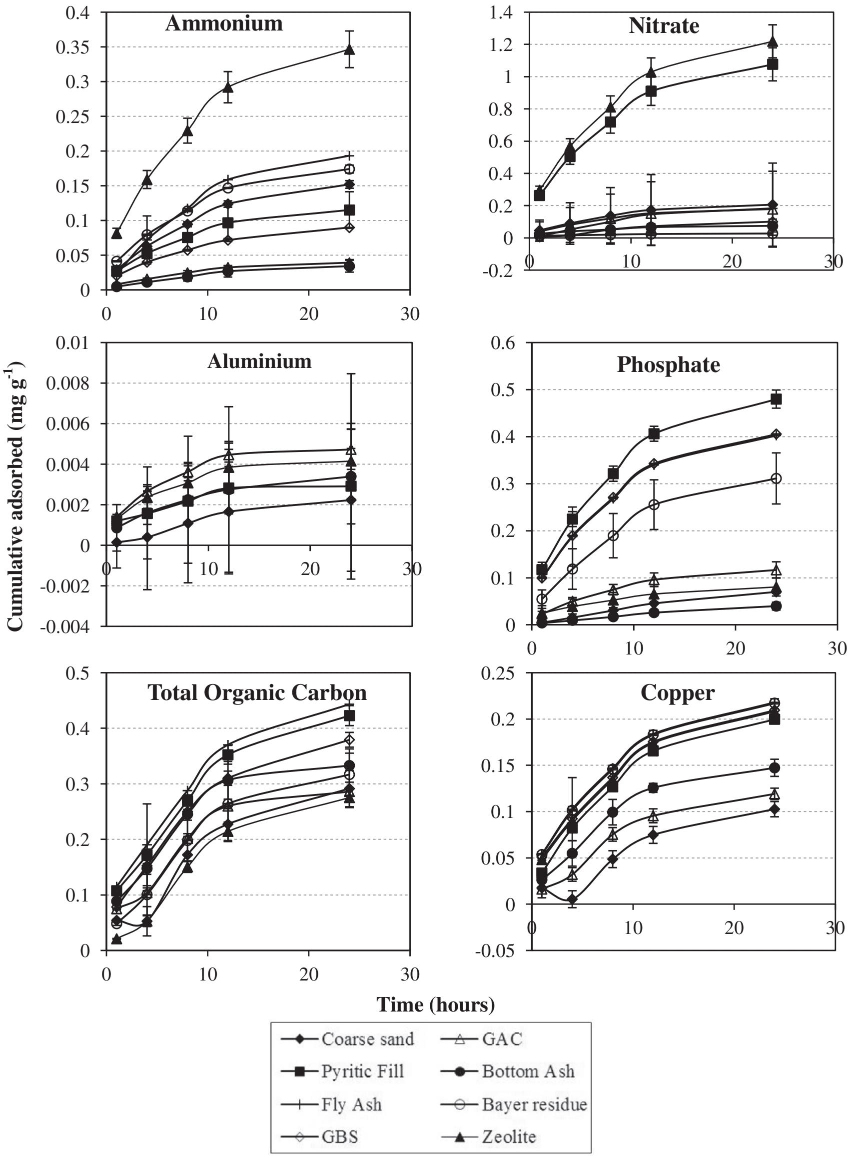

Fig. 1. Kinetic results over a 24 hour period at 19 °C.

3.2. Kinetics of adsorption

Fig. 1 shows the kinetic results for the contaminants and media tested. All the media adsorbed 60% of the NH_4^+-N within 8 h of contact. Nitrate, Al and P adsorption followed the same trend. Copper adsorption was slightly different, in that for zeolite, pyritic fill, GBS, Bayer residue and fly ash, almost all adsorption had taken place after 4 h. Total organic carbon adsorption by fly ash occurred almost immediately, with 96% of adsorption occurring within one hour. There was a decrease in the rate of adsorption for all media after 8 h. This was most likely due to adsorption sites becoming unavailable. This was to be expected, as initially, the concentration of the adsorbate is high, and all sites are vacant (Widiastuti et al., 2011).

3.3. Effect of pH on adsorption

Table 3 shows the effect reducing pH had on the adsorption of each contaminant for each media. For TOC adsorption, bottom ash (without pH modification) was modelled by Langmuir isotherm. However, the data were modelled to Freundlich when the pH was adjusted. This was based on the fit of the regression coefficient. Coarse sand desorbed TOC at unadjusted pH, but some adsorption activity was observed when the pH was adjusted to 4. For the other media (zeolite, fly ash, GAC, GBS, pyritic fill and Bayer residue), pH adjustment allowed for increased adsorption of TOC. This was to be expected as the TOC comprised mainly humic acid, and acidic species are known to adsorb more effectively at lower pH (Cooney, 1999). These results indicate that the benefits of adjusting the pH would likely not be a cost-effective intervention in improving adsorption kinetics.

Nitrate did not model well to any of the above isotherms following pH adjustment. Where modelling was successful, the differences between the unadjusted and adjusted K values from the Freundlich isotherm were small.

In general, NH_4^+-N adsorption did not improve with pH adjustment. Zeolite modelled well to Langmuir isotherm following pH adjustment, and demonstrated improved adsorption characteristics, reflecting observations in literature (Widiastuti et al., 2011).

pH adjustment allowed Bayer residue to slightly adsorb Al (1 $\mu g\ g^{-1}$), which desorbed at an unadjusted pH. pH adjustment had a tendency to improve Al adsorption except in the case of GAC, where the adsorption capacity was halved with pH adjustment. pH adjustment was not necessary to improve PO_4^{3-}-P removal, except with bottom ash, where it improved adsorption. Previous studies have noted a positive relationship between pH and retention capacity for P with rates of adsorption increasing with pH (Egemose et al., 2012). Copper adsorption proved to be more effective at a unadjusted pH, reflecting other studies, where it has been found that adsorption can increase as much as 85% when the pH is increased from 2.5 to 8 (Chen et al., 1996).

Table 3
Isotherm constant comparisons for unadjusted isotherm tests (pH 6–11) and pH adjusted (pH 3.5–4).

Contaminant	Media	Langmuir Q_{max} adjusted	Q_{max} unadjusted	Freundlich K adjusted	K unadjusted
TOC	Zeolite	0.141	0.037		
	Fly ash			2.9	0.26
	GAC	0.298	0.327		
	GBS			0.075	0.101
	Pyritic fill			0.178	0.152
	Bayer residue			0.132	0.019
Nitrate	Pyritic fill			0.094	0.009
	Bayer residue			0.032	$3.41 * 10^{-5}$
Ammonium	Sand	0.054	0.044		
	Fly ash	0.0002	0.0129		
	GBS	0.0003	0.0029		
	Pyritic fill	0.0003	0.004		
Aluminium	Sand	0.0031	0.0006		
	Zeolite	0.0025	0.0012		
	Bottom ash	0.0010	0.0001		
	GAC	0.0018	0.0036		
	Pyritic fill	0.0013	0.0014		
Phosphate	Zeolite	0.05	0.01		
	GAC	0.04	0.04		
	GBS	0.21	3.61		
	Bayer residue	0.17	0.20		
Copper	Sand	0.020	0.020		
	Zeolite	0.020	0.771		
	Bottom ash	0.010	0.079		
	GAC	0.019	0.022		

3.4. Effect of temperature on adsorption

Table 4 displays the data from the thermodynamic study. The data analysis was limited due to the use of the Langmuir adsorption isotherm to calculate the equilibrium constant used in Eq. (4). Therefore, data not modelled to Langmuir across more than one temperature range were excluded from the table for clarity. The negative values of the adsorption energy ($\Delta G°$) indicate that the adsorption process was of a spontaneous nature, and heat energy was released, for each set of reactions modelled (Widiastuti et al., 2011). Coarse sand adsorption is more energetically favourable at lower temperatures for both NH_4^+-N and Cu, as indicated by decreasing values at lower temperatures. Zeolite adsorption was more energetically favourable with increasing temperature for PO_4^{3-}-P, similar to earlier studies investigating zeolite adsorption of nutrients (Widiastuti et al., 2011). It has been noted that Cu adsorption is not radically affected by temperature (Gündoğan et al., 2004). However, the results of the current study indicate that it is more favourable at a lower temperature — a positive result for a filtration unit that would most likely be located outdoors. Granular activated carbon adsorption tended to be more energetically favourable at lower temperatures, as expected, as adsorption onto carbon is likely to be lower as the temperature increases (Cooney, 1999). For pyritic fill, the lower temperatures were also more effective.

3.5. Impact of adsorption isotherm studies on filter design

Based on the adsorption isotherms developed in this study, the media may be used in filters to target specific problematic contaminants that may be present in abstraction water. These media can be layered to create an effective, sustainable and multifunctional treatment system, using alternative media, without, as demonstrated in this study, the need for adjustment of the pH of the water prior to filtration. A layered configuration would also allow the utilisation of adsorption properties from each of the media, while having the ability to control any potential metal leaching. The kinetics study indicate that as long as the average hydraulic retention time within a filter exceeds eight hours, effective water treatment will occur.

Table 4
Thermodynamic data analysis at 10 °C, 19 °C and 29 °C.

Media	Contaminant	ΔG @ 10 °C	ΔG @ 19 °C	ΔG @ 29 °C
Coarse sand	Ammonium	−36.00	−21.78	
	Copper	−37.04	−32.54	
Zeolite	Phosphate	−23.59	−25.94	
	Copper	−33.72	−27.12	
Fly ash	Copper	−35.41	−18.76	
GAC	Aluminium	−29.69	−30.82	−30.77
	Phosphate	−32.32	−21.71	−26.18
	Copper	−33.11	−18.79	
Pyritic fill	Aluminium		−36.62	−41.67
	Phosphate	−36.00	−15.31	
	Copper	−33.44	−18.66	−39.45
Bayer residue	Ammonium	−17.87	−23.34	−11.75
	Phosphate	−22.65	−17.94	−20.88
	Copper		−18.15	−29.01

The study investigated a variety of media, impacts of temperature and pH on each, as well as a variety of compounds commonly found in contaminated water. Some of the media investigated currently poses problems with disposal and/or storage. The potential use of these media in the water sector may result in a more sustainable option for what are otherwise considered to be waste materials. The wide variety of materials explored in this study could enable designers use locally sourced material depending on the availability in the area. Work following on from this study will focus on laboratory and site-scale trials and desorption mechanisms to enable media reuse. These studies will focus on long-term issues such as sustainability, robust operation in the natural climate, and filter clogging.

4. Conclusions

The main conclusions from the study were:

- Fly ash and Bayer residue, which have been previously identified as having adsorption potential, were shown in this study to successfully adsorb TOC, nutrients and Cu, and thus, improving environmental quality by re-using industrial waste products for pollution control.
- Granular blast furnace slag and pyritic fill have good adsorption potential (unreported to date). Granular activated carbon and zeolite, known ion exchangers and adsorptive media, proved successful with each contaminant analysed in this study.
- Improved adsorption occurs at lower pH for TOC. However, for other water parameters, depending on the media, pH adjustment is not necessary for optimal adsorption. In this study, there was no instance in which pH adjustment was necessary for adsorption; therefore adjusting pH is unlikely to be a cost-effective intervention to improve adsorption kinetics. In the case of Cu and PO_4^{3-}-P, it was found that optimal adsorption occurred at the unadjusted pH.
- Kinetic adsorption studies showed that at least 60% of adsorption (where adsorption occurred) had taken place after eight hours. This would be useful in designing a filter using these media, as the retention time can be adjusted to achieve the required adsorption.

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Performance and surface clogging in intermittently loaded and slow sand filters containing novel media

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Performance and surface clogging in intermittently loaded and slow sand filters containing novel media

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ABSTRACT

Slow sand filers are commonly used in water purification processes. However, with the emergence of new contaminants and concern over removing precursors to disinfection by-products, as well as traditional contaminants, there has recently been a focus on technology improvements to result in more effective and targeted filtration systems. The use of new media has attracted attention in terms of contaminant removal, but there have been limited investigations on the key issue of clogging. The filters constructed for this study contained stratified layers comprising combinations of Bayer residue, zeolite, fly ash, granular activated carbon, or sand, dosed with a variety of contaminants (total organic carbon (TOC), aluminium (Al), ammonium (NH_4^+-N), nitrate (NO_3^--N) and turbidity). Their performance and clogging mechanisms were compared to sand filters, which were also operated under two different loading regimes (continuous and intermittently loaded). The study showed that the novel filter configurations achieved up to 97% Al removal, 71% TOC removal, and 88% NH_4^+-N removal in the best-performing configuration, although they were not as effective as sand in terms of permeability. Deconstruction of the filters revealed that the main clogging mechanism was organic matter build-up at the uppermost layer of the filters. The clogging layer formed more quickly on the surface of the novel media when compared to the sand filters, but extended further into the sand filters, the extent dependent on the loading regime. The study shows the potential for an alternative filtration configuration, harnessing the adsorption potential of industrial waste products and natural media.

1. Introduction

Slow sand filters are commonly used in water treatment to remove contaminants by physical, chemical and biological mechanisms (EPA, 1995), but they may not be effective in the removal of specific contaminants, 'emerging contaminants' (EC), or precursors to disinfection by-products (DBP), such as dissolved organic carbon (DOC) (Gang et al., 2003; Chuang et al., 2011; EPA, 2015). Consequently, there has been much research into the use of alternative media, particularly industrial by-products and waste products, or coated media, for use in filters for the treatment of targeted contaminants (Bhatnagar and Sillanpää, 2010; Fu and Wang, 2011; Rahman et al., 2013). Although these media have been examined extensively at bench-scale level, their efficacy has been infrequently examined in laboratory, pilot or large-scale filters (Bailey et al., 1999; Bhatnagar et al., 2011). This is a major knowledge gap, as a layered configuration in a water filter may allow the utilisation of adsorption properties from each of the media, and may have the ability to control any potential metal leaching. Moreover, the use of waste materials in a filtration unit is potentially an effective and sustainable means of water treatment. While the viability of these media for use in filters depends on their efficacy in the removal of contaminants, it equally depends on their capacity to treat water without clogging.

Clogging mechanisms in sand filters for the treatment of wastewater (Hatt and Fletcher, 2008; Leverenz et al., 2009) and vertical flow constructed wetlands, which operate in a similar way to filters (Turon et al., 2009; Pedescoll et al., 2009; Hua et al., 2010; Knowles et al., 2011), have been well researched. However, clogging mechanisms in filters for drinking water treatment have not been examined to the same extent. Biological clogging has been the main focus of the research to date (Thullner et al., 2002; Kildsgaard and Engesgaard, 2002; Mauclaire et al., 2004); however, clogging may also occur by chemical and physical mechanisms (Mauclaire et al., 2004; Le Coustumer et al., 2012). This may be particularly

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relevant for water filters. Chemical clogging can affect the shapes and stabilities of the pores in the media, in turn, affecting the flow paths (Baveye et al., 1998). Adsorption of substances and metal precipitation from the influent water may also contribute to clogging within filters (Noubactep et al., 2010). Physical clogging may result from compaction due to loads on the surface of the filter and migration of the fine media into the filter. Therefore, the use of a particularly fine media at the surface may result in a filter cake forming at the media-water interface, contributing to physical clogging (Baveye et al., 1998). Where organic carbon is a component of the influent water, clogging is expected (McKinley and Siegrist, 2011), which may be due to the extracellular polymer substances (EPS) sometimes present in humic acid. These may form a gel-like, hydrophilic structure as the humic acid accumulates (Tanner et al., 1998), increasing the retardation of flow within the filter.

Filter head loss is the most common method of determining clogging at operational facilities (EPA, 1995). Clogging of filter media may be investigated in a number of ways. One of the most common methods is to measure the field saturated hydraulic conductivity (K_{fs}) (Rodgers et al., 2004; Pedescoll et al., 2009; Le Coustumer et al., 2012). As the filter clogs over time, K_{fs} decreases (Knowles et al., 2011). This can be measured using either a falling head test (ASTM, 2007) or constant head test (British Standard Institution, 1990b), depending on the permeability of the media under consideration. Other common methods of analysis include loss-on-ignition (LOI), chemical analysis of the media at different depths throughout the filter, scanning electron microscopy (SEM) of the biofilm layer, and X-Ray diffraction (XRD) analysis (Rodgers et al., 2004; Pedescoll et al., 2009; Knowles et al., 2010; Nivala et al., 2012).

Clogging becomes evident in filters as surface ponding occurs (for intermittent filters) and the outflow flow rate decreases (Knowles et al., 2011). It is important to ascertain how deep the clogging layer is within the filter, as the filter can be regenerated and the hydraulic conductivity restored. This may be accomplished by replacing the clogging layer of the filter with fresh media (Mauclaire et al., 2004). Current guidelines advise the removal and re-sanding of slow sand filters once a predetermined design head loss has been reached (EPA, 1995). However, re-sanding beyond the clogging layer leads to excessive and unnecessary cost.

In the current paper, the water contaminants studied were DOC, aluminium (Al), nitrate-nitrogen (NO_3^--N), ammonium-nitrogen (NH_4^+-N) and turbidity. Dissolved organic carbon present in source water causes formation of DBPs such as trihalomethanes and haloacetic acids following chlorination, and oral ingestion of DBPs can lead to cancer (Wang et al., 2007). Removal of DOC at filtration stage would reduce the potential of DBP formation, which has been the main source of non-compliance in Irish water treatment plants (WTPs) in recent years (Water_Team, 2012). Aluminium is added to water during the treatment processes, but only represents a problem when it is present in the source water due to geological leaching (Calderon, 2000). The maximum allowable concentration (MAC) for Al in water is 200 $\mu g\ L^{-1}$ (SI No 278 of 2007), and epidemiological studies have previously established a link between excessive Al and Alzheimer's disease (Flaten, 2001; Bondy, 2010; Exley and Vickers, 2014), as well as having other human toxicity effects (Nayak, 2002). The MAC for NO_3^--N in drinking water is 10 mg L^{-1} (SI No 278 of 2007), as consumption of high levels of NO_3^--N may cause methemoglobinemia, and can have significant environmental impacts on agricultural and aquatic life (Bhatnagar and Sillanpää, 2011). Ammonium has a MAC of 0.3 mg L^{-1} in drinking water, and is generally present in source water due to anthropogenic activities. A residual presence of NH_4^+-N at the disinfection stage can cause extra chlorine consumption, and may have a negative effect on the disinfection process (Feng et al., 2012), and can suppress pH and dissolved oxygen in the supply system (Wilczak et al., 1996). Legislation states that turbidity must be acceptable to consumers and have no abnormal change (SI No 278 of 2007), except in the case of surface water treatment where 1.0 NTU should be achieved. However, turbidity can also be an indication of likely DBP formation, and excessive turbidity can also inhibit disinfection (EPA, 2011).

This paper focuses on the use of two industrial by-products, Bayer residue ('red mud') and fly ash, and a natural medium, zeolite, combined with granular activated carbon (GAC) and sand, in layered filter configurations. Bayer residue is a waste product of the Al production industry, and is often stored in bauxite residue storage areas close to the production site (EAA, 2013). Fly ash, a by-product of incineration, is most commonly used in the manufacture of concrete (Mehta, 2002). Natural zeolites are known adsorbents of contaminants in water and wastewater treatment (Wang and Peng, 2010). Each of these has been used previously for adsorption of contaminants, although not in stratified filter configurations operated at laboratory-scale, and their maximum adsorption capacities are summarised in Table 1.

While the performance of slow and intermittently loaded filters is important in the selection of suitable filter media, the hydraulic function and permeability are also crucial parameters that need to be considered. Therefore, the aim of this study was to (1) determine the mechanisms of clogging of the filters and (2) assess the performance of intermittently and constantly loaded filters, each containing the novel filter media and operated for a period of 90 days, in the removal of contaminants (DOC, Al, NH_4^+-N, NO_3^--N and turbidity) of water.

2. Materials and methods

2.1. Filter construction

Three filter configurations, each replicated at $n = 3$, were examined with constantly loaded and intermittently loaded operational regimes, giving a total of 18 filters (Fig. 1). The first configuration ('Config 1') was a three-layer stratified filter (each layer had a depth of 0.33 m) containing (downwards from the filter surface) Bayer residue, zeolite and coarse sand. The second configuration ('Config 2') was a four-layer filter, with equal layers of 0.25 m media, containing (downwards from the filter surface) flyash (from coal combustion), GAC, zeolite and coarse sand. The effective particle sizes (d_{10}) of each medium are given in Table 2. The third configuration ('Control') was a 1-m deep single layer sand filter with an d_{10} of 0.18 mm and uniformity coefficient of 2.19 (EPA, 1995). The filter configurations were chosen based on adsorption results obtained by Grace et al. (2015), where NH_4^+-N removal was focused at the surface of the filter, and Al, TOC, and NO_3^--N further down through the media. Locally available media were chosen, where possible. The configurations took cognisance of the K_{fs} of each media, which was measured prior to the experiment. Each filter had a free-board depth of 0.5 m above the filter surface. Physical and chemical characteristics of the media are detailed in Table 2.

2.2. Filter operation

The intermittently loaded filters were subjected to an initial loading rate (day 1 of experiment) of 0.1 m h^{-1} following the Irish EPA guidelines for slow sand filters (intermittent filters are not currently used for large-scale drinking water treatment) (EPA, 1995). The intermittent filters were dosed for 10 min every 2 h using a peristaltic pump (7528-10, Masterflex L/S Variable-Speed Drive). A head of water of 0.5 m was maintained above the constantly loaded filters.

Table 1
Previous use of media for adsorption.

Media	Contaminant	Adsorption capacity (mg g^{-1})	Comment	Reference
Bayer Residue	Phosphorus	1.1	Initial Concentrations between 0.1 and 1 mg L^{-1}	Huang et al., 2008
		345.5	Activated Bayer residue	Li et al., 2006
	Nitrate	115.3	Raw Bayer residue	Cengeloglu et al., 2006
		363.2	Activated bayer residue	Cengeloglu et al., 2006
	Al	0.064		Komnitsas et al., 2004
Fly Ash	Phosphorus	75.4	Activated fly ash	Li et al., 2006
		42.6	Raw fly ash	Vohla et al., 2011
	Flouride	20.3		Bhatnagar et al., 2011
	Copper	2.36		Gupta and Ali 2000
	Zinc	2.54		Gupta and Ali 2000
Zeolites	Ammonium	2.13		Widiastuti et al., 2011
	Lead	9.97		Nguyen et al., 2015
	Copper	8.53		Nguyen et al., 2015
	Zinc	5.83		Nguyen et al., 2015

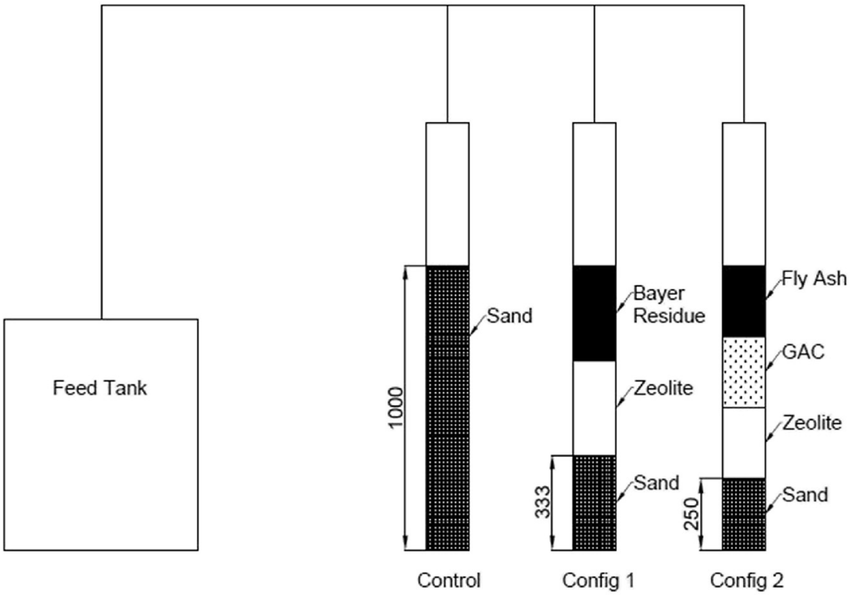

Fig. 1. Filter configurations.

The water feed, the same for both loading regimes, comprised tap water dosed with NH_4^+-N (synthesised using laboratory-grade NH_4Cl to a concentration of 5 mg L^{-1}), NO_3^--N (synthesised using laboratory-grade KNO_3 to a concentration of 20 mg L^{-1}), Al (synthesised using laboratory-grade aluminium powder to a concentration of 2 mg L^{-1}), and DOC (synthesised using laboratory-grade humic acid to a concentration of 10 mg L^{-1}). These concentrations were based on maximum exceedances reported by the Irish EPA (Water_Team, 2012). The humic acid was prepared using a method adapted from Abdul et al. (1990), to remove as much of the non-water soluble fraction as possible. This involved mixing the humic acid with deionised water for 25 min and then centrifuging at 1000 RCF for 30 min before filtering through 0.45 μm filter paper. Using humic acid as the DOC source resulted in influent suspended solids of approximately 200 mg L^{-1}, greater than would be present in a standard groundwater or surface water source, allowing an investigation of clogging occurrence at a high mass loading rate. Irish water quality reports indicate that in surface water, suspended solids concentrations do not often exceed 35 mg L^{-1} (EPA, 2008). The two loading regimes were operated in parallel for 90 days.

2.3. Statistical analysis

Statistical analysis was carried out using SPSS 22 software (IBM, 2014). The data were checked for normal distribution using the Shapiro-Wilk test. The Kruskal-Wallis test for non-parametric data was used, where the null hypothesis is that the distribution, and the medians of the test fields are the same across groups.

2.4. Hydraulic conductivity

The variety of media used in this study meant that both the constant head test (appropriate for media with a K_{fs} of between 10^{-2} and 10^{-5} m s^{-1} (British Standard Institution, 1990b) and the falling head test (appropriate for media with a $K_{fs} \leq 10^{-5}$ m s^{-1}, ASTM, 2007) were required to analyse the K_{fs} of the filters. Samples of the virgin media were tested initially for K_{fs}. At the end of the 90 day trial, samples of media were collected at incremental depths to analyse K_{fs} variation with depth. The sample collection in each filter was terminated when the K_{fs} measured at a given depth returned to that of the virgin sample.

For the constant head test, two undisturbed media cores, 0.5 m

Table 2
Characterisation of media.

Media	Sand[a]	Zeolite[b]	Bayer residue[c]	Fly ash[d]	GAC[e]
Chemical					
SiO_2 (%)	97.72	65–72	8.9	60.37	–
Fe_2O_3 (%)	1.26	0.8–1.9	43.8	8.27	–
Al_2O_3 (%)	0.21	10.0–12	15.04	20.53	–
K_2O (%)	0.05	2.3–3.5	–	1.89	–
L.O.I[f] (%)	0.36	9.0–12	9.5	–	–
CaO (%)	–	2.5–3.7	6.6	2.26	–
MgO (%)	–	0.9–1.2	0.09	1.95	–
Na_2O (%)	–	0.3–0.65	5.32	0.65	–
TiO_2 (%)	–	0–0.1	9.2	1	–
MnO (%)	–	0–0.08	–	–	–
SO_4 (%)	–	–	0.41	2.15	–
P_2O_5 (%)	–	–	0.36	0.22	–
Iodine No (mg gm^{-1})	–	–	–	–	1100
Moisture (%)	–	–	–	–	5
Ash (%)	–	–	–	–	4
Un-determined		–	–	0.71	–
Ca (%)*	–	–	–	–	9.85
K (%)*	–	–	–	–	77.73
Al (mg kg^{-1})*	87	263	8388	1223	49
Cu (mg kg^{-1})*	4.65	1.18	4.17	4.35	0.55
Fe (mg kg^{-1})*	39	23	59	189	14
Mg (mg kg^{-1})*	22.57	12.8	0.18	13.59	3.78
Mn (mg kg^{-1})*	3	15	1	22	2
Na (mg kg^{-1})*	15	655	18,280	175	219
P (mg kg^{-1})*	4	3	10	1044	87
Zn (mg kg^{-1})*	1.37	1.64	0.4	4.43	0.4
Total exchange capacity (meq 100 g^{-1})*	0.96	22.13	108.8	0.06	0.58
Organic matter (%)*	0.1	0.1	5.7	0.22	72.3
Effective size, d_{10} (mm)	1.31	1.02	0.06	0.06	0.58

*Analysis by Brookside Laboratories.

[a] Irwin's Quality Aggregates.

[b] Zeolite Ireland Ltd.

[c] Rusal Aughinish.

[d] ESB Energy International Moneypoint

[e] Indo German Carbons Ltd.

[f] Loss on Ignition.

in diameter, were taken at 0.02 m incremental depths from the filter surface. Water was kept at a constant head over the top of the sample, using an overflow valve to maintain the head of water. The sample was retained in an open-ended vessel to allow the water to flow freely through the sample. The hydraulic gradient was defined as (Rodgers et al., 2004):

$$\frac{dH}{dZ} = 1 + \frac{z}{l}$$

where dH/dZ is the hydraulic gradient, z is the head of water, and l is the height of the sample. The hydraulic gradient was calculated using Darcy's law (Craig, 2004):

$$\frac{Q}{A} = K_{fs}\left(\frac{dH}{dZ}\right)$$

where Q is the volume of water flowing per unit time ($m^3\ s^{-1}$), A is the cross-sectional area (m^2), K_{fs} is the field-saturated hydraulic conductivity (m s^{-1}), and dH/dZ is the hydraulic gradient (m m^{-1}).

The falling head test was carried out at incremental depths of 0.05 m from the surface (the difference in incremental depths between constant and falling head tests was due to limitations with the laboratory apparatus). The samples were saturated for 24 h before being placed in an overflow vessel, which was clamped in an apparatus that allowed a free flow through the base. The reservoir water was de-aired and the manometer was filled. The test was then carried out by allowing the de-aired water in the manometer to flow through the sample. The time taken for the meniscus to fall between two measurements on the manometer was recorded, and the K_{fs} was calculated using (ASTM, 2007):

$$K_{fs} = 2.3\frac{A_2}{A_1}\frac{L}{T}log\left(\frac{h_1}{h_2}\right)$$

where K_{fs} is the field-saturated hydraulic conductivity (m s^{-1}), A_2 is the cross-sectional area of the manometer (m^2), A_1 is the cross sectional area of the sample (m^2), L is the height of the sample (m), T is the time taken for the water level to fall (s), h_1 is the height of the water in manometer at $t = 0$ (m), and h_2 is the height of the water in the manometer at $t = T$ (m).

2.5. *Chemical composition*

Media samples were taken at incremental depths of 0.02 m from the surface. Organic matter analysis was carried out by LOI, as described in Schulte and Hopkins (1996). Metal analysis was carried out using the Mehlich soil extractant method (Mehlich, 1984). Total exchange capacity was carried out using the method described in Ross (1995). Ammonium was analysed using the 1 N KCl method (Dahnke, 1990) and NO_3^--N was analysed using the saturated paste extract method (Gavlak et al., 2003). The media characteristics were determined using BS 1377:2 (British Standard Institution, 1990a).

3. Results and discussion

3.1. Filter performance

The performance of each filter configuration is summarised in Table 3. Turbidity removal was effective among all configurations, although it did not reduce to below the MAC of 1.0 NTU (SI No 278 of 2007). However, the initial turbidity of the synthetic water was much higher than would be expected in raw water prior to treatment. Dissolved organic carbon removal was most effective in Config 2, where higher percentage removals were exhibited in both loading regimes, in comparison to the other configurations. These removal rates, of 63–71%, were also higher than those found in conventional WTPs, which can be expected to remove 10–50% of DOC (Kim and Kang, 2008). Effective DOC removal is important, given that DOC is a pre-cursor to many DBP, and has been identified as a major problem in Irish drinking water treatment plants (EPA, 2015).

Aluminium removal was greater than 94% in all filters, and there was no significant difference in the performance of Config 1 and 2 ($p = 0.114$). In all cases the filters were able to reduce the concentration of Al to below the MAC of 200 μg Al L^{-1} (SI No 278 of 2007). Aluminium removal could attributed to ion exchange, a common practice for Al removal from aqueous solutions (Pesavento et al., 1998). This is particularly likely in the case of Bayer residue which exhibits a high total exchange capacity (Table 1). Aluminium adsorption may also have been enhanced by molecular interaction with humic acid present in the water feed (Elfarissi et al., 1998; Tombácz et al., 2000).

All filters were capable of NH_4^+-N removal, with significantly higher removal of NH_4^+-N occurring in Config 1 and 2, versus the Control, when operated under intermittent loading ($p = 0.01$). The trend of NO_3^--N production, coupled with high NH_4^+-N present in the influent supply and a carbon source, suggested that nitrification was occurring within the filters.

3.2. Visual observation

After 90 days of operation, clogging was observed across all filter configurations. The clogging layer was most likely caused by a build-up of organic matter, due to the loading of humic acid with high suspended solids, and biomass accumulation (Mauclaire et al., 2004). Despite the filters not being seeded with biomass, the occurrence of nitrification indicates that a biomass layer was present. This was evident in both Config 1 and 2, where a gel-like layer was visible on the surface of each column operated in either loading regime (Fig. S1). The Control was slightly different, in that a colour change was evident at the uppermost layer, but the larger particle size meant the gel-like layer was less obvious. This was verified by the organic matter analysis (Section 3.4) on all three configurations, where the organic matter content decreased with depth from the surface in the filter.

3.3. Hydraulic conductivity

The K_{fs} results are displayed in Fig. 2. The results are normalised against the K_{fs} of the virgin media, where K is the hydraulic conductivity of the clogged media and K_v is the K_{fs} of the virgin media. There was some variation in the K_{fs} of the Control filters, which could be due to the arrangement of the coarse and fine sand during column construction, followed by migration of the fines. There is also evidence of scatter in Config 1. This may be due to the nature of the Bayer residue (which has a mud-like texture) and voids within the layer of media that were evident upon deconstruction. However, a general trend of increasing conductivity with depth below the surface was observed.

The extent of clogging in the Control filters differed depending on the operational regime (Fig. 2). The constantly loaded filters showed that the clogging layer extended further, to approximately 0.3 m below the surface of the filter, whereas the K_{fs} of the intermittent filters returned to that of the virgin media between 0.15 and 0.2 m below the surface of the media. This was evident by both a colour change of the sand and the hydraulic conductivity results. This was greater than the clogging depth reported by Zhao et al. (2009), who observed a decreasing K_{fs} near the filter surface of an organically-loaded, continuously fed, laboratory-scale, vertical flow constructed wetland, operated for 2 months, and concluded clogging occurred in the top 0.15 m layer. The clogging mechanisms of Config 1 and Config 2, i.e. the gel-like layer on the surface of the media, did not differ much between the two loading regimes. This is most likely due to the nature of the media; both fly ash and Bayer residue having a small particle size (Table 2) meant that the clogging layer formed more quickly on the surface of the media (Hand et al., 2008; Thullner, 2010).

Nieć and Spychała (2014) found that for medium to high permeability of sand and gravels, the constant head method is reliable, but that a method taking into account capillary rise measurements is more acceptable for fine sands. Methods that take into

Table 3
Filter Performance after 90 days of operation with standard deviation.

		Continuous loading			Intermittent loading		
		Control	Config 1	Config 2	Control	Config 1	Config 2
Average hydraulic loading rate[a] ($L\ m^{-2}\ d^{-1}$)		1424 ± 48	600 ± 268	577 ± 12	676 ± 30	592 ± 228	655 ± 208
Influent ($mg\ L^{-1}$)	DOC	5.7 ± 2.2	5.7 ± 2.2	5.7 ± 2.2	6 ± 1.7	6 ± 1.7	6 ± 1.7
	Al	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2	1.5 ± 0.2
	NH_4^+-N	5.9 ± 2	5.9 ± 2	5.9 ± 2	5.8 ± 1.3	5.8 ± 1.3	5.8 ± 1.3
	NO_3^-N	19.9 ± 3.2	19.9 ± 3.2	19.9 ± 3.2	18.3 ± 4.1	18.3 ± 4.1	18.3 ± 4.1
Turbidity (NTU)	Influent	19 ± 7	19 ± 7	19 ± 7	19 ± 4	19 ± 4	19 ± 4
	Effluent	6 ± 1	4 ± 2	2 ± 1	6 ± 1	5 ± 3	4 ± 3
% Removal	DOC	16.7 ± 3.3	34.9 ± 10.9	71.5 ± 4.8	24.3 ± 2.5	34.4 ± 4.8	63.3 ± 10
	Al	93.6 ± 3.0	93.5 ± 3.2	97.6 ± 0.2	94 ± 0.8	94.7 ± 4.4	96.4 ± 2.9
	NH_4^+-N	56.5 ± 1.9	75.9 ± 10.9	88.5 ± 1.9	60.2 ± 3	84.7 ± 2.1	84.8 ± 2.8
	NO_3^-N	−29.8 ± 10.3	−28.1 ± 5.4	12 ± 1.6	−30.6 ± 13.9	−44.3 ± 5.4	−16.3 ± 19.3
Avg mass removal ($g\ m^{-3}\ d^{-1}$)	DOC	1.6 ± 0.25	1.3 ± 0.36	2.4 ± 0.15	1.0 ± 0.08	1.2 ± 0.13	2.4 ± 0.38
	Al	2.6 ± 0.06	0.9 ± 0.02	0.9 ± 0.003	1.0 ± 0.01	0.9 ± 0.04	1.0 ± 0.03
	NH_4^+-N	4.6 ± 0.45	2.7 ± 0.33	3.0 ± 0.09	2.4 ± 0.19	2.9 ± 0.07	3.2 ± 0.09
	NO_3^-N	−7.9 ± 5.73	−3.3 ± 0.73	1.8 ± 0.12	−3.5 ± 1.82	−4.4 ± 0.51	−1.7 ± 2.23

[a] Average hydraulic loading rate was calculated from the initial and final hydraulic loading rates, to best describe the columns as clogging occurred.

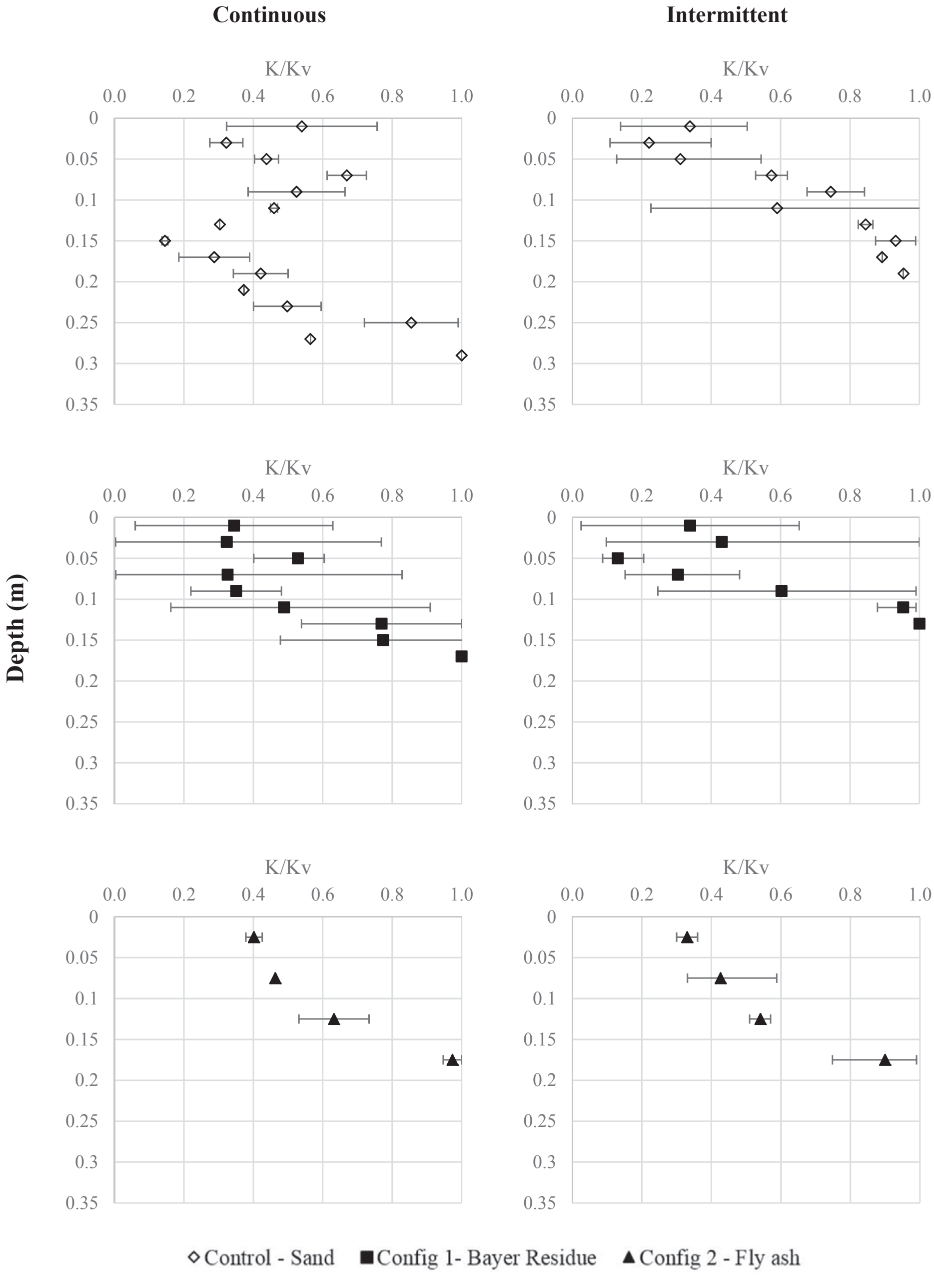

Fig. 2. Relative hydraulic conductivity variation in the uppermost layer with maximum and minimum values.

account filter resistance may also be appropriate in estimating the true permeability, which could be used in filter design (Li et al., 2005). These could be investigated in future filter designs.

3.4. Organic matter composition

Fig. 3 displays the organic matter composition (percentage organic matter per dry weight) of samples taken throughout the clogging layer. In each configuration and each loading rate, more organic matter was measured on the surface of the filter than at further depths. This is consistent with the hydraulic conductivity and observation results, which report a layer of organic matter at the surface, leading to the clogging of the filters. The Bayer residue in Config 1 had higher initial concentrations of organic matter present, which appeared to leach down as water passed through the filter, shown by the percentage decreasing below that of the virgin media with depth from the surface.

3.5. Performance outlook

The performance results indicate that Bayer residue and fly ash are the two most feasible media for use in water filters, based on contaminant removal. However, these two media were also prone to clogging. To carry these media forward to a pilot-scale study, a redesign of the filter configuration is required, to assess whether clogging is as likely to occur if these media were not at the uppermost layer of the filter. In some locations, the removal of DOC may be more important than the footprint of the filter, in which case these media may indeed be the most successful. The adsorption capacity of both media is undoubtedly powerful, as shown in

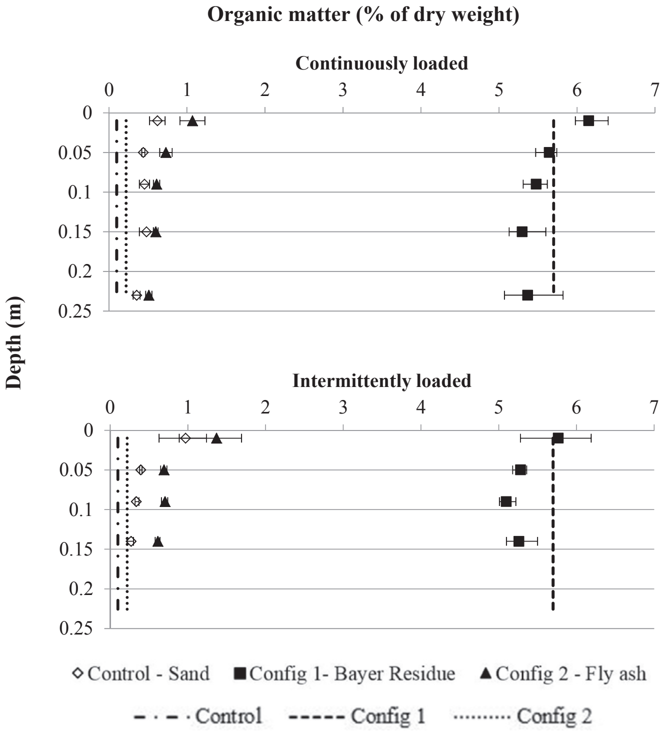

Fig. 3. Organic matter percentages of dry weight of media (with max and min) per depth in each configuration, with initial concentrations shown as vertical lines.

the filter performance in this study, and is well documented in literature (Cengeloglu et al., 2006; Li et al., 2006; Kurniawan et al., 2006; Bhatnagar and Sillanpää, 2010). Laboratory-scale configurations have not been previously investigated, and a lack of follow-through from bench-scale adsorption testing to laboratory or pilot-scale continuous flow experiments has been noted in the literature (Ali, 2012; Bhatnagar and Sillanpää, 2010). However, for some treatment plants, footprint of the filter is essential, and the permeability of the media may be most important. Cost may also be a criterion in filter selection, as media costs can differ extensively from location to location. For example, countries with reserves of natural zeolite may find it an extremely low cost material, whereas countries relying on production of synthetic zeolites may find it to be an expensive resource and it may not be feasible for use (Misaelides, 2011). It is also important to note the risks that may be present when dealing with industrial by-products such as Bayer residue and fly ash, namely, the potential for metal leaching from the media. Aluminium and iron were the only metals found in desorption studies (Grace et al., 2015), but these can be absorbed using a combination of filter media. In order to harness the adsorption potential of filter media, yet prevent any leaching of contaminants, a stratified filter must be carefully designed to target the removal of specific contaminants, and toxicity analysis of the final effluent must be conducted, particularly during the initial stages of operation.

Across all configurations and both loading regimes, the build-up of organic matter was the main clogging mechanism, shown by observation, hydraulic conductivity analysis, and chemical characterisation of the percentage organic matter present. Based on performance alone, Config 2 was the most effective filter configuration, and continuous loading was most effective regarding DOC removal. However, the fine particles of fly ash meant that clogging was a significant problem, meaning that this option is not viable for long-term use. Config 1 was consistent across both loading regimes and the clogging layer did not extend as deeply as in Config 2. This means it would be more cost effective for replenishment. The Control performed best in the constantly loaded regime, although the clogging layer extended 0.1 m deeper in this regime than in the intermittently loaded regime. This would suggest that the current method of removing 0.15–0.3 m of sand, in 20 or 30 stages, is in fact, a conservative estimate of the extent of clogging, and that intermittently loaded filters would require less sand removal than constantly loaded filters.

4. Conclusion

The current model of a sand filter for water treatment is very effective for certain contaminants. However with urbanisation, population growth and industrial development, there is constant pressure on current water resources and infrastructure to meet the demand for supply and treatment quality. With variations from place to place in contaminants and source water quality, a more effective approach may be to focus on site-specific designs. The use of novel media could allow this, as well as targeting contaminants that fail to be removed by traditional sand filters. For a thorough approach to media selection, it is important to look at performance potential, but it is also vital to understand the clogging mechanisms. To date there has been little prior research on clogging of drinking water filters. This study focuses on clogging of novel media, while maintaining efficient water treatment.

A layer-by-layer deconstruction of the filters showed that the main clogging mechanism in all cases was a build-up of organic matter on the surface of the media. Although Configuration 2 (fly ash, GAC, zeolite and sand) was effective in DOC removal, this configuration was more likely to clog than the Control (sand), therefore requiring a larger area for filtration. The flow regime had an impact on the extent of clogging in the sand filters, with constantly loaded sand filters found to have clogged to a deeper depth below the surface than those that were intermittently loaded. The current method of re-sanding the slow sand filter (wherein 20 or 30 scrapings are carried out, removing 0.010–0.015 m each time) may be conservative, as the clogging layer did not extend below 0.3 m, despite a high suspended solids concentration in the influent. Further research should investigate the potential of using these media in an alternative configuration to harness the positive adsorption of the media, while reducing the potential for clogging. Following this, given the variable nature of both the media and the water supply, site-specific testing is essential to the development of a design.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.05.018.

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A novel filtration configuration for targeted humic acid removal from drinking water

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Article associated with Chapter 4.

A novel filtration configuration for targeted humic acid removal from drinking water

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Abstract
Natural organic matter (NOM) has been identified as a precursor to disinfection by-product (DBP) formation in a potable water purification system, and can be measured on site as dissolved organic carbon (DOC). Disinfection by-products are harmful to human health and have been linked to cancer and genetic mutations. To eliminate the potential for DBP formation in the plant, it is necessary to design a treatment system targeting DOC removal prior to disinfection. This study investigates the use of filtration as a mechanism to remove DOC. Based on a bench-scale adsorption study of a variety of media, two filter configurations, each containing layers of novel adsorptive media, were designed to target the removal of DOC. The filters contained a variety of media, including natural materials and industrial waste products. The results of the novel configurations were compared to those from a conventional sand filter (the study control), constructed as per Irish Environmental Protection Agency (EPA) guidelines. With percentage removals as high as 70% in some instances, the new filters, developed in this study, have the potential to remove DOC from drinking water.

Keywords
Filtration, drinking water, humic acid, natural organic matter

INTRODUCTION

Raw sources for drinking water generally comprise ground or surface waters. The very nature of this means that there will be a microbial community present, resulting from agriculture, anthropogenic and environmental sources (Pandey 2006). Disinfection of potable water is used to inactivate any pathogens that may be present in the microbial community (EPA 2011). Chemical disinfectants are used more often than physical disinfectants, with chlorine being the most commonly used worldwide (Sincero & Sincero 2002; de la Rubia et al. 2008). Disinfection normally occurs at the last stage of treatment within the water treatment plant, and can also be followed up with a 'boost' along the distribution network, ensuring that the required residual remains at the tap (EPA 2011).

However, a problem associated with all types of chemical disinfectants, is the formation of disinfection by-products (DBPs) following disinfection. The occurrence of trihalomethanes (THM), following chlorination, was first reported in 1974 (Minear & Amy 1996). Trihalomethanes, like other DBPs, are toxic compounds, and long-term exposure has been linked to elevated cancer risk (Wang et al. 2007) and reproductive and developmental defects in people and animals (Wang et al. 2007). The maximum allowable concentration of THM in Ireland, and the European Union, is currently 100 μg L^{-1} (European Communities 1998; SI No 278 of 2007), however, this will likely be reduced to align with the United States Environmental Protection Agency (USEPA) MAC of 80 μg L^{-1} (USEPA 2009).

Natural organic matter (NOM), the precursor to the formation of DBPs, is present in all raw waters from various sources and can be due to impacts of plant and animal decomposition leachates (Chen et al. 2002). Natural organic matter is usually measured by the concentration of total organic carbon (TOC) in water and primarily comprises humic substances, which are classed as humic and fulvic acids (Chen et al. 2002). The ratio of humic to fulvic acids depends on a variety of environmental conditions including temperature, soil-type and rainfall (Minear & Amy 1996). Seasonal changes to this ratio in raw water are also likely to affect DBP formation (Jacangelo et al. 1995). Humic substances can be particularly problematic where much of the raw water for treatment is sourced from peatland areas (for example in Ireland) (Gough et al. 2014). Humic substances are difficult to remove at the filtration stage of a conventional water treatment plant (WTP), without resorting to expensive ultrafiltration membranes, due to the small particle size, which falls in the molecular to macromolecular range (<0.01 – 1 μm) (Jacangelo et al. 1995).

Disinfection by-product formation is a growing concern for the authorities, with exceedances in WTPs being reported every year (Water_Team 2012). Much of the current research proposes methods of removing THM and other DBPs post-disinfection, using techniques such as ozonation reactors, and submerged membrane photocatalytic reactors (Reguero et al. 2013). Many of these are capital-rich, difficult to maintain, and are unsustainable technologies. Other studies suggest changing the form of disinfection. However, this may result in the formation of other DBPs, not yet discovered, as it is thought that all disinfectants will produce some form of DBP (Ivančev-Tumbas 2014). Such technologies may not provide residual effects, and technology upgrades can incur more capital expense. With removal of TOC in conventional WTPs reported to be as low as 8 – 48 % (Jacangelo et al. 1995), targeting TOC removal appears to be a more sustainable approach.

This study investigates the potential of redesigning filtration systems in WTPs, by replacing sand with a combination of novel media, to remove specific contaminants, such as TOC, and to compare its performance against filters constructed as per EPA guidelines (EPA 1995). Such a technology would be adaptable to use in small and large-scale WTPs, would be sustainable, and would require little maintenance. Moreover, depending on the media and distance to the plant from source, capital expenditure would be greatly reduced.

MATERIALS AND METHODS

Media selection

In a preliminary study (Grace et al. 2015), the adsorption of humic acid on a selection of novel media was modelled using Langmuir and Freundlich adsorption isotherms (Table 1). Based on the results in Table 1, laboratory filters were constructed using stratified layers of sand, zeolite, fly ash, granular activated carbon (GAC), or Bayer residue as filter media.

Table 1 Results of Langmuir and Freundlich adsorption models for TOC adsorption on a variety of media (adapted from (Grace et al. 2015)).

Media	*Isotherm*	*R^2*	*Q_{max} ($\mu g\ g^{-1}$)*	*1/n*	*K*
Sand	Desorption				
Zeolite	Langmuir	0.71	37		
Fly ash	Freundlich	0.73		1.17	0.262
GAC	Langmuir	0.42	327		
Bayer residue	Freundlich	0.83		0.68	0.019

Filter construction

Filter columns, each with 1 m depth of media, were constructed in triplicate. Filters (also at n=3) containing one layer of unstratified sand, with an effective size (d_{10}) of 0.18 mm and a uniformity coefficient of 2.19, were also constructed as per Irish EPA guidelines (EPA 1995), and acted as the study control ('Control'). 'Config 1' consisted of three equal layers of Bayer residue, zeolite and sand, and 'Config 2' consisted of four equal layers of fly ash, GAC, zeolite and sand (Figure 1). The filter columns were fitted with sample ports at the media interfaces (at 250 mm or 330 mm intervals, depending on the configuration), in order to gain a clear understanding of what was happening within each layer of media. The Control was instrumented in a similar way to Config 1, with sample ports at 330 and 660 mm below the surface of the filter.

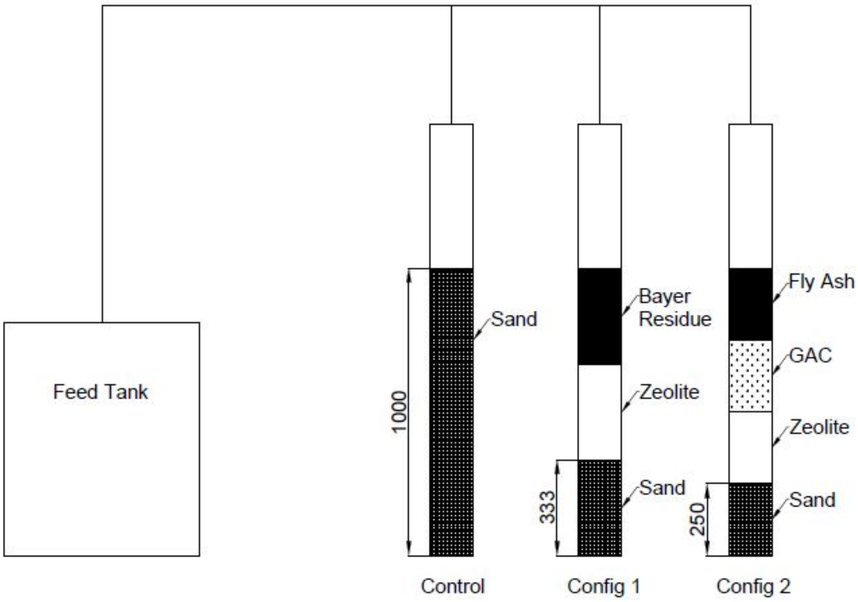

Figure 1 Profile design of Control, Config 1 and Config 2.

Filter operation

The filters were operated under two loading regimes: constantly loaded and intermittently loaded. The constantly loaded filters had a head of 500 mm of water maintained above the filter surface at all times. The intermittently loaded filters were dosed with a peristaltic pump (7528-10, Masterflex L/S Variable-Speed Drive) for 10 min every 2 hr, at an average loading rate of 641 L m^{-2} d^{-1}. The filters were dosed with a synthetic water mix, containing, among other water contaminants, TOC at the concentrations stated in Table 2. To properly assess the efficacy of the novel filter configuration to remove DBP formation potential, laboratory-grade humic acid (Sigma Aldrich) was used as the TOC source in the synthetic water. Humic acid was prepared using a method adapted from Abdul et al. (1990), where humic acid was added to water and stirred for 25 min before being centrifuged at 1000 RPM for 30 min. The mixture was then filtered through a 0.45 µm filter to remove as much of the non-water soluble fraction as possible, and to conform to standard specification for dissolved organic carbon (DOC) (de la Rubia et al. 2008). The influent and effluent DOC concentrations were measured using a BioTector TOC analyser (BioTector Analytical Systems, Ireland).

RESULTS AND DISCUSSION

The influent and effluent DOC concentrations from each filter configuration and loading regime are shown in Table 2. The four-layer filter (Config 2) had the best DOC removal, although removal was also evident in Config 1. However, both removals were greater than the Control. The continuous loading regime was more effective than an intermittent loading regime, particularly in the case of Config 2. The average removal of 70% of Config 2 was comparable to the bench-scale membrane photocatalytic reactor of Reguero et al. (2013), yet Config 2 would be a less expensive technology.

Towards the end of the experiment, clogging was observed across all filter configurations. This can be attributed to the high suspended solids in the humic acid mix (approx. 200 mg L^{-1}), which was significantly higher than would normally be found at the filtration stage in a standard WTP, and also to the small particle size at the uppermost layer in Configs 1 and 2, both of which clogged more quickly than the sand.

Table 2 Influent and effluent DOC removal concentrations for three configurations*, loaded continuously and intermittently.

Loading Regime		*Average concentrations mg DOC L^{-1}*	*St. Dev*
Continuous	Influent Concentration	5.78	2.2
	Effluent Concentration		
	Control	4.16	1.87
	Config 1	3.7	1.81
	Config 2	1.7	1.61
Intermittent	Influent Concentration	6.01	1.72
	Effluent Concentration		
	Control	4.51	1.82
	Config 1	3.95	1.77
	Config 2	2.3	1.63

*Control = sand filter; Config 1 = three-layer filter containing Bayer residue, zeolite and sand, and Config 2 = four-layer filter containing flyash, granular activated carbon, zeolite and sand.

Figure 2 shows the percentage removal of DOC at different depths within the filters when operated continuously and intermittently, at day 0, 45 and 90 of operation. Sampling at depths in intermittently loaded Config 2 filters was not possible. The uppermost section of the Control filters (measured from the filter surface to the 330 mm sample port) had a lower uptake rate at the end of the experiment than at the start, indicating that the media in the layer may have become saturated.

The DOC removal in Config 1 and 2 generally decreased over time, which would be expected as the adsorptive potential of the media may have been greatly reduced and much of the chemical removal would have lessened. The 90-day removal data for both Config 1 and 2 suggest that there was less removal at the lower layers than at the top layers, indicating that there may have been some leaching of DOC back into the water by the time it reached the base. This may have been due to media saturation, with more specific surface area available in the uppermost layer, because of the fine particles.

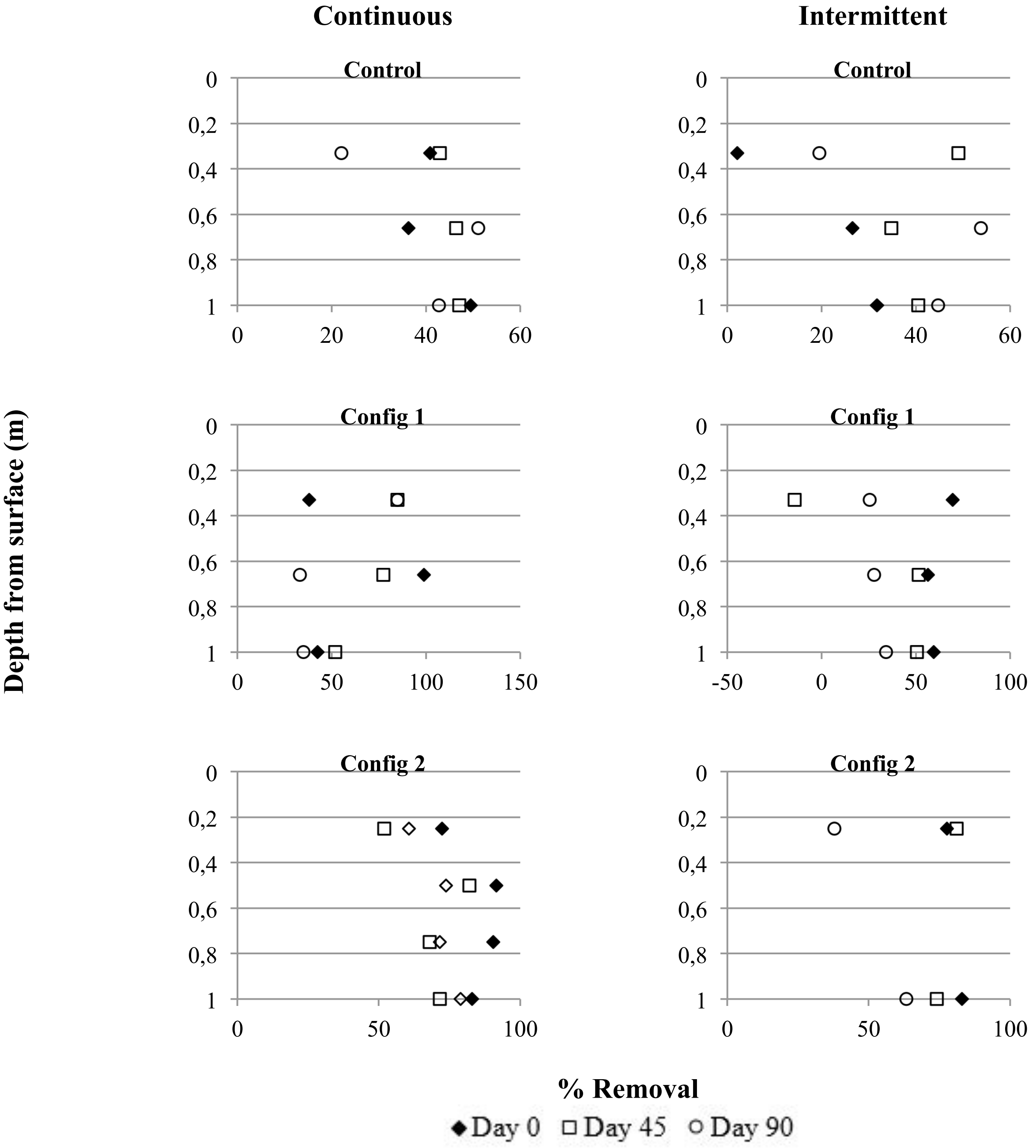

Figure 2 Profile results for each configuration in both loading regimes, showing percentage removal at depths throughout the columns at day 0, day 45 and day 90 of the experiment.

Outlook for adoption of technology

These results show that alternative filter media may be employed in WTPs to remove DOC. Dissolved organic carbon removal at filtration stage is essential to reduce the potential for DBP formation post-disinfection in a WTP. The DOC removals in Config 1 and Config 2 were greater than a standard sand filter, subjected to high suspended solids and high humic acid concentrations. Profile results show that media can become saturated with contaminants, though this can be fixed by replacing the clogged layer within the filter, before the DOC breaks through and releases back into the water from the saturated layer.

Further investigation into the design is necessary as these configurations are not sustainable, given the potential for clogging (due to the low saturated hydraulic conductivity of the fly ash). However, this study showed that novel media can be used, and repositioning these within the filter may be an option. Future work will involve testing an alternative configuration to assess the potential of a successful design. This can be used to inform future developments in filtration technologies that use specific media to remove targeted compounds.

CONCLUSION

This study showed that Bayer residue, fly ash, zeolite, GAC and sand, in layered filter configurations, can remove DOC from drinking water sources. The most effective configuration was fly ash, GAC, zeolite and sand (Config 2). However, there is a potential issue with clogging of the filters, although this may be solved by removing the clogged layer of the filter, provided that clogging is restricted to the uppermost layer. To create a realistically viable filter configuration, it is imperative to redesign the filter to mitigate the effects of clogging. It was also shown that Bayer residue, zeolite and sand (Config 1) were more effective that the control study at removing DOC, although it was not as successful as Config 2.

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The potential for the use of waste products from a variety of sectors in water treatment processes

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Review

The potential for the use of waste products from a variety of sectors in water treatment processes

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ABSTRACT

This review examines the utilisation of waste products from three sectors (industry, agriculture, and construction and demolition) in filters for the removal of contaminants from water. Sand is commonly used in drinking water filtration in water treatment plants. However, the use of alternative, low-cost materials could address the limitations of sand, particularly for the removal of emerging contaminants, and address European legislation which fosters the development of a 'circular' economy, in which materials are used effectively. This review assesses the suitability of potential media by quantifying their adsorption potential across a variety of common drinking water contaminants. The media investigated were fly ash, Bayer residue, ground granular blast furnace slag, coconut shell, tea/coffee waste, rice husk, crushed concrete, masonry waste, and wood waste. There is a potential for the use of these media in the water treatment sector, although certain precautions must be taken to ensure any concerns are mitigated, such as release of metals into water. Recommendations, following this review, include testing the media in large-scale applications, and also constructing filters so as potential media are placed in layers to harness their contrasting adsorptive potentials.

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1. Introduction

The European Union (EU) produces 2.3 billion tonnes of waste annually, of which 10% (or 250 million tonnes) includes municipal waste, and 90% includes industrial, commercial, agricultural, and other business related waste (Ruggiero, 2013). In agriculture, wastes are generated at production, post-harvest and processing stages (Parfitt et al., 2010), and amount to 1.3 billion tonnes per year worldwide (FAO, 2011). About 850 million tonnes of construction and demolition (C&D) waste is generated in the EU per year, representing 31% of the total waste generation in the EU (Fischer and Werge, 2009). However, the level of recycling and reuse of C&D waste varies greatly (between less than 10% to over 90%) across the EU. The concept of a 'zero waste' industry is not feasible, and while industries such as the C&D industry have a policy of reduction, reuse, recycle and disposal (Yuan and Shen, 2011), there is a tendency amongst stakeholders to only consider the use of wastes within the same sector (Duran et al., 2006), without considering their use in other sectors. One such avenue for the use of these wastes is in the water treatment sector, particularly as less than half the population of some countries in the developing world have access to clean, potable water (FAO, 2015), and as a need has been identified for cost-effective and robust solutions to improve water purification in both the developed and developing world (Shannon et al., 2008). Although drinking water improvement trends are increasing, in 2015, 663 million people were deprived of good quality drinking water, leaving much scope for improvements (WHO/UNICEF, 2015).

Improvements must include sophisticated strategies to combine water and energy savings, while striving for the ultimate goal of a circular economy (Bagatin et al., 2014). Although a 'zero-waste' society is not yet achievable, steps in this direction are continuing. Total recycling of used products and an entirely circular economy may not be realistic in all scenarios, but it is possible to achieve a sustainable future by attempting to reach this goal (Reh, 2013). It is also important to maintain environmental and economic benefits while investigating material recovery concepts (Dahlbo et al., 2015), and so, either disposal or use post-treatment must also be considered to ensure a holistic design approach. It is also necessary to ensure new production processes do not create extra environmental impacts, which could even undermine those beneficial changes found by utilizing waste products (Mirabella et al., 2014).

Sand filtration is commonly used in drinking water purification. However, it can have shortfalls regarding the removal of certain contaminants (Water_Team, 2012). The use of a multi-layer filter containing a variety of media may have the potential to tackle problematic contaminants. Anthracite and coal are most commonly used in multi-layer filters, but these are costly and unsustainable adsorbents (EPA, 1995). The use of adsorption is evolving, as it produces satisfactory results while being cost-efficient and easy to design and operate (Bibi et al., 2015). The exploration of different adsorbents, both manufactured and recycled, is paving the way for a new generation of filters, containing a variety of media from many different sources (Bhatnagar and Sillanpää, 2010). The utilisation of waste from sectors such as industry, agriculture and C&D as adsorbents allows for the development of sustainable and effective treatment technologies. The use of waste from certain processes could provide a more sustainable alternative for water treatment systems than abstraction of sand, for example by providing a use for an otherwise landfilled waste material.

There is increasing interest in the utilisation of waste materials, and there is a gap in knowledge in terms of the application to water treatment processes. This paper investigates a variety of media from three sectors (industry, agriculture and C&D) that could be used in filters for the removal of contaminants from water.

1.1. *Adsorption classification and contaminant definitions*

The potential adsorption capacity of media can be classified mathematically using a number of adsorption isotherm models (Foo and Hameed, 2010), allowing for a comparison between the theoretical adsorption capacity of novel versus traditional media. In turn, these data would allow the relative efficacy of one type of filter media over another to be evaluated. There has been considerable research into the adsorption capacities of a huge variety of media to adsorb a variety of contaminants, such as clays, zeolites and chitosan for nitrate removal (Bhatnagar and Sillanpää, 2011), carbon nanotubes, biosorbents and low cost adsorbents for heavy metal removal (Fu and Wang, 2011), and agricultural wastes for water purification (Bhatnagar et al., 2015). However, for the purposes of this review, common drinking water contaminants will be investigated against a selection of media arising from industrial, C&D, and agricultural sectors.

The legislation discussed in the current review is Irish drinking water legislation (SI No 278 of 2007, 2007); however, this is based on the European Communities (Drinking Water) (No 2) Regulations 2007. Discrepancies between these and United States regulations, where they arise, are stated in the current paper. The European Communities set out clear quality standards for water for human consumption. A total of 39 parameters must be tested for on a regular basis, and 95% of samples must comply with the regulations. There are further requirements for those samples which do not pass. To allow for a broad overview of media and contaminants, a small selection has been chosen on which the review is based.

Phosphorus (P) is not currently legislated for under drinking water quality legislation. However, given that most potable water uses surface- or ground-water as its abstraction source, P is likely to be found in abstraction water. The Water Framework Directive (2000/60/EC; EC, 2000) states the threshold level of P in water to be 0.035 mg L^{-1}. However there is a likelihood that certain locations in the EU will not meet this objective, based on current trends (EPA, 2015a). Phosphorus causes detrimental eutrophication effects when present in surface water sources, and can have negative effects following human consumption. Phosphorus is also likely to cause problems in the water distribution network, with excessive amounts increasing microbial growth (Miettinen et al., 1997).

Nitrogen (N) can be present in water as ammonium (NH_4^+-N), nitrate (NO_3^--N) and nitrite-N (NO_2^--N) and organic nitrogen. The maximum allowable concentration (MAC) for NH_4^+-N in drinking water is 0.3 mg L^{-1}. The presence of NH_4^+-N in water treatment plants can have a negative impact on (i) disinfection by resulting in increased chlorine consumption or reducing the effect of chlorine-based disinfection systems (Wilczak et al., 1996) and (ii) both pH and dissolved oxygen (DO) in the distribution system (Feng et al., 2012). The MAC for NO_3^--N in drinking water is 11 mg L^{-1}. Nitrate can enter drinking water abstraction sources from anthropogenic sources, generally from municipal wastewater treatment plants where denitrification was incomplete, and from agricultural land (Bagatin et al., 2014). The MAC for NO_2^--N in drinking water is 0.5 mg L^{-1}, and its presence has also been linked to blue-baby syndrome (Fan and Steinberg, 1996). Nitrogen is most commonly removed at filtration stage by a combination of biological and chemical removal mechanisms, with the biological activity occurring at the surface of the filters.

There is no MAC for dissolved organic carbon (DOC), with legislation stating “no abnormal change” must be observed. However, the presence of organic carbon in water can, following disinfection, result in the formation of multiple disinfection by-products (DBP) (EPA, 2012). Total trihalomethanes (TTHM) are the most commonly occurring disinfection by-products, and are the only ones regulated by legislation, with a MAC of TTHM in Ireland of 0.1 mg L^{-1} (SI No 278 of 2007, 2007) and in the United States of 0.08 mg L^{-1} (USEPA, 2009). Disinfection by-products are carcinogenic and have been linked to reproductive issues and birth defects (Richardson, 2003). The composition of DOC has an impact on the formation potential of DBP, with the hydrophobic fraction, comprising mainly humic substances, most likely to form DBP (Tran et al., 2015). Humic acid is a constituent of natural organic matter in surface and ground water sources, and is often used in adsorption studies. The potential formation will also differ depending on temperature, rainfall, pH, alkalinity, surrounding soils, and time of year (EPA, 2012). For the purposes of this paper, the focus is on DOC adsorption, rather than the by-products.

Metals are most likely to enter drinking water abstraction sources by anthropogenic sources, such as mining, drainage, corrosion of pipes (EPA, 2015b), and by industrial processes (Mohod and Dhote, 2013). In legislation, each metal has a different MAC, depending on the severity of the effects on human health. For example, the MAC of aluminium (Al) is 200 μg L^{-1}, chromium (Cr) is 50 μg L^{-1}, copper (Cu) is 2 mg L^{-1}, lead (Pb) is 10 μg L^{-1}, and iron (Fe) is 200 μg L^{-1}. The presence of metals in water can be associated with many physiological illnesses attacking the major organs of the human body (Mohod and Dhote, 2013).

Although adsorption of individual contaminants onto various media is well examined in the literature, reviews tend to group the literature based on a single contaminant or in terms of wastewater treatment, and often investigates commercial adsorbents. This review focuses on a variety of drinking water contaminants, solely from the point-of-view of reusing by-products or waste material, and it provides researchers and practitioners with a comprehensive overview on a number of different materials. This would not only allow for improved water treatment, but also improvements for the environment as a whole, by aiming to reduce waste products and disposal of same.

2. Methodology

A detailed literature search was carried out by initially selecting several key words. Those used include: adsorption, waste products, waste reuse, water treatment, regeneration, agricultural-based adsorbents, construction-based adsorbents, and industrial-based adsorbents. Each media mentioned was also included in a search. The search was limited to papers published in the last ten years, where possible. Exceptions were made for highly cited papers and areas where there was limited research available. No geographical limitations were applied. Search engines used included databases such as Scopus, as well as publisher-specific search engines such as ScienceDirect, Royal Society of Chemistry, American Chemical Society, and Materials Research Society, and the Boolean operator “AND” was used to include several keywords in one search. References from selected papers were also explored for relevant information.

Articles were selected based on relevance to the review, with a focus on the selected media from industry, agriculture, and construction and demolition sectors. Particular attention was paid to those contaminants of concern, although all adsorption studies were considered for inclusion. Post-treatment use and regeneration were also considered when selecting articles. A total of 210 references were selected, of which most are journal papers from chemistry, engineering, and material science research areas. A small number of books and reports were also included.

3. Industrial waste

Industrial activities generate products and residues from both production and consumption. As industrial activity continues to increase, so too does the creation of excessive waste. In 2012, 48% of total waste in the EU was disposed, and the remainder was either recycled, or used for energy recovery, backfilling or incineration (Eurostat, 2015). The utilisation of industrial by-products and wastes in water treatment is infrequently examined in the literature. The wastes that will be considered in this paper are fly ash and ground granular blast furnace slag (GGBS), and Bayer residue. Fly ash was chosen as it comprises 85% of all ash produced in coal combustion products (CCP), with approximately 780 million tonnes produced worldwide (Heidrich et al., 2013). Ground granular blast furnace slag was chosen as it is a product of over 1 billion tonnes of steel produced (Juckes, 2011), and Bayer residue because of the increasing accumulation of the waste (EAA, 2013).

3.1. Fly ash

Fly ash (specifically coal fly ash) is a waste product of the incineration process. It is defined as a non-hazardous mineral combustion waste, with coal fly ash falling under the category of slags and ashes from thermal treatment combustion (Eurostat, 2010). It has a recognised potential use as a raw/construction material in applications such as cement and concrete addition (ESB Moneypoint, 2012), with more than half of the concrete used in the USA containing fly ash (World Coal Association, 2015). The current utilisation rate for fly ash use in the EU is approximately 43%, leaving over 17 million tonnes for disposal or stockpiling (Ecoba, 2015).

Fly ash is produced by the incineration process when coal is burned as a power source, and in incineration of municipal solid wastes, sugar cane bagasse, rice husks and tea dusts. For many years production has exceeded utilisation capabilities, meaning a large proportion is landfilled (Ecoba, 2015). For the purposes of this review, power station fly ash (coal combustion) is of most interest, as it is the largest source of fly ash production (Iyer and Scott, 2001). The major components are silica, Al, Fe oxides, carbon, calcium (Ca), magnesium (Mg), and sulphur in varying amounts, depending on the original source (Iyer and Scott, 2001). Chemical characteristics are detailed in Table 1. With such a large variety of elements, fly ash has potential for many uses (Fig. 1), and efforts should be made to avoid landfilling.

3.1.1. *Current uses*

In the construction industry, fly ash is mostly used in concrete addition (35.9% of total use of fly ash in 2010), with other uses including blended cement, road construction and concrete blocks (Ecoba, 2015). Research has been carried out on increasing the amount of fly ash in certain concrete mixtures to increase performance (Mehta, 2002). This must be cautioned however, as fly ash can adsorb concrete surfactants which may have negative effects on the mixture (Ahmed and Hand, 2014). The fine nature and elemental composition of fly ash has led to investigations into the use of fly ash as a fertiliser (Jala and Goyal, 2006) and for soil conditioning, which has demonstrated positive results on a short-term basis (Kalra et al., 1998), though this should only be used where the fly ash will not compromise the soil quality (Pandey and Singh, 2010).

3.1.2. *Potential for use in water treatment*

Fly ash has been well recognised for its efficacy as an adsorptive material for various contaminants in aqueous solutions (Ahmaruzzaman, 2010). Table 2 gives an overview of the adsorption potential, based on adsorption isotherm modelling, targeting in particular those contaminants of interest in this review. Fly ash also has the ability to uptake metals, such as Pb and Cu (Alinnor, 2007), and zinc (Zn) and manganese (Nascimento et al., 2009) from aqueous solutions, and its capacity may be improved by the presence of humic acid in water (Wang et al., 2008a). Metal removal using fly ash can also be enhanced by coating with chitosan (Adamczuk and Kołodyńska, 2015). Lignin removal can be achieved by fly ash (Andersson et al., 2011), as can phenanthrene (An and Huang, 2012). Little research has been carried out on NH_4^+-N adsorption, other than cation exchange capacity (CEC) investigations with synthesised zeolite from fly ash.

Many studies have been carried out to investigate the efficacy of zeolite that is synthesised from fly ash (ZFA), for example to remove heavy metals from wastewater (Querol et al., 2002), phosphate from an aqueous solution (Chen et al., 2006), and for humic acid removal from water (Li et al., 2011). Synthetic zeolites from fly ash have been shown to have a CEC of up to 3 meq g^{-1}, allowing for the uptake of heavy metals and cations such as NH_4^+-N (Querol et al., 2002). Wu et al. (2006) investigated the increase of CEC of ZFA by salt treatment, and simultaneous P and NH_4^+-N removal, which was particularly effective at low concentrations. A mild acid treatment has been shown to have a similar effect on ZFA (Zhang et al., 2007).

The main disadvantage to using fly ash in water treatment is the potential for metal leaching. By its nature, metals are an intrinsic

Table 1
Media characterisation.

	Fly ash	GGBS	Bayer residue	Coconut shell	Coffee waste	Rice husk	Crushed concrete	Masonry waste
SiO_2	44.5–67%	35%	5-30%					66.52%
Al_2O_3	22.2–30.7%	10%	10-22%					14.2%
Fe_2O_3	1.1–14.4%		20-45%					5.45%
CaO	0.4–4.2%	40%	0-14%					6.06%
BaO	0–0.5%							
MgO	0.3–1.6%	8%						2.35%
Na_2O	0.2–0.9%		2-8%					0.67%
K_2O	0.5–2.9%							2.09%
TiO_2	0.9–1.9%		4-20%					
P_2O_5	0.1–2.7%							
SO_3	0.1–0.5%							0.75%
Carbon %				48.6	57–59	35		
Hydrogen %				6.5	7.1–7.6	4–5		
Oxygen %				44.6	26–23	31–37		
Nitrogen %				0.1	1.2–1.3	0.23–0.32		
Sulphur %				0.1		0.04–0.08		
Ash %						22–29		
Moisture						8–9		
Ca g kg^{-1}							240–551	
Fe g kg^{-1}							17–29	
Al g kg^{-1}							18–30	
P g kg^{-1}							1–13	
Cu mg kg^{-1}							37–87	
Pb mg kg^{-1}							33–87	
Cr mg kg^{-1}							22–115	
Cd mg kg^{-1}							1–20	
Reference	Ward and French (2006)	Ecocem (2015)	EAA (2013)	Daud (2004)	Pujol et al. (2013)	Kumar et al. (2012)	Egemose et al. (2012)	Naceri and Hamina (2009)

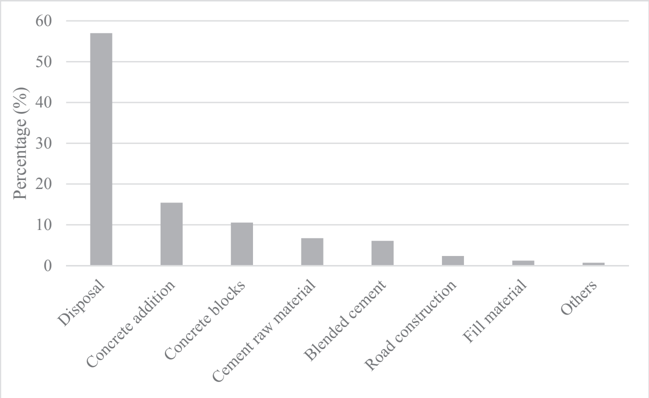

Fig. 1. Disposal and utilisation of fly ash in the construction industry and underground mining in Europe (EU 15) in 2010 (Ecoba, 2015).

characteristic of fly ash (Chou et al., 2009). However, with the introduction of some precautionary measures, where necessary, this can be mitigated. Measures may include a leaching behaviour test (for example, where systems may contain other adsorptive media), forced extraction, immobilisation of elements, and destruction of persistent pollutants (Wang and Wu, 2006).

Acid, heat, and activation all have a positive effect on the adsorption capacity of fly ash (Li et al., 2006). However, for the most sustainable and cost-effective approach, the raw state is generally stated to be most desirable (Alinnor, 2007). Phosphorus and humic acid can also be successfully removed from water (Table 2) using fly ash. However, there is little investigation of co-adsorption and contaminant interaction. Wang et al. (2008a) studied the positive effect of humic acid presence on metal adsorption, but to comprehensively assess the potential for the use of fly ash in a sustainable technology, it is necessary to study the raw water contaminants in a combined and natural environment.

3.2. *Ground granulated blast furnace slag*

Ground granular blast furnace slag is a waste product of the steel production industry. It is non-hazardous, and is a finely ground powder. Similar to fly ash, GGBS falls under the category of mineral combustion wastes, and is hazardous if it contains toxic heavy metals (Eurostat, 2013). Over a billion tonnes of steel is manufactured per annum, leading to the availability of a large amount of GGBS (Juckes, 2011).

Ground granulated blast furnace slag is produced from blast furnaces used in Fe production. Molten slag is produced when iron-ore, coke and limestone are melted in a blast furnace. Slag floats on the molten iron, and once removed, is granulated and ground to produce GGBS (Siddique and Bennacer, 2012). Ground granulated blast furnace slag typically contains oxides of calcium, silica, Al and Mg in varying proportions (Ecocem, 2012).

3.2.1. *Current uses*

In Europe, almost 18 million tonnes of GGBS is currently used in the cement and concrete industries (Ecocem, 2015). This is the most common use for GGBS. It acts as a direct replacement for cement, and has many advantages including extending the life cycle of concrete, making concrete more durable, and reducing the carbon and energy footprint of concrete production (Ecocem, 2015). Blended cements (GGBS and ordinary Portland cement) have a superior resistance to sulphates and an increased chloride binding capacity (Siddique and Bennacer, 2012).

3.2.2. *Potential for use in water treatment*

Ground granulated blast furnace slag has not been previously identified as an adsorptive material, and little research has been carried out in this regard. The chemical composition of GGBS would indicate potential for a strong CEC for cation and metal adsorptions. Grace et al. (2015) found that GBS (granular blast furnace slag) had good adsorption properties but solidified upon immersing in water, which would counteract the usefulness in a water treatment system. Further research is necessary to investigate pre-treatments which would allow the adsorption potential of GGBS to be harnessed and utilised.

3.3. *Bayer residue*

Bayer residue (also called bauxite residue or red mud) is a primary waste product of the Al production industry. Accumulation of the residue is estimated to be increasing by 110 million tonnes per annum, with 2700 million tonnes already in storage in 2010 (EAA, 2013). Bayer residue is highly alkaline and has a fine particle size, leading to environmental issues around disposal and storage.

Aluminium is most often refined from bauxite ore, which is readily available all over the world. The ore contains high levels of Al oxides, which can be extracted by the Bayer process. This involves heating the bauxite in caustic soda under high temperature and pressure, to form sodium aluminate and an insoluble residue - known as Bayer residue (Deelwal et al., 2014). The sodium aluminate is further treated to form Al hydroxide or oxide. The Bayer residue typically contains Fe oxide, Al oxide, titanium oxide, calcium oxide, silica oxide and sodium oxide (EAA, 2013).

3.3.1. *Current uses*

Bayer residue is stored at or close to the alumina manufacturing facility in a bauxite residue storage area or in dry stacking facilities (Nikraz et al., 2007). Bauxite residue storage areas should be carefully controlled, with hydrosphere monitoring to avoid any negative environmental or ecological impacts (EAA, 2013). It is a concerning issue for many nations; indeed the Chinese government set a target of utilizing 20% of fresh mud by the end of 2015 (Liu et al., 2014). Approximately 110 million tonnes of Bayer residue are produced and stored worldwide annually (EAA, 2013), and amount currently in storage is expected to increase to 4 billion tonnes by 2015 (Liu and Naidu, 2014). Therefore, it is the subject of ongoing research to identify potential uses and alternative disposal mechanisms such as soil amelioration, construction and groundworks restoration (EAA, 2013). Work has been carried out on the use of Bayer residue as a construction additive or filling material (Deelwal et al., 2014). Limited work has been carried out on the use of Bayer residue as a coagulant or as an industrial catalyst, showing it may have potential in this area (Wang et al., 2008b), for example to purify a bio-diesel waste stream (Resende et al., 2013). Work has also been carried out on iron recovery from Bayer residue (Liu and Naidu, 2014).

3.3.2. *Potential for use in water treatment*

Previous studies indicate that Bayer residue has potential as an adsorptive material for removal of contaminants from water supplies, and it has been suggested that exhausted material be re-used in the construction sector (Ali and Gupta, 2006). Metal removal from aqueous solution has been examined successfully (Hua et al., 2014), although further work is required to understand the removal techniques and consequences (Brunori et al., 2005). Phosphorus removal is very effective using Bayer residue (Table 3), and limited studies of NO_3^--N, along with other anion adsorption studies (Bhatnagar et al., 2011), have produced positive results. Gaps exist in the adsorption potential of NH_4^+-N and DOC, although Lopez et al.

Table 2
Previous studies of fly ash adsorption.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Phosphate	63.2 mg g^{-1}	Raw	Langmuir	Li et al. (2006)
	58.9 mg g^{-1}	Heat activated at 700 °C	Langmuir	
	78.4 mg g^{-1}	Acid activated with 0.25 M HCl	Langmuir	
	27.4 g g^{-1}	At 40 °C, with initial concentration of 100 mg/L	Langmuir	Ugurlu and Salman (1998)
	20 mg g^{-1}	Raw fly ash	Langmuir	Wu et al. (2006)
	35.3 mg g^{-1}	Salt treated zeolite synthesised from fly ash	Langmuir	
	42 mg g^{-1}	Raw fly ash	Langmuir	Chen et al. (2007)
Humic Acid	126.6 mg g^{-1}	zeolite synthesised from (high calcium) fly ash	Langmuir	Li et al. (2011)
	31.6 mg g^{-1}	zeolite synthesised from (low calcium) fly ash	Langmuir	
	36.6 mg g^{-1}	Raw, single pollutant system	Langmuir	Wang et al. (2008a)
	45.5 mg g^{-1}	Raw, all unburned carbon present	Langmuir	Wang and Zhu (2007)
DOC	0.3 mg g^{-1}	Hydrophobic acid fraction of DOC. Fly ash eluted with methanol	Langmuir	Wei et al. (2011)

(1998) observed NH_4^+-N removal from secondary effluent from a wastewater treatment plant. Bayer residue can also achieve more than 90% bromate removal from aqueous solutions (Chen et al., 2016). The positive results indicate that further research should be carried out to assess the removal capabilities of a spectrum of contaminants.

The most relevant disadvantage to using Bayer residue in water treatment processes is reflected in environmental concerns (Liu et al., 2011). Its chemical and mineralogical characteristics require treatment before storage and it is important to ensure it does not further pollute water or leach contaminants. The adsorption potential may outweigh the concerns, and carefully designed systems could mitigate any possible concerns.

4. Agricultural waste

The agricultural sector is constantly growing, particularly as trade relations strengthen between countries and demographics continue to put pressure on food production systems. Thirty-eight percent of the EU budget is spent on agriculture, with exports steadily rising and currently estimated to have a value of €122 billion (European Commission, 2015a). Globally, trade flow values have increased fivefold in the past 50 years (United Nations, 2015). Twelve percent of the total land area of the world is used for crop production in the agricultural sector (United Nations, 2015). This produces many different types of wastes and by-products. In this review, those examined are coconut shell, tea and coffee wastes, and rice husk.

4.1. Coconut shell

Coconut shell is frequently used as a carbonaceous source for activated carbon, as it results in a strong, dense carbon (Cooney, 1999). Although powdered coconut shell can be used for adsorption, the most common use is as an activated carbon source. This is a successful adsorbent, but the activation process can be expensive, and using the raw material as is would be a more sustainable approach.

Activated carbon is manufactured in a two-step process. First, raw materials go under a carbonization process in an inert environment, and then the carbonized product is activated with oxidising gases (Hu and Srinivasan, 1999). The oxidation process erodes a network of internal channels and pores, while creating a surface of oxides, to increase the surface area and make the material more suitable for adsorption (Cooney, 1999).

4.1.1. Current uses

In developing countries, coconut shells have practical uses such as bowls and utensils, but the most common large-scale use for coconut shell is the production of activated carbon. More than 61 million tonnes of coconuts are grown worldwide annually, most commonly used for drinking, coconut oil, and dessicated coconut (UNCTAD, 2012). This volume of raw material gives much scope for activated carbon production. Coconut shells have also been used in construction, to create coconut shell aggregate concrete; however, this is not commonly used (Gunasekaran et al., 2012).

4.1.2. Potential for use in water treatment

Table 4 presents a selection of previous studies investigating adsorption using coconut shell in terms of relevant contaminants for drinking water treatment. Coconut-based adsorbents are well studied in terms of biosorption for water treatment. Bhatnagar et al. (2010) reviewed a variety of coconut biosorbents for removal of metals, dyes, pollutants, anions and radionuclides from water, concluding that the potential for use is great, although knowledge gaps still exist in terms of real effluent use, regeneration and

Table 3
Previous studies of Bayer residue adsorption.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Phosphate	113.9 mg g^{-1}	Raw Heat activated at 700 °C	Langmuir	Li et al. (2006)
	345.5 mg g^{-1}	Acid activated with 0.25 M HCl	Langmuir	
	161.6 mg g^{-1}		Langmuir	
	K = 0.47	Acid activated with 2M HCl, experiment @ 30 °C	Freundlich	Huang et al. (2008)
	K = 0.62	Acid activated with 2M HCl, experiment @ 40 °C	Freundlich	
	K = 0.24	Raw, adsorption experiment @ 30 °C	Freundlich	
	K = 0.33	Raw, adsorption experiment @ 40 °C	Freundlich	
	75.9 mg g^{-1}	Acid activated with 20% HCl	Langmuir	Pradhan et al. (1998)
	58.1 mg g^{-1}	Neutralised and aggregated, 48 h study	Langmuir	Lopez et al. (1998)
Nitrate	365.8 mg g^{-1}	Acid activated with 20% HCl @ 40 °C	Langmuir	Cengeloglu et al. (2006)
	117.8 mg g^{-1}	Original red mud	Langmuir	
Ammonium	18% removal efficiency	Packed column	N/A	Lopez et al. (1998)

K: Freundlich adsorption capacity factor.

recovery studies.

Coconut shell has been successfully used in adsorption of metals such as Cu, Pb, cadmium (Cd) and Zn (Sousa et al., 2010), and dye adsorption (Cazetta et al., 2011), various anions such as those mentioned in Table 4, and fluoride (Sathish et al., 2007). Nickel can also be adsorbed using coconut shell (Vocciante et al., 2014). Adsorption of dyes can be indicative of an adsorbent's affinity to adsorb various molecular weights of organic matter (Zhang et al., 2007), thus activated carbon from coconut shell has good potential to adsorb natural organic matter (NOM). Studies have shown that the presence of NOM in aqueous solutions can inhibit or at least compete with adsorption of other trace organic compounds that are commonly found in drinking water by pore blockage and site competition (Quinlivan et al., 2005).

Evidence suggests that coconut shell-derived activated carbon is useful in terms of water treatment. However, the carbonization and activation process can be expensive and technology-intensive, meaning that it is not as sustainable as other by-products. It is also likely to become saturated and exhausted, requiring a regeneration treatment. Coconut shell could be combined with another adsorbent to reduce the need for regeneration yet achieve effective and sustainable water treatment.

4.2. *Tea/coffee wastes*

Worldwide coffee and tea production is a large industry, with the total coffee production per crop year 2014/15 at 141.7 million 60 kg bags (ICO, 2015) and world tea crop production in 2013 was 5.3 million tonnes (FAOSTAT, 2015). The chemical composition of tea varies depending on the type, but the largest proportion generally comprises polyphenols, as well as sugars, some amino acids, lipids and some minerals (Harbowy et al., 1997). Similarly, coffee varies depending on the type, but major constituents are fatty acids, hydrocarbons and sterols (Pujol et al., 2013).

4.2.1. *Current uses*

Coffee and tea grounds/leaves are most commonly disposed of in compost or in landfill disposal. Coffee grains can be beneficial for vermi-composting, by allowing the kitchen waste to become more stable for earthworm populations (Adi and Noor, 2009). Biofuel production has also proved successful with coffee grains (Caetano et al., 2014). However, if a potential use is identified, it would reduce the need for landfill. Studies have also been carried out to investigate the preparation of activated carbon from these wastes by pyrolysis (Reffas et al., 2010) and acid impregnation for improved adsorption of dyes (Ma and Ouyang, 2013).

4.2.2. *Potential for use in water treatment*

Coffee grounds (Safarik et al., 2012) and tea grains have been used successfully in dye adsorption (Nasuha et al., 2010), which can be used to indicate a potential for use in cationic adsorption requirements (Franca et al., 2009). Metal removal has been achieved using both coffee grounds and tea leaf wastes (Djati Utomo and Hunter, 2010). Phenol removal has also been successful with activated carbon prepared from coffee residue (Lamine et al., 2014). Wang et al. (2014) reported a NO_3^--N removal efficiency of almost 52% using green tea extract.

The above evidence would suggest that there is scope for tea and coffee wastes to be used in a technology for water treatment, particularly for adsorption of cationic compounds; however, further analysis is required on nutrient and carbon adsorption to fully understand the benefits.

4.3. *Rice husk*

Rice husks (hulls) are the outer covering on the grain, separated from rice during milling. In Asia, 700 million tonnes of rice husk are produced annually (Santiaguel, 2013), accounting for 92% of the worldwide rice production (Ricehusk.com, 2015). The chemical composition of rice husk includes cellulose, hemicellulose, lignin, silica, ash, and protein (Krishnani et al., 2008).

4.3.1. *Current uses*

Rice husk was generally considered a waste product, but in recent years, it has become a commodity, and has uses such as power production (from biomass gasification) and a raw material for chopstick manufacture (Santiaguel, 2013). It can also be used in horticulture, animal bedding, and as a material in composites (Ricehusk.com, 2015). Thermal treatment of the husk can aid in oil (Angelova et al., 2011) and petroleum adsorption (Kenes et al., 2012).

When rice husk is burnt, it produces an ash, with a high silica content, that can be used in concrete production and insulation products (Singhania, 2004). The ash has also been used in purification methods, such as the preparation of biodiesel from frying oil (Manique et al., 2012). Similarly, oil polluted water can be cleaned using the ash (Vlaev et al., 2011).

4.3.2. *Potential for use in water treatment*

From various studies and reviews, it is clear that rice husk is a successful adsorbent (Ahmaruzzaman and Gupta, 2011). Table 5 details the previous adsorption studies of the contaminants examined in this review, indicating that rice husk can be used in a treatment technology.

Rice husk has proven to adsorb metals from wastewater successfully, particularly when used as a starting material for activated carbon preparation (Daifullah et al., 2003). A partial alkali digestion of rice husk also improved the metal binding ability, showing a

Table 4
Previous studies of coconut shell activated carbon adsorption.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Ammonium	K = 44.9	Activated carbon from coconut shell, at pH 9	Freundlich	Boopathy et al. (2013)
	K = 1875	5:3 Limestone:GAC mix	Freundlich	Hussain et al. (2007)
Nitrate	33.7 mg g^{-1}	NaOH modified coconut shell powder	Langmuir	de Lima et al. (2012)
	10.3 mg g^{-1}	$ZnCl_2$ activated coir pith (from coconut husk)	Langmuir	Namasivayam and Sangeetha (2008)
	18.6 mg g^{-1}	Activated carbon from coconut shell, at pH 2-4	Langmuir	Ohe et al. (2003)
	55.8 mg g^{-1}	Anion exchanger produced from coconut shell	Langmuir	Orlando et al. (2002)
	6.2 mg g^{-1}	Anion exchanger produced from coconut shell	Langmuir	Orlando et al. (2003)
Phosphate	3.0 mg g^{-1}	5:3 Limestone:GAC mix	Langmuir	Hussain et al. (2011)
	200 mg g^{-1}	NaOH modified coconut shell powder	Langmuir	de Lima et al. (2012)
	5.1 mg g^{-1}	$ZnCl_2$ activated coir pith (from coconut husk)	Langmuir	Namasivayam and Sangeetha (2004)
	K = 0.0001 L g^{-1}	Activated carbon from coconut shell	Frumkin	Agrawal et al. (2011)

K: Freundlich adsorption capacity factor.

good affinity for eight different heavy metals (Krishnani et al., 2008). Mohan and Sreelakshmi (2008) found that treating rice husk with P increased its affinity for metal adsorption. Other studies confirm the affinity of rice husk for adsorption of metals such as Cd (Ye et al., 2010), nickel and Zn (Srivastava et al., 2007), and Pb and mercury (Feng et al., 2004), and also for dye adsorption (Kumar et al., 2014). Rice husk ash can also be used as a precursor to activated carbon, which has been successful for dye removal (Liu et al., 2012).

To further assess the potential of using rice husk in a water treatment technology, it is necessary to compare the advantages to its current uses, to ensure it is a viable adsorption source. It is also necessary to assess the cost of having to modify the husk, compared to using a raw, untreated material.

5. Construction and demolition waste

Construction and demolition wastes encompass a wide variety of media, from wood, metals and plastics, to textiles and paper, oils and minerals (Eurostat, 2013). Fig. 2 shows the composition of C&D wastes, for EU member states, excluding Estonia and Finland (European Commission, 2011). Large quantities of C&D waste is produced every year and it accounts for 25–30% of all waste in the EU (European Commission, 2015b). Although recycling efforts are substantial (greater than 50%), there is still a necessity for further re-use of some of this material (Fischer and Werge, 2009). In 2012 in Europe, 40 million tonnes, of a total 295 million tonnes, of mineral waste from C&D was deposited onto or into land, meaning there is a large quantity of potential mineral waste available (Eurostat, 2015). This will allow for compliance with the EU Waste Framework Directive (2008/98/EC; EC, 2008), which states that recycling efforts must be raised to at least 70% (Fischer and Werge, 2009). To aid in reaching this target, it is necessary to examine the potential for certain C&D wastes for other purposes, such as water and wastewater treatment. The wastes of interest in this review are crushed concrete, masonry waste and wood waste.

5.1. *Crushed concrete*

Crushed concrete is a waste product from the C&D industry, resulting from the demolition of buildings and concrete structures. Crushed concrete comprises the largest fraction of C&D waste (Fig. 2), so finding an alternative use is extremely important. It comprises the standard components of a concrete mixture, aggregates, water, cement and sand. This results in a chemical composition of Ca oxides, Al oxides and Fe oxides (Egemose et al., 2012).

Production of crushed concrete arises from the need to reduce landfill waste from all industries, including the C&D industry, with crushing meaning it is more suitable for use elsewhere. Debris and rubble from buildings that have been damaged in destructive earthquakes, along with regeneration demolition, and rebuilding roads and runways result in large amounts of waste. The debris is crushed and ground using various techniques dependent on the required use (Topçu and Şengel, 2004).

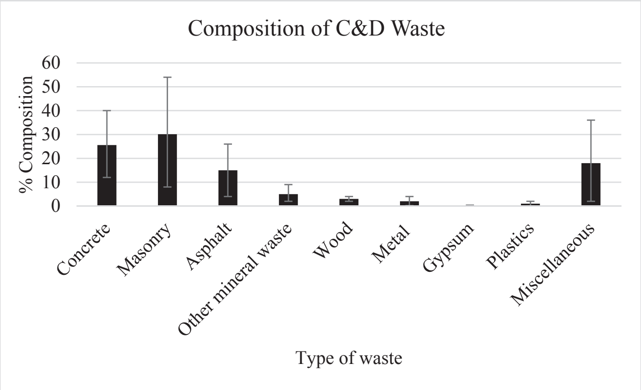

Fig. 2. Composition of C&D waste from EU member states excluding Estonia and Finland (Adapted from (European Commission, 2011)).

5.1.1. *Current uses*

A certain amount of old concrete from the C&D sector still goes to landfill. Crushed concrete can be reused as a form of aggregate; however, this must be done with caution, as increasing amounts of waste concrete aggregate can decrease density, workability, hardness and compressive strength (Topçu, 1997).

5.1.2. *Potential for use in water treatment*

Table 6 details previous work on adsorption studies using crushed concrete. Egemose et al. (2012) investigated the use of crushed concrete as a filter material for urban and agricultural runoff. The study found that it was effective in P removal, but observed that caution must be taken to ensure the pH and alkalinity of the effluent is controlled. During a column study to treat secondary effluent wastewater from a municipal wastewater treatment plant, Berg et al. (2005) discovered that although crushed gas concrete (lightweight concrete) was effective at reducing the concentration of P by 80–100%, the DOC was unchanged, meaning crushed concrete may not be effective as a stand-alone filter media, depending on the contaminants in question. Crushed concrete has shown potential for metal adsorption, with successful adsorption of Cu, Zn and Pb (Coleman et al., 2005). There are indications that crushed concrete may be a successful filter media for removal of contaminants from aqueous solutions, but further work would have to be carried out across a broad spectrum of contaminants to fully assess its potential.

Table 5
Previous adsorption studies using rice husk.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Nitrate	55.6 mg g^{-1}	Anionic sorbent prepared with rice husk	Langmuir	Katal et al. (2012)
	74.4 mg g^{-1}	Anion exchanger produced from rice husk	Langmuir	Orlando et al. (2002)
	6.2 mg g^{-1}	Anion exchanger produced from rice husk	Langmuir	Orlando et al. (2003)
	70.2 mg g^{-1}	Activated carbon prepared from rice husk	Langmuir	Zhang et al. (2013)
Phosphate	89.6% removal	Chemically activated rice husk	Not specified	Yadav et al. (2015)
	64.3% removal	Raw rice husk	Not specified	
Ammonium	39.8 mg g^{-1}	Biochar prepared from rice husk	Langmuir	Kizito et al. (2015)
	2.6 mg g^{-1}	Rice husk charcoal	Langmuir	Han et al. (2013)
	1.4 mg g^{-1}	Activated carbon prepared from rice husk	Pseudo-second order	Zhu et al. (2012)
Humic acid	45.5 mg g^{-1}	Activated carbon prepared from rice husk	Langmuir	Daifullah et al. (2004)
	8.2 mg g^{-1}	Modified rice husk ash	Langmuir	Imyim and Prapalimrungsi (2010)

5.2. Masonry

Masonry waste comprises a large proportion of the C&D waste generated in the EU (Fig. 2), approximately 30%, and is classified under the same waste stream as concrete and gypsum-based materials. It refers to a mixed waste comprising bricks, tiles and ceramics, and any other masonry rubble; and can arise from construction of civil infrastructure, or from demolition (European Commission, 1999). The properties of masonry, both physical and chemical, vary depending on the proportions of the components present in any one sample (del Rio Merino et al., 2010). It can also vary depending on location, given that different regions may use different types of bricks. In some countries, such as Pakistan, brick powder is readily available and may have few costs associated with its use (Bibi et al., 2015). In general, it comprises silicate minerals, rich in silicon, Al oxides and hydroxides (Naceri and Hamina, 2009).

5.2.1. Current uses

Masonry waste from the C&D industry can be reused in the same industry, particularly as aggregate for concrete production, mortars, roof elements, concrete blocks and concrete tiles (del Rio Merino et al., 2010). There have also been studies carried out to investigate the use of masonry waste as a replacement of clinker in cement (Naceri and Hamina, 2009), and as a pozzolonic admixture (Lavat et al., 2009).

5.2.2. Potential for use in water treatment

Table 7 details the studies which have investigated those contaminants of interest in this review. Crushed brick has been used to remove dye from aqueous solutions effectively (Hamdaoui, 2006). Metals, such as Cu (Djeribi and Hamdaoui, 2008) and mercury (Labidi, 2008), have also been removed from aqueous solutions using crushed brick. Brick has also been used for microbiological adsorption, with *Clostridium beijerinckii* found to adsorb onto the surface (Qureshi et al., 2000). Ceramics have also been used in contaminant removal from aqueous solutions. Fluoride has been successfully adsorbed by granular ceramic (Chen et al., 2011), and silica ceramic has been used to remove arsenic from aqueous solution (Salim and Munekage, 2009). Brick powder has also been successfully used for both fluoride and arsenic removal (Bibi et al., 2015).

It is clear that there is potential in the use of masonry waste as an adsorbent for water treatment. With the ability to adsorb such a variety of contaminants, the next step would be to assess its potential to adsorb multiple contaminants simultaneously. The biggest disadvantage, however, is the lack of uniformity. Depending on the source, the masonry waste composition could have a huge variance, which will in turn affect the potential for use.

5.3. Wood waste

Although wood waste only accounts for 2% of the EU C&D waste (Fig. 2), it is a relevant waste to investigate, given that in certain countries this figure may be higher. For example, in Ireland, in 2010, wood accounted for 5% of total C&D waste collected, amounting to 45,000 tonnes (EPA, 2010). Wood waste can arise from discarded treated and untreated wood products, off-cuts, shavings, chip and dust from wood processing and virgin wood mixed in with waste wood (EPA, 2013). The composition of wood varies depending on the source of the timber. It is imperative to encourage the use of wood in a material recovery sense, as currently a significant proportion is used in energy (Dahlbo et al., 2015).

5.3.1. Current uses

Waste wood has many different uses, including fuel, landscaping, bedding, composite boarding manufacture, landfill cover and composting. It can be used both as biofuel and as a fuel in its raw state (Lippke et al., 2012). However, the use of waste wood as fuel brings environmental concerns, given the likelihood of halogenated organic compounds or heavy metals to be present, following preservation methods (EPA, 2013).

5.3.2. Potential for use in water treatment

Wood waste, in the form of wood chips, has been successfully used in adsorption of dye from aqueous solutions (Nigam et al., 2000). Sawdust has been successfully used in the same way (Hanafiah et al., 2012). Wood also has good capacities for metal adsorption (Rafatullah et al., 2012). Alternative methods for using wood waste in water treatment would be as a biochar, for nutrient (Wang et al., 2015a), perchlorate (Fang et al., 2014), or metal adsorption (Jiang et al., 2015); or as an activated carbon, for dye (Ma et al., 2014) and metal adsorption (Lo et al., 2012). Table 8 details adsorption studies that have been carried out using relevant contaminants, mainly in the form of biochar adsorption, indicating that there is a possibility of using this material, though further research should be carried out.

It is clear that waste wood does have potential for use in water treatment. However, there will be a lot of variability depending on the original type of wood used. Another issue could be the release of organics into the water. To avoid a release, a pre-treatment could be advised and perhaps the use of a multi-media technology to harness different sorption capacities.

6. Post-treatment use of media

It is clear from the review of previous studies that the scope for alternative media use as adsorbents in water treatment is broad, encompassing many types of media and contaminants. However, a problem still remains with disposal of the media post-treatment. The recycling of waste does often create larger environmental benefits, particularly than energy recovery methods, but this is not always the case and should be carefully analysed (Dahlbo et al., 2015). Although adsorption can create a purpose for an otherwise discarded material, adsorption is not an infinite solution. Once used in an adsorption system in water treatment, it will be necessary to either regenerate or find a safe disposal mechanism for the media. This will also ensure any contaminants adsorbed onto the media will not pollute land or water.

The use of the media post-treatment depends on the constituents of the water it was used to treat. If the raw water contained heavy metals, it is necessary to ensure that metals would not pose a threat to the next purpose of the media. In the case of adsorption of

Table 6
Previous adsorption studies using crushed concrete.

	Adsorption capacity	Comment/conditions	Isotherm	Reference
Phosphate	19.6 mg g^{-1}	Initial P concentration of 1000 mg L^{-1}	Not specified	Egemose et al. (2012)
	17.3 mg g^{-1}	Initial P concentration of 100 mg L^{-1}	Langmuir	Oguz et al. (2003)
	70.9 mg g^{-1}	Initial P concentration of 10 mg L^{-1}	Langmuir	Renman and Renman (2012)
	α:4.976 and β:0.0042	Ordinary Portland cement	Frumkin	Agyei et al. (2002)

Table 7
Previous adsorption studies with masonry waste.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Nitrate	14.1 mg g^{-1}	Brick with particle size <710 μm	Langmuir	Selvaraju and Pushpavanam (2009)
Phosphate	18.2 mg g^{-1}	Brick with particle size <710 μm	Langmuir	Selvaraju and Pushpavanam (2009)
	0.9 mg g^{-1}	La(III) loaded granular ceramic	Langmuir	Chen et al. (2012)
Ammonium	112.4 mg g^{-1}	Novel ceramic adsorbent	Langmuir	Zhao et al. (2013)
	35% removal	Broken brick as biofilter	Not specified	Savage and Tyrrel (2005)

organic pollutants, successful regeneration and desorption techniques, such as biological degradation, chemical desorption, oxidation, and thermal desorption, may be used to restore the quality of the media (Zhu et al., 2009). Where nutrients are problematic contaminants, land fertilisation may be a potential area of utilisation post-treatment. This would be doubly beneficial as it would improve the land quality and provide a useful purpose for what is otherwise a waste material.

6.1. Regeneration

It is recognised that there exists a knowledge gap on large-scale regeneration of adsorbents, particularly non-carbonaceous adsorbents (Omorogie et al., 2014). Traditional regeneration techniques include thermal, chemical, and bioregeneration. Emerging regeneration techniques include electrochemical, ultrasound, oxidation, and supercritical fluid methods (Duan et al., 2013). Although many of these techniques have proved effective, it is necessary to implement large-scale regeneration of media, for both economic and environmental benefits (Omorogie et al., 2014).

Regeneration of metal oxides, such as fly ash and Bayer residue, has not been extensively studied. The studies which have been carried out tend to refer to treated media, such as impregnated fly ash (Yang et al., 2016) or activated carbon prepared from fly ash (Aslam et al., 2015). However, it has been found that where these media have been used to adsorb various metals, it can make the media more stable (Jacukowicz-Sobala et al., 2015). It has also been shown that methods such as thermal desorption can be used to restore the media to its previous condition (Yang et al., 2016). This can result in the media being used for land reclamation, or in construction methods such as those mentioned in the “current uses” sections above. Fly ash, once exhausted from certain adsorbents, can be used as a filler in paper-making with few side-effects (Saakshy et al., 2015). Although similar studies have not been carried out in relation to GGBS, the chemical composition would suggest similar potential. The United States Environmental Protection Agency (USEPA) have developed a number of tests which can be used to investigate the potential leaching and toxicity of spent sorption material and suitability for use on land (Jacukowicz-Sobala et al., 2015).

Regeneration of coconut shell activated carbon is well researched, with up to five adsorption-regeneration cycles being tested. For adsorption of gaseous sulphur, complete regeneration can be achieved using water vapour (Shi et al., 2015). Microwave regeneration was not as effective when used to regenerate from benzene and toluene adsorption, achieving just 50% removal efficiency after five cycles (Mohammed et al., 2015). Thermal regeneration with 0.1M NaOH was very effective for regeneration from Pb removal, with removal efficiencies of over 90% after cycling (Itodo et al., 2014). Other activated carbons have been regenerated successfully by electrical-assisted acid washing (Weng et al., 2014), supercritical carbon dioxide operating conditions (Carmona et al., 2014), and pyrite-activated sodium persulfate oxidation (Liang and Chen, 2010).

Similar to the other agricultural wastes, several regeneration techniques have proved successful for both tea wastes (Fadhil et al., 2012) and coffee wastes (Plaza et al., 2012). These wastes can be used as a source material for activated carbon and so respond well to regeneration. Although regeneration can still mean the pollutant is present, it becomes concentrated, and thus may be more easily disposed of (Kyzas, 2012), while the material can be returned to its original state. Alternative disposal mechanisms include manufacturing blended fuel briquettes from tea and coffee wastes, due to high calorific values (Nandal et al., 2014).

Bioregeneration has successfully been used for rice husk regeneration (Aktas and Cecen, 2007), as have chemical techniques. Chemically modified rice husk for mercury adsorption was successfully regenerated using 0.1M HCl, only losing 10% adsorption capacity (Song et al., 2016). Regeneration by NaOH has been successfully used for rice husk that has been used for arsenate (Luo et al., 2016) and Pb adsorption (Masoumi et al., 2016). Rice husk ash, a product of the incineration of rice husk, has many uses including catalyst carriers, fillers in cement, fertilisers, and production of gels and polymers (Kumar et al., 2016). This would be a useful post-treatment use of rice husk, provided that the contaminants would be contained and not leached to the environment.

Construction and demolition wastes are not well researched in terms of regeneration processes. Where an activated carbon was produced from wood waste, regeneration would be most likely successful. For concrete and masonry, depending on the source water contaminants, there is potential for use as aggregate or fill in the construction industry. However, extensive testing would be necessary to ensure no damage would occur to the environment.

6.2. Economic and environmental outlook

When considering regeneration techniques, it is important to recognise the economic and environmental costs of regeneration

Table 8
Previous studies of adsorption using wood waste.

Contaminant	Adsorption capacity	Comment/conditions	Isotherm	Reference
Ammonium	5.4 mg g^{-1}	Biochar from maple wood, pH adjusted	Langmuir	Wang et al. (2015a)
	54.8 mg g^{-1}	Biochar from mixed wood, 1400 mg L^{-1} initially	Langmuir	Kizito et al. (2015)
	5.3 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015b)
Nitrate	8.9 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015b)
	43.5 mg g^{-1}	Activated biochar from pine wood	Langmuir	Chintala et al. (2013)
Phosphate	32 mg g^{-1}	Untreated biochar from oak sawdust	Langmuir	Wang et al. (2015b)

Table 9
A brief summary of media potentials.

Media	Opportunities	Advantages	Disadvantages
Fly ash	17 M t	Nutrient, metal and humic acid removal Disadvantages may be mitigated by pretreatment	Potential for metal leaching
GGBS	<18 M t used in Europe	Limited research available	Solidification in water Potential for metal leaching
Bayer residue	>2700 M t	Phosphorus and metal removal	Potential for contaminant leaching
Coconut shell	>60 M t of coconut grown per annum	Metal, dye and anion removal	Expensive carbonization and activation processes required
Tea/Coffee wastes	>5 M t of tea produced per annum	Metal and cation removal Dye removal when pretreated	Expensive pre-treatments may be required
Rice husk	>700 M t	Metal and dye removal	Expensive pre-treatments may be required
Crushed concrete	25% of all C&D waste	Phosphorus and metal removal	Potential for contaminant leaching from concrete constituents
Masonry	30% of all C&D waste	Nutrient, metal and microbiological removal	Variation in raw material
Wood waste	2% of all C&D waste	Nutrient and metal removal	Variation in raw material Expensive pre-treatments may be required

techniques. Where acid regeneration is used, it can be corrosive and difficult to store. Thermal regeneration techniques can require complex instrumentation and large capital expenditure (Aslam et al., 2015). Regeneration can also produce a high concentrate waste stream, which can bring about further issues of waste management (Igunnu and Chen, 2012). Therefore, it is important to analyse filter media holistically, including potential regeneration and costs, to ensure the most sustainable approach is taken.

It is important ensure that the use of the media in water treatment does not devalue the original product. Desorption techniques may be used to restore the product, although it may create another issue regarding waste creation as the pollutant will now be concentrated. In some instances, the original product may become more stable, and may still be useful in its current uses. In other cases, for example when used for nutrient capture, the media may then be used as a fertiliser. The ultimate use of the media will depend on the raw water being treated, and how that impacts on the media. However, it is clear that this is an area worth researching with clear gaps in knowledge evident.

The notion of a ‘circular economy’ requires products, materials, and services to be maintained within the economy for as long as possible, and is a major step towards a zero-waste society (European Commission, 2015c). Although the utilisation of these products does not result in an infinitely long solution, and further disposal mechanisms must be investigated, it does result in a more sustainable use for waste products. Evidently, in certain circumstances, regeneration of adsorption material is a possibility, although there is a large scope for further research in this area. The European Commission have identified waste management as a critical aspect of the circular economy, and recognises the need to involve public authorities, businesses, and investors (European Commission, 2015c). In order to fully engage these entities, it is important to have a viable solution to a difficult-to-solve problem. If the media can be sufficiently exploited to treat water in a sustainable fashion, those entities will have an invested interest in aiming to develop the technologies to their full potential. There is a recognised lack of studies considering industrial symbiosis, logistics and large-scale operation (Mirabella et al., 2014), and it is clear from the review that there is a large scope for development in this area. In this instance, the combination of research and industry, along with public authorities, could work together to fully develop a sustainable method of removing contaminants from water, while avoiding the creation of waste, and therefore leading towards a circular economy.

7. Conclusion

A brief summary of the advantages and disadvantages of each media, along with the raw material availability, is presented in Table 9. Where definite amounts are not available, figures for the parent material have been given. This review indicates that there is a large scope for use of media in water treatment, therefore mitigating current environmental issues such as waste disposal and storage, while aiming to improve water treatment services globally.

It is important to note that some media can also be successfully regenerated, once the adsorption potential has been reached, meaning that the filter can be used incurring much less cost than a full replacement. With the use of alternative media, clogging should also be considered. Certain media, although successful adsorbants, may have too fine a particle size, and become clogged within a short period of operation. This can be tested fully at a pilot-scale test.

It is, however, important to proceed with caution regarding some of the media, where there is a potential release of toxins or where the pre-treatment costs may not allow for a sustainable approach to be taken. Further recommendations, following this review, are to test the media at larger scale, both individually and also in a multi-layer configuration, where it would be possible to harness the varying adsorptive qualities of different media.

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Appendix B

Notation used in Appendix B

Conc: Concentration
Ce: Final concentration
x: mass removed
Vol: volume
NO3--N: Nitrate-nitrogen
NH4+-N: Ammonium-nitrogen
DOC: Dissolved organic carbon
Al: Aluminium
Cu: Copper
PO43--P: Phosphate-phosphorus
GAC: Granular activated carbon
GBS: Granular blast furnace slag

Table B1: Results from room temperature adsorption isotherms

Media	Contaminant	Initial conc (mg L^{-1})	Ce, Final Conc (mg L^{-1})	% reduction	mg/L removed	x, mass removed (mg)
Fine Sand	NO3-N	66.5	61.6	7.37	4.9	0.1225
		23	22	4.35	1	0.025
		66.5	60.4	9.17	6.1	0.1525
		43.2	41.8	3.24	1.4	0.035
		36.8	34.3	6.79	2.5	0.0625
		23	21.6	6.09	1.4	0.035
		36.8	35.5	3.53	1.3	0.0325
		23	22.2	3.48	0.8	0.02
Coarse Sand	NO3-N	66.5	63.7	4.21	2.8	0.07
		36.8	35.8	2.72	1	0.025
		23	22.3	3.04	0.7	0.0175
		9.6	9.1	5.21	0.5	0.0125
		66.5	64.2	3.46	2.3	0.0575
		23	22.2	3.48	0.8	0.02
		9.6	8.9	7.29	0.7	0.0175
		66.5	64.1	3.61	2.4	0.06
		36.8	34.9	5.16	1.9	0.0475
		23	22	4.35	1	0.025
		9.6	9.1	5.21	0.5	0.0125
Fine Sand	PO4-P	91.2	85.7	6.03	5.5	0.1375
		53.7	52.2	2.79	1.5	0.0375
		46.3	43	7.13	3.3	0.0825
		26.8	24.9	7.09	1.9	0.0475
		16.7	15.7	5.99	1	0.025
		91.2	84	7.89	7.2	0.18
		53.7	52.5	2.23	1.2	0.03
		46.3	42.9	7.34	3.4	0.085
		26.8	25.3	5.60	1.5	0.0375
		91.2	86.4	5.26	4.8	0.12
		53.7	52.3	2.61	1.4	0.035
		46.3	45.3	2.16	1	0.025
		26.8	25.4	5.22	1.4	0.035
		46.8	45	3.85	1.8	0.045
		27.2	26.1	4.04	1.1	0.0275

		18.2	16.1	11.54	2.1	0.0525
		9.3	8.7	6.45	0.6	0.015
Coarse Sand	PO4-P	91.2	65.8	27.85	25.4	0.635
		53.7	48.3	10.06	5.4	0.135
		46.3	38.5	16.85	7.8	0.195
		26.8	21.8	18.66	5	0.125
		16.7	14.4	13.77	2.3	0.0575
		91.2	77.1	15.46	14.1	0.3525
		53.7	47.9	10.80	5.8	0.145
		26.8	24.4	8.96	2.4	0.06
		16.7	15.6	6.59	1.1	0.0275
		91.2	83.2	8.77	8	0.2
		46.3	42	9.29	4.3	0.1075
		26.8	24.1	10.07	2.7	0.0675
		16.7	16.4	1.80	0.3	0.0075
		10.9	9.9	9.17	1	0.025
		47.1	43.4	7.86	3.7	0.0925
		27.1	24.9	8.12	2.2	0.055
		18.1	16.2	10.50	1.9	0.0475
		9.2	9.1	1.09	0.1	0.0025
Zeolite	PO4-P	47.1	43.7	7.22	3.4	0.085
		27.1	25.7	5.17	1.4	0.035
		18.1	16.8	7.18	1.3	0.0325
		9.2	9.1	1.09	0.1	0.0025
		100	69.9	30.10	30.1	0.7525
		60	56.2	6.33	3.8	0.095
Bottom Ash	PO4-P	47.1	43.1	8.49	4	0.1
		27.1	25.3	6.64	1.8	0.045
		18.1	16.2	10.50	1.9	0.0475
		9.2	9	2.17	0.2	0.005
		100	90.6	9.40	9.4	0.235
		60	58.5	2.50	1.5	0.0375
GAC	PO4-P	46.8	43.5	7.05	3.3	0.0825
		27.2	25.9	4.78	1.3	0.0325
		18.2	16.8	7.69	1.4	0.035
		9.3	8.1	12.90	1.2	0.03
Fine Sand	NH4-N	56.1	53.2	5.17	2.9	0.0725
		42.4	24.3	42.69	18.1	0.4525
		17	15.8	7.06	1.2	0.03
		9.5	9.3	2.11	0.2	0.005
		93.4	89.9	3.75	3.5	0.0875
		57.5	57	0.87	0.5	0.0125
Coarse Sand	NH4-N	47.4	43.2	8.86	4.2	0.105
		31.4	23.6	24.84	7.8	0.195
		17.9	14.4	19.55	3.5	0.0875
		9.09	8.8	3.19	0.29	0.00725
		93.4	86.2	7.71	7.2	0.18
		57.5	55.9	2.78	1.6	0.04
Fly Ash	NH4-N	47.4	40.3	14.98	7.1	0.1775
		31.4	24.6	21.66	6.8	0.17
		17.9	12.5	30.17	5.4	0.135
		9.09	7.6	16.39	1.49	0.03725

		93.4	62.5	33.08	30.9	0.7725
		57.5	34.7	39.65	22.8	0.57
Bottom Ash	NH4-N	47.4	44.8	5.49	2.6	0.065
		31.4	30.7	2.23	0.7	0.0175
		17.9	16.2	9.50	1.7	0.0425
		9.09	9	0.99	0.09	0.00225
		93.4	84.6	9.42	8.8	0.22
		57.5	52.5	8.70	5	0.125
		45.9	42.8	6.75	3.1	0.0775
		31.2	27.4	12.18	3.8	0.095
		17.8	16.1	9.55	1.7	0.0425
		8.5	8.4	1.18	0.1	0.0025
GAC	NH4-N	56.1	54.7	2.50	1.4	0.035
		42.4	24.7	41.75	17.7	0.4425
		17	16.5	2.94	0.5	0.0125
		9.5	9.4	1.05	0.1	0.0025
		93.4	91.1	2.46	2.3	0.0575
		57.5	57	0.87	0.5	0.0125
GBS	NH4-N	93.4	84.8	9.21	8.6	0.215
		57.5	55.8	2.96	1.7	0.0425
		45.9	40.8	11.11	5.1	0.1275
		31.2	28.6	8.33	2.6	0.065
		17.8	16.5	7.30	1.3	0.0325
		8.5	16	-88.24	-7.5	-0.1875
Bayer Residue	NH4-N	47.4	30.1	36.50	17.3	0.4325
		31.4	18.9	39.81	12.5	0.3125
		17.9	12.9	27.93	5	0.125
		9.09	9	0.99	0.09	0.00225
		93.4	65.6	29.76	27.8	0.695
		57.5	47.7	17.04	9.8	0.245
Pyritic Fill	NH4-N	93.4	86.2	7.71	7.2	0.18
		57.5	53.8	6.43	3.7	0.0925
		45.9	43.6	5.01	2.3	0.0575
		31.2	27.4	12.18	3.8	0.095
		17.8	16.3	8.43	1.5	0.0375
		8.5	8.4	1.18	0.1	0.0025
Fine Sand	DOC	5	6.048	-20.96	-1.048	-0.0393
		5	6.191	-23.82	-1.191	-0.04466
		10	12.237	-22.37	-2.237	-0.08389
		10	11.977	-19.77	-1.977	-0.07414
		20	24.791	-23.96	-4.791	-0.17966
		20	24.637	-23.19	-4.637	-0.17389
		50	61.206	-22.41	-11.206	-0.42023
		50	56.461	-12.92	-6.461	-0.24229
		100	109.939	-9.94	-9.939	-0.37271
		100	116.917	-16.92	-16.917	-0.63439
Coarse Sand	DOC	2.5	3.774	-50.96	-1.274	-0.03185
		2.5	3.396	-35.84	-0.896	-0.0224
		5	7.008	-40.16	-2.008	-0.0502
		5	6.125	-22.50	-1.125	-0.02813
		10	11.357	-13.57	-1.357	-0.03393
		10	10.934	-9.34	-0.934	-0.02335

		25	60.419	-141.68	-35.419	-0.88548
		25	33.672	-34.69	-8.672	-0.2168
Zeolite	DOC	2.5	2.294	8.24	0.206	0.007725
		5	4.042	19.16	0.958	0.035925
		5	3.14	37.20	1.86	0.06975
		5	3.915	21.70	1.085	0.040688
		10	4.357	56.43	5.643	0.211613
		10	4.911	50.89	5.089	0.190838
		10	5.452	45.48	4.548	0.17055
		25	23.684	5.26	1.316	0.04935
		25	23.58	5.68	1.42	0.05325
Fly Ash	DOC	5	0.716	85.68	4.284	0.16065
		5	0.589	88.22	4.411	0.165413
		10	0.957	90.43	9.043	0.339113
		10	0.652	93.48	9.348	0.35055
		20	1.434	92.83	18.566	0.696225
		20	2.856	85.72	17.144	0.6429
		50	3.796	92.41	46.204	1.73265
		50	1.692	96.62	48.308	1.81155
		100	7.69	92.31	92.31	3.461625
		100	4.506	95.49	95.494	3.581025
Bottom Ash	DOC	5	2.768	44.64	2.232	0.0837
		5	3.364	32.72	1.636	0.06135
		10	6.489	35.11	3.511	0.131663
		10	6.482	35.18	3.518	0.131925
		20	16.436	17.82	3.564	0.13365
		20	14.674	26.63	5.326	0.199725
		50	49.235	1.53	0.765	0.028688
		100	97.284	2.72	2.716	0.10185
GAC	DOC	5	3.169	36.62	1.831	0.068663
		5	3.285	34.30	1.715	0.064313
		10	9.204	7.96	0.796	0.02985
		20	13.041	34.80	6.959	0.260963
		20	0.788	96.06	19.212	0.72045
		50	2.744	94.51	47.256	1.7721
		100	89.281	10.72	10.719	0.401963
		100	90.629	9.37	9.371	0.351413
GBS	DOC	5	1.284	74.32	3.716	0.13935
		5	1.078	78.44	3.922	0.147075
		5	1.279	74.42	3.721	0.139538
		10	1.885	81.15	8.115	0.304313
		10	2.05	79.50	7.95	0.298125
		10	1.827	81.73	8.173	0.306488
		20	1.512	92.44	18.488	0.6933
		20	2.073	89.64	17.927	0.672263
		20	1.9	90.50	18.1	0.67875
		50	5.929	88.14	44.071	1.652663
		50	4.066	91.87	45.934	1.722525
		50	3.487	93.03	46.513	1.744238
		100	10.05	89.95	89.95	3.373125
		100	7.407	92.59	92.593	3.472238
		100	5.687	94.31	94.313	3.536738
PYR	DOC	5	1.134	77.32	3.866	0.144975

		5	0.867	82.66	4.133	0.154988
		10	1.239	87.61	8.761	0.328538
		10	1.11	88.90	8.89	0.333375
		20	1.881	90.60	18.119	0.679463
		20	1.296	93.52	18.704	0.7014
		50	3.686	92.63	46.314	1.736775
		50	3.37	93.26	46.63	1.748625
Bauxite	DOC	2.5	1.659	33.64	0.841	0.031538
		2.5	1.808	27.68	0.692	0.02595
		2.5	1.528	38.88	0.972	0.03645
		5	2.627	47.46	2.373	0.088988
		5	2.897	42.06	2.103	0.078863
		5	2.905	41.90	2.095	0.078563
		10	5.931	40.69	4.069	0.152588
		10	7.425	25.75	2.575	0.096563
		10	7.108	28.92	2.892	0.10845
		25	19.826	20.70	5.174	0.194025
		25	21.528	13.89	3.472	0.1302
		25	21.804	12.78	3.196	0.11985
		50	36.649	26.70	13.351	0.500663
		50	38.089	23.82	11.911	0.446663
		50	38.642	22.72	11.358	0.425925
Fine Sand	NO3-N	66.5	61.6	7.37	4.9	0.1225
		23	22	4.35	1	0.025
		66.5	60.4	9.17	6.1	0.1525
		43.2	41.8	3.24	1.4	0.035
		36.8	34.3	6.79	2.5	0.0625
		23	21.6	6.09	1.4	0.035
		36.8	35.5	3.53	1.3	0.0325
		23	22.2	3.48	0.8	0.02
		9.6	10	-4.17	-0.4	-0.01
		6.4	6.9	-7.81	-0.5	-0.0125
Coarse Sand	NO3-N	66.5	63.7	4.21	2.8	0.07
		36.8	35.8	2.72	1	0.025
		23	22.3	3.04	0.7	0.0175
		9.6	9.1	5.21	0.5	0.0125
		66.5	64.2	3.46	2.3	0.0575
		23	22.2	3.48	0.8	0.02
		9.6	8.9	7.29	0.7	0.0175
		66.5	64.1	3.61	2.4	0.06
		36.8	34.9	5.16	1.9	0.0475
		23	22	4.35	1	0.025
		9.6	9.1	5.21	0.5	0.0125
		6.4	6.6	-3.12	-0.2	-0.005
Zeolite	NO3-N	86.9	92.6	-6.56	-5.7	-0.1425
		58.8	62.9	-6.97	-4.1	-0.1025
		50.6	56.4	-11.46	-5.8	-0.145
		29.6	33.1	-11.82	-3.5	-0.0875
		19.2	19.6	-2.08	-0.4	-0.01
		8.4	9.1	-8.33	-0.7	-0.0175
		86.9	88.4	-1.73	-1.5	-0.0375
		58.8	63.3	-7.65	-4.5	-0.1125
		50.6	54.1	-6.92	-3.5	-0.0875

		29.6	31.7	-7.09	-2.1	-0.0525
		19.2	20.9	-8.85	-1.7	-0.0425
		8.4	8.5	-1.19	-0.1	-0.0025
		86.9	90.8	-4.49	-3.9	-0.0975
		58.8	59.9	-1.87	-1.1	-0.0275
		50.6	52.9	-4.55	-2.3	-0.0575
		29.6	31.6	-6.76	-2	-0.05
		19.2	20.4	-6.25	-1.2	-0.03
		8.4	9.6	-14.29	-1.2	-0.03
Fly Ash	NO3-N	86.9	92.6	-6.56	-5.7	-0.1425
		58.8	62.8	-6.80	-4	-0.1
		50.6	49.2	2.77	1.4	0.035
		29.6	29.5	0.34	0.1	0.0025
		19.2	18.9	1.56	0.3	0.0075
		8.4	8.3	1.19	0.1	0.0025
		86.9	86.2	0.81	0.7	0.0175
		58.8	59.2	-0.68	-0.4	-0.01
		50.6	48	5.14	2.6	0.065
		29.6	30.1	-1.69	-0.5	-0.0125
		19.2	19.9	-3.65	-0.7	-0.0175
		8.4	8.9	-5.95	-0.5	-0.0125
		86.9	89.7	-3.22	-2.8	-0.07
		58.8	60.9	-3.57	-2.1	-0.0525
		50.6	49.5	2.17	1.1	0.0275
		29.6	32.5	-9.80	-2.9	-0.0725
		19.2	21.6	-12.50	-2.4	-0.06
		8.4	22.8	-171.43	-14.4	-0.36
Bottom Ash	NO3-N	91	87	4.40	4	0.1
		91	86.2	5.27	4.8	0.12
		61.4	59.2	3.58	2.2	0.055
		49.4	48	2.83	1.4	0.035
		31.6	31.1	1.58	0.5	0.0125
		91	87.9	3.41	3.1	0.0775
		61.4	59	3.91	2.4	0.06
		49.4	46.2	6.48	3.2	0.08
		31.6	32.4	-2.53	-0.8	-0.02
		19.8	23.2	-17.17	-3.4	-0.085
		9.3	47	-405.38	-37.7	-0.9425
GAC	NO3-N	91	58.5	35.71	32.5	0.8125
		61.4	37.4	39.09	24	0.6
		49.4	29.6	40.08	19.8	0.495
		31.6	9.3	70.57	22.3	0.5575
		19.8	7.6	61.62	12.2	0.305
		9.3	5.5	40.86	3.8	0.095
		91	57.6	36.70	33.4	0.835
		61.4	37.8	38.44	23.6	0.59
		49.4	30.3	38.66	19.1	0.4775
		31.6	9.9	68.67	21.7	0.5425
		19.8	8.4	57.58	11.4	0.285
		9.3	8	13.98	1.3	0.0325
		91	55.2	39.34	35.8	0.895
		61.4	38.9	36.64	22.5	0.5625
		49.4	30.6	38.06	18.8	0.47

		31.6	20.7	34.49	10.9	0.2725
		19.8	8.3	58.08	11.5	0.2875
		9.3	8.4	9.68	0.9	0.0225
GBS	NO3-N	60.2	58.5	2.82	1.7	0.0425
		40.2	39.7	1.24	0.5	0.0125
		33.3	32.1	3.60	1.2	0.03
		21.6	9.5	56.02	12.1	0.3025
		8.9	7.7	13.48	1.2	0.03
		6.4	5.4	15.63	1	0.025
		60.2	57	5.32	3.2	0.08
		40.2	39.2	2.49	1	0.025
		33.3	31.3	6.01	2	0.05
		21.6	9.4	56.48	12.2	0.305
		8.9	8.2	7.87	0.7	0.0175
		6.4	9.2	-43.75	-2.8	-0.07
		60.2	58.5	2.82	1.7	0.0425
		40.2	39	2.99	1.2	0.03
		33.3	32.3	3.00	1	0.025
		21.6	9.8	54.63	11.8	0.295
		8.9	8.2	7.87	0.7	0.0175
		6.4	8.8	-37.50	-2.4	-0.06
PYR	NO3-N	60.3	7.2	88.06	53.1	1.3275
		41.2	6.3	84.71	34.9	0.8725
		34.1	5	85.34	29.1	0.7275
		21.3	3.7	82.63	17.6	0.44
		8.6	3.2	62.79	5.4	0.135
		5.6	2.1	62.50	3.5	0.0875
		60.3	6.7	88.89	53.6	1.34
		41.2	6	85.44	35.2	0.88
		34.1	5.6	83.58	28.5	0.7125
		21.3	4.2	80.28	17.1	0.4275
		8.6	3.5	59.30	5.1	0.1275
		5.6	3.5	37.50	2.1	0.0525
		60.3	6.9	88.56	53.4	1.335
		41.2	5.7	86.17	35.5	0.8875
		34.1	5.4	84.16	28.7	0.7175
		21.3	4.4	79.34	16.9	0.4225
		8.6	3.5	59.30	5.1	0.1275
		5.6	3.5	37.50	2.1	0.0525
BAUX	NO3-N	60.3	56.5	6.30	3.8	0.095
		41.2	39.5	4.13	1.7	0.0425
		34.1	33.1	2.93	1	0.025
		21.3	21.2	0.47	0.1	0.0025
		8.6	8.5	1.16	0.1	0.0025
		60.3	56.9	5.64	3.4	0.085
		41.2	39.6	3.88	1.6	0.04
		34.1	31.6	7.33	2.5	0.0625
		21.3	20	6.10	1.3	0.0325
Fine Sand	PO4-P	16.6	15.7	5.42	0.9	0.0225
		8.1	6.9	14.81	1.2	0.03
		4.1	3.5	14.63	0.6	0.015
		30.7	27.9	9.12	2.8	0.07
		20	22.9	-14.50	-2.9	-0.0725

		11.4	12.2	-7.02	-0.8	-0.02
		30.7	28.3	7.82	2.4	0.06
		20	19.7	1.50	0.3	0.0075
		11.4	9.9	13.16	1.5	0.0375
Coarse Sand	PO4-P	16.6	10.7	35.54	5.9	0.1475
		8.1	3.1	61.73	5	0.125
		4.1	1.6	60.98	2.5	0.0625
		30.7	21.5	29.97	9.2	0.23
		20	16.3	18.50	3.7	0.0925
		11.4	9.9	13.16	1.5	
		30.7	21.5	29.97	9.2	0.23
		20	14.9	25.50	5.1	0.1275
		11.4	7.9	30.70	3.5	
Fine Sand	NH4-N	10	9	10.00	1	0.025
		9.8	8.6	12.24	1.2	0.03
		5.1	4.3	15.69	0.8	0.02
		17.9	17.3	3.35	0.6	0.015
		8.9	8.1	8.99	0.8	0.02
		4.3	3.6	16.28	0.7	0.0175
		17.9	16.9	5.59	1	0.025
		8.9	8.2	7.87	0.7	0.0175
		4.3	3.3	23.26	1	0.025
Coarse Sand	NH4-N	20	12	40.00	8	0.2
		10	5	50.00	5	0.125
		19.3	9.5	50.78	9.8	0.245
		9.5	3.9	58.95	5.6	0.14
		4.6	1.2	73.91	3.4	0.085
		17.9	10.7	40.22	7.2	0.18
		8.9	3.4	61.80	5.5	0.1375
		17.9	12	32.96	5.9	0.1475
		8.9	4.2	52.81	4.7	0.1175
Zeolite	NH4-N	56.4	1.4	97.52	55	1.375
		19	0.1	99.47	18.9	0.4725
		19	0.2	98.95	18.8	0.47
		9.1	0.3	96.70	8.8	0.22
		4.3	0	100.00	4.3	0.1075
		183.8	11.2	93.91	172.6	4.315
		96.9	4.1	95.77	92.8	2.32
		183.8	11.3	93.85	172.5	4.3125
		96.9	4.5	95.36	92.4	2.31
Fly Ash	NH4-N	41	12	70.73	29	0.725
		20	9	55.00	11	0.275
		10	5	50.00	5	0.125
		19	6.2	67.37	12.8	0.32
		9.1	3.3	63.74	5.8	0.145
		4.3	1.1	74.42	3.2	0.08
		19	6.2	67.37	12.8	0.32
		9.1	2.7	70.33	6.4	0.16
		4.3	1.2	72.09	3.1	0.0775
Bottom Ash	NH4-N	20	17	15.00	3	0.075
		10	8	20.00	2	0.05
		18.7	16.2	13.37	2.5	0.0625

		4.4	3.1	29.55	1.3	0.0325
		19	15.9	16.32	3.1	0.0775
		9.1	7	23.08	2.1	0.0525
		19	15.8	16.84	3.2	0.08
		9.1	7.3	19.78	1.8	0.045
		4.3	3.2	25.58	1.1	
GAC	NH4-N	41	38	7.32	3	0.075
		20	17	15.00	3	0.075
		19.9	18.3	8.04	1.6	0.04
		9.7	8.9	8.25	0.8	0.02
		4.7	4.4	6.38	0.3	0.0075
		17.9	15.6	12.85	2.3	0.0575
		8.9	7.8	12.36	1.1	0.0275
		4.3	4.1	4.65	0.2	0.005
		19	17.1	10.00	1.9	0.0475
GBS	NH4-N	41	22	46.34	19	0.475
		20	15	25.00	5	0.125
		10	7	30.00	3	0.075
		19.3	13	32.64	6.3	0.1575
		9.6	6.5	32.29	3.1	0.0775
		19	11.3	40.53	7.7	0.1925
		9.1	4.5	50.55	4.6	0.115
		4.3	3	30.23	1.3	0.0325
		19	11.2	41.05	7.8	0.195
		9.1	5.8	36.26	3.3	0.0825
		4.3	2.6	39.53	1.7	0.0425
Bayer Residue	NH4-N	20	10	50.00	10	0.25
		19.3	8	58.55	11.3	0.2825
		9.6	3.8	60.42	5.8	0.145
		4.7	1.7	63.83	3	0.075
		17.9	8.1	54.75	9.8	0.245
		8.9	1.2	86.52	7.7	0.1925
		4.3	0.4	90.70	3.9	0.0975
		17.9	2.6	85.47	15.3	0.3825
		8.9	0.6	93.26	8.3	0.2075
		4.3	0.3	93.02	4	0.1
Pyritic Fill	NH4-N	41	21	48.78	20	0.5
		20	14	30.00	6	0.15
		10	7	30.00	3	0.075
		19.3	12.2	36.79	7.1	0.1775
		9.6	5.6	41.67	4	0.1
		5	2.6	48.00	2.4	0.06
		19	12.9	32.11	6.1	0.1525
		9.1	5.6	38.46	3.5	0.0875
		4.3	2.5	41.86	1.8	0.045
		19	12.6	33.68	6.4	0.16
		9.1	5.7	37.36	3.4	0.085
		4.3	2.5	41.86	1.8	0.045
Fine Sand	NO3-N	66.5	61.6	7.37	4.9	0.1225
		23	22	4.35	1	0.025
		66.5	60.4	9.17	6.1	0.1525
		43.2	41.8	3.24	1.4	0.035

		36.8	34.3	6.79	2.5	0.0625
		23	21.6	6.09	1.4	0.035
		36.8	35.5	3.53	1.3	0.0325
		23	22.2	3.48	0.8	0.02
		9.6	10	-4.17	-0.4	-0.01
		6.4	6.9	-7.81	-0.5	-0.0125
Coarse Sand	NO3-N	66.5	63.7	4.21	2.8	0.07
		36.8	35.8	2.72	1	0.025
		23	22.3	3.04	0.7	0.0175
		9.6	9.1	5.21	0.5	0.0125
		66.5	64.2	3.46	2.3	0.0575
		23	22.2	3.48	0.8	0.02
		9.6	8.9	7.29	0.7	0.0175
		66.5	64.1	3.61	2.4	0.06
		36.8	34.9	5.16	1.9	0.0475
		23	22	4.35	1	0.025
		9.6	9.1	5.21	0.5	0.0125
		6.4	6.6	-3.12	-0.2	-0.005
Zeolite	NO3-N	86.9	92.6	-6.56	-5.7	-0.1425
		58.8	62.9	-6.97	-4.1	-0.1025
		50.6	56.4	-11.46	-5.8	-0.145
		29.6	33.1	-11.82	-3.5	-0.0875
		19.2	19.6	-2.08	-0.4	-0.01
		8.4	9.1	-8.33	-0.7	-0.0175
		86.9	88.4	-1.73	-1.5	-0.0375
		58.8	63.3	-7.65	-4.5	-0.1125
		50.6	54.1	-6.92	-3.5	-0.0875
		29.6	31.7	-7.09	-2.1	-0.0525
		19.2	20.9	-8.85	-1.7	-0.0425
		8.4	8.5	-1.19	-0.1	-0.0025
		86.9	90.8	-4.49	-3.9	-0.0975
		58.8	59.9	-1.87	-1.1	-0.0275
		50.6	52.9	-4.55	-2.3	-0.0575
		29.6	31.6	-6.76	-2	-0.05
		19.2	20.4	-6.25	-1.2	-0.03
		8.4	9.6	-14.29	-1.2	-0.03
Fly Ash	NO3-N	86.9	92.6	-6.56	-5.7	-0.1425
		58.8	62.8	-6.80	-4	-0.1
		50.6	49.2	2.77	1.4	0.035
		29.6	29.5	0.34	0.1	0.0025
		19.2	18.9	1.56	0.3	0.0075
		8.4	8.3	1.19	0.1	0.0025
		86.9	86.2	0.81	0.7	0.0175
		58.8	59.2	-0.68	-0.4	-0.01
		50.6	48	5.14	2.6	0.065
		29.6	30.1	-1.69	-0.5	-0.0125
		19.2	19.9	-3.65	-0.7	-0.0175
		8.4	8.9	-5.95	-0.5	-0.0125
		86.9	89.7	-3.22	-2.8	-0.07
		58.8	60.9	-3.57	-2.1	-0.0525
		50.6	49.5	2.17	1.1	0.0275
		29.6	32.5	-9.80	-2.9	-0.0725
		19.2	21.6	-12.50	-2.4	-0.06

		8.4	22.8	-171.43	-14.4	-0.36
Bottom Ash	NO3-N	91	87	4.40	4	0.1
		91	86.2	5.27	4.8	0.12
		61.4	59.2	3.58	2.2	0.055
		49.4	48	2.83	1.4	0.035
		31.6	31.1	1.58	0.5	0.0125
		91	87.9	3.41	3.1	0.0775
		61.4	59	3.91	2.4	0.06
		49.4	46.2	6.48	3.2	0.08
		31.6	32.4	-2.53	-0.8	-0.02
		19.8	23.2	-17.17	-3.4	-0.085
		9.3	47	-405.38	-37.7	-0.9425
GAC	NO3-N	91	58.5	35.71	32.5	0.8125
		61.4	37.4	39.09	24	0.6
		49.4	29.6	40.08	19.8	0.495
		31.6	9.3	70.57	22.3	0.5575
		19.8	7.6	61.62	12.2	0.305
		9.3	5.5	40.86	3.8	0.095
		91	57.6	36.70	33.4	0.835
		61.4	37.8	38.44	23.6	0.59
		49.4	30.3	38.66	19.1	0.4775
		31.6	9.9	68.67	21.7	0.5425
		19.8	8.4	57.58	11.4	0.285
		9.3	8	13.98	1.3	0.0325
		91	55.2	39.34	35.8	0.895
		61.4	38.9	36.64	22.5	0.5625
		49.4	30.6	38.06	18.8	0.47
		31.6	20.7	34.49	10.9	0.2725
		19.8	8.3	58.08	11.5	0.2875
		9.3	8.4	9.68	0.9	0.0225
GBS	NO3-N	60.2	58.5	2.82	1.7	0.0425
		40.2	39.7	1.24	0.5	0.0125
		33.3	32.1	3.60	1.2	0.03
		21.6	9.5	56.02	12.1	0.3025
		8.9	7.7	13.48	1.2	0.03
		6.4	5.4	15.63	1	0.025
		60.2	57	5.32	3.2	0.08
		40.2	39.2	2.49	1	0.025
		33.3	31.3	6.01	2	0.05
		21.6	9.4	56.48	12.2	0.305
		8.9	8.2	7.87	0.7	0.0175
		6.4	9.2	-43.75	-2.8	-0.07
		60.2	58.5	2.82	1.7	0.0425
		40.2	39	2.99	1.2	0.03
		33.3	32.3	3.00	1	0.025
		21.6	9.8	54.63	11.8	0.295
		8.9	8.2	7.87	0.7	0.0175
		6.4	8.8	-37.50	-2.4	-0.06
Fine Sand	Al	1.04	0.106	89.81	0.934	0.02335
		0.339	0.202	40.41	0.137	0.003425
		1.1	0.106	90.36	0.994	0.02485
		0.741	0.087	88.26	0.654	0.01635
		0.388	0.13	66.49	0.258	0.00645

		0.292	0.13	55.48	0.162	0.00405
		0.741	0.123	83.40	0.618	0.01545
		0.388	0.268	30.93	0.12	0.003
		0.292	0.024	91.78	0.268	0.0067
Coarse Sand	Al	0.452	0.13	71.24	0.322	0.00805
		0.339	0.036	89.38	0.303	0.007575
		1.01	0.035	96.53	0.975	0.024375
		0.741	0.005	99.33	0.736	0.0184
		0.388	0.102	73.71	0.286	
		1.01	0.106	89.50	0.904	0.0226
		0.741	0.005	99.33	0.736	0.0184
		0.388	0.268	30.93	0.12	0.003
		0.292	0.01	96.58	0.282	0.00705
		0.292	0.024	91.78	0.268	0.0067
Zeolite	Al	1.04	0.024	97.69	1.016	0.0254
		0.452	0.003	99.34	0.449	0.011225
		0.339	0.001	99.71	0.338	0.00845
		0.35	0.162	53.71	0.188	0.0047
		0.47	0.145	69.15	0.325	0.008125
		0.457	0.114	75.05	0.343	0.008575
		0.184	0.042	77.17	0.142	0.00355
		1000	0.069	99.99	999.931	24.99828
		0.47	0.067	85.74	0.403	0.010075
		0.467	0.067	85.65	0.4	0.01
Pyritic Fill	Al	1.04	0.03	97.12	1.01	0.02525
		0.452	0.029	93.58	0.423	0.010575
		0.339	0.025	92.63	0.314	0.00785
		0.897	0.068	92.42	0.829	0.020725
		0.462	0.087	81.17	0.375	0.009375
		0.382	0.061	84.03	0.321	0.008025
		0.189	0.031	83.60	0.158	0.00395
		0.897	0.03	96.66	0.867	0.021675
		0.462	0.078	83.12	0.384	0.0096
		0.382	0.128	66.49	0.254	0.00635
Bottom Ash	Al	0.452	0.416	7.96	0.036	0.0009
		0.339	0.227	33.04	0.112	0.0028
		1.01	0.093	90.79	0.917	0.022925
		0.388	0.253	34.79	0.135	0.003375
		0.292	0.211	27.74	0.081	0.002025
		0.897	0.034	96.21	0.863	0.021575
		0.462	0.1	78.35	0.362	0.00905
		0.382	0.102	73.30	0.28	0.007
		0.189	0.108	42.86	0.081	0.002025
		0.897	0.093	89.63	0.804	0.0201
		0.462	0.253	45.24	0.209	0.005225
		0.382	0.098	74.35	0.284	0.0071
		0.189	0.069	63.49	0.12	0.003
GAC	Al	1.04	0.374	64.04	0.666	0.01665
		0.452	0.025	94.47	0.427	0.010675
		0.339	0.009	97.35	0.33	0.00825
		1.01	0.123	87.82	0.887	0.022175
		0.741	0.104	85.96	0.637	0.015925

		0.388	0.076	80.41	0.312	0.0078
		0.292	0.05	82.88	0.242	0.00605
		1.01	0.146	85.54	0.864	0.0216
		0.741	0.112	84.89	0.629	0.015725
		0.388	0.07	81.96	0.318	0.00795
		0.292	0.088	69.86	0.204	0.0051
		0.35	0.03	91.43	0.32	0.008
		0.47	0.078	83.40	0.392	0.0098
		0.457	0.128	71.99	0.329	0.008225
		0.35	0.01	97.14	0.34	0.0085
		0.47	0.031	93.40	0.439	0.010975
		0.457	0.061	86.65	0.396	0.0099
Fine Sand	Cu	2.9	2.8	3.45	0.1	0.0025
		3	1.8	40.00	1.2	0.03
		4.9	4.8	2.04	0.1	0.0025
		3.9	2.9	25.64	1	0.025
		3	2.2	26.67	0.8	0.02
Coarse Sand	Cu	4.9	1	79.59	3.9	0.0975
		3.9	0.7	82.05	3.2	0.08
		3	0.5	83.33	2.5	0.0625
		4.9	0.8	83.67	4.1	0.1025
		3.9	0.3	92.31	3.6	0.09
		3	0.1	96.67	2.9	0.0725
Zeolite	Cu	32.9	4.13	87.45	28.77	0.71925
		20.58	2.74	86.69	17.84	0.446
		9.75	0.19	98.05	9.56	0.239
		5.52	0.2	96.38	5.32	0.133
		32.9	4	87.84	28.9	0.7225
		20.58	1.28	93.78	19.3	0.4825
		9.75	0.08	99.18	9.67	0.24175
		5.52	0.18	96.74	5.34	0.1335
Fly Ash	Cu	32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		500	336	32.80	164	4.1
		1000	682	31.80	318	7.95
Bottom Ash	Cu	32.9	29.1	11.55	3.8	0.095
		20.58	11.95	41.93	8.63	0.21575
		9.75	5.04	48.31	4.71	0.11775
		5.52	0.14	97.46	5.38	0.1345
		32.9	30.12	8.45	2.78	0.0695
		20.58	15.9	22.74	4.68	0.117
		9.75	3.07	68.51	6.68	0.167
		5.52	0.05	99.09	5.47	0.13675
GAC	Cu	4.9	1.7	65.31	3.2	0.08
		3.9	1.2	69.23	2.7	0.0675
		3	0.7	76.67	2.3	0.0575

		4.9	1.4	71.43	3.5	0.0875
		3.9	0.9	76.92	3	0.075
		3	0.7	76.67	2.3	0.0575
GBS	Cu	32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		500	246	50.80	254	6.35
		1000	436	56.40	564	14.1
Bayer Residue	Cu	32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		500	374	25.20	126	3.15
		1000	692	30.80	308	7.7
Pyritic Fill	Cu	32.9	0.01	99.97	32.89	0.82225
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		32.9	0.1	99.70	32.8	0.82
		20.58	0.1	99.51	20.48	0.512
		9.75	0.1	98.97	9.65	0.24125
		5.52	0.1	98.19	5.42	0.1355
		500	335	33.00	165	4.125
		1000	692	30.80	308	7.7
Fine Sand	PO4-P	16.6	15.7	5.42	0.9	0.0225
		8.1	6.9	14.81	1.2	0.03
		4.1	3.5	14.63	0.6	0.015
		30.7	27.9	9.12	2.8	0.07
		30.7	28.3	7.82	2.4	0.06
		11.4	9.9	13.16	1.5	0.0375
Coarse Sand	PO4-P	16.6	10.7	35.54	5.9	0.1475
		8.1	3.1	61.73	5	0.125
		4.1	1.6	60.98	2.5	0.0625
		30.7	21.5	29.97	9.2	0.23
		20	16.3	18.50	3.7	0.0925
		30.7	21.5	29.97	9.2	0.23
		20	14.9	25.50	5.1	0.1275
		11.4	7.9	30.70	3.5	0.0875
Zeolite	PO4-P	12.9	3.3	74.42	9.6	0.24
		7.3	0.9	87.67	6.4	0.16
		3.6	0.1	97.22	3.5	0.0875
		30.7	25.1	18.24	5.6	0.14
		20	18.5	7.50	1.5	0.0375

		11.4	8.8	22.81	2.6	0.065
		30.7	28.3	7.82	2.4	0.06
		11.4	8.7	23.68	2.7	0.0675
Fly Ash	PO4-P	850	2.84	99.67	847.16	21.179
		370	0.6	99.84	369.4	9.235
		81	0.1	99.88	80.9	2.0225
Bottom Ash	PO4-P	16.9	13.9	17.75	3	0.075
		7.8	5.6	28.21	2.2	0.055
		4	2.8	30.00	1.2	0.03
		30.7	25.5	16.94	5.2	0.13
		30.7	25.5	16.94	5.2	0.13
		20	17.9	10.50	2.1	0.0525
		11.4	8.4	26.32	3	0.075
GAC	PO4-P	13.8	9.7	29.71	4.1	0.1025
		7.7	2.9	62.34	4.8	0.12
		3.9	0.2	94.87	3.7	0.0925
		30.7	22.6	26.38	8.1	0.2025
		20	13.2	34.00	6.8	0.17
		11.4	5.3	53.51	6.1	0.1525
		30.7	22.2	27.69	8.5	0.2125
		20	14.9	25.50	5.1	0.1275
		11.4	4.4	61.40	7	0.175
GBS	PO4-P	848.5	140.2	83.48	708.3	17.7075
		850	78.9	90.72	771.1	19.2775
		730	0.5	99.93	729.5	18.2375
		81	0.2	99.75	80.8	2.02
Pyritic Fill	PO4-P	31.5	0.1	99.68	31.4	0.785
		7.7	0.1	98.70	7.6	0.19
		5	0.1	98.00	4.9	0.1225
		163.8	13.6	91.70	150.2	3.755
		93.5	3.8	95.94	89.7	2.2425
		49	0.8	98.37	48.2	1.205
		163.8	12.5	92.37	151.3	3.7825
		93.5	2.3	97.54	91.2	2.28
		49.1	1	97.96	48.1	1.2025
Bayer Residue	PO4-P	20.6	5.6	72.82	15	0.375
		8	3.2	60.00	4.8	0.12
		4.4	2	54.55	2.4	0.06
		163.8	128.6	21.49	35.2	0.88
		93.5	58.1	37.86	35.4	0.885
		49	26.1	46.73	22.9	
		163.8	129.8	20.76	34	0.85
		93.5	59	36.90	34.5	0.8625
		49	27.1	44.69	21.9	0.5475
Fine Sand	NH4-N	10	9	10.00	1	0.025
		9.8	8.6	12.24	1.2	0.03
		5.1	4.3	15.69	0.8	0.02
		17.9	17.3	3.35	0.6	0.015
		8.9	8.1	8.99	0.8	0.02
		4.3	3.6	16.28	0.7	0.0175
		17.9	16.9	5.59	1	0.025
		8.9	8.2	7.87	0.7	0.0175

		4.3	3.3	23.26	1	0.025
Coarse Sand	NH4-N	20	12	40.00	8	0.2
		10	5	50.00	5	0.125
		19.3	9.5	50.78	9.8	0.245
		9.5	3.9	58.95	5.6	0.14
		4.6	1.2	73.91	3.4	0.085
		17.9	10.7	40.22	7.2	0.18
		8.9	3.4	61.80	5.5	0.1375
		4.3	1.3	69.77	3	0.075
		17.9	12	32.96	5.9	0.1475
		8.9	4.2	52.81	4.7	0.1175
		4.3	1.7	60.47	2.6	0.065
Zeolite	NH4-N	56.4	1.4	97.52	55	1.375
		19	0.1	99.47	18.9	0.4725
		19	0.2	98.95	18.8	0.47
		9.1	0.3	96.70	8.8	0.22
		4.3	0.1	97.67	4.2	0.105
		183.8	11.2	93.91	172.6	4.315
		96.9	4.1	95.77	92.8	2.32
		183.8	11.3	93.85	172.5	4.3125
		96.9	4.5	95.36	92.4	2.31
Fly Ash	NH4-N	41	12	70.73	29	0.725
		20	9	55.00	11	0.275
		10	5	50.00	5	0.125
		19	6.2	67.37	12.8	0.32
		9.1	3.3	63.74	5.8	0.145
		4.3	1.1	74.42	3.2	0.08
		19	6.2	67.37	12.8	0.32
		9.1	2.7	70.33	6.4	0.16
		4.3	1.2	72.09	3.1	0.0775
Bottom Ash	NH4-N	20	17	15.00	3	0.075
		10	8	20.00	2	0.05
		18.7	16.2	13.37	2.5	0.0625
		4.4	3.1	29.55	1.3	0.0325
		19	15.9	16.32	3.1	0.0775
		9.1	7	23.08	2.1	0.0525
		19	15.8	16.84	3.2	0.08
		9.1	7.3	19.78	1.8	0.045
		4.3	3.2	25.58	1.1	0.0275
GAC	NH4-N	41	38	7.32	3	0.075
		20	17	15.00	3	0.075
		19.9	18.3	8.04	1.6	0.04
		9.7	8.9	8.25	0.8	0.02
		4.7	4.4	6.38	0.3	0.0075
		17.9	15.6	12.85	2.3	0.0575
		8.9	7.8	12.36	1.1	0.0275
		4.3	4.1	4.65	0.2	0.005
		19	17.1	10.00	1.9	0.0475
GBS	NH4-N	41	22	46.34	19	0.475
		20	15	25.00	5	0.125
		10	7	30.00	3	0.075
		19.3	13	32.64	6.3	0.1575
		9.6	6.5	32.29	3.1	0.0775

		19	11.3	40.53	7.7	0.1925
		9.1	4.5	50.55	4.6	0.115
		4.3	3	30.23	1.3	0.0325
		19	11.2	41.05	7.8	0.195
		9.1	5.8	36.26	3.3	0.0825
		4.3	2.6	39.53	1.7	0.0425
Pyritic Fill	NH4-N	41	21	48.78	20	0.5
		20	14	30.00	6	0.15
		10	7	30.00	3	0.075
		19.3	12.2	36.79	7.1	0.1775
		9.6	5.6	41.67	4	0.1
		5	2.6	48.00	2.4	0.06
		19	12.9	32.11	6.1	0.1525
		9.1	5.6	38.46	3.5	0.0875
		4.3	2.5	41.86	1.8	0.045
		19	12.6	33.68	6.4	0.16
		9.1	5.7	37.36	3.4	0.085
		4.3	2.5	41.86	1.8	0.045
Bayer residue	NH4-N	20	10	50.00	10	0.25
		19.3	8	58.55	11.3	0.2825
		9.6	3.8	60.42	5.8	0.145
		4.7	1.7	63.83	3	0.075
		17.9	8.1	54.75	9.8	0.245
		8.9	1.2	86.52	7.7	0.1925
		4.3	0.4	90.70	3.9	0.0975
		17.9	2.6	85.47	15.3	0.3825
		8.9	0.6	93.26	8.3	0.2075
		4.3	0.3	93.02	4	0.1

Table B2: Results from 10°C adsorption isotherms

Media	Contaminant	Initial conc (mg/L)	Ce, Final Conc (mg/L)	% reduction	mg/L removed	x, mass removed (g)
Coarse sand	NH4N	36	18	50	18	4.50E-04
		21	13	38.1	8	2.00E-04
		11	6	45.5	5	1.25E-04
		18.9	10.9	42.3	8	2.00E-04
		9.5	4.7	50.5	4.8	1.20E-04
		4.9	1.8	63.3	3.1	7.75E-05
		18.9	11.6	38.6	7.3	1.83E-04
		9.5	4.8	49.5	4.7	1.18E-04
		4.9	1.9	61.2	3	7.50E-05
	Cu	4.78	0.18	96.2	4.6	1.15E-04
		3.82	0.12	96.7	3.7	9.25E-05
		3.08	0.07	97.7	3.01	7.53E-05
		4.78	0.04	99.2	4.7	1.19E-04
		3.82	0.02	99.5	3.8	9.50E-05
		3.08	0.02	99.4	3.06	7.65E-05
Zeolite	PO4P	30.2	27.1	10.3	3.1	7.75E-05
		20.1	16.8	16.4	3.3	8.25E-05
		9.7	7.5	22.7	2.2	5.50E-05
		30.2	28.4	5.9	1.8	4.50E-05
		20.1	17.5	12.9	2.6	6.50E-05
		9.7	5.3	45.4	4.4	1.10E-04
	Cu	5.2	1.2	76.1	3.96	9.90E-05
		4.2	0.24	94.3	3.96	9.90E-05
		3.14	0.04	98.7	3.1	7.75E-05
		5.2	1.04	80	4.16	1.04E-04
		4.2	0.52	87.6	3.68	9.20E-05

		3.14	0.244	92.4	2.90	7.25E-05
Fly ash	Cu	5.2	0.3	94.2	4.9	1.23E-04
		4.2	0.12	97.2	4.08	1.02E-04
		3.14	0.05	98.4	3.09	7.73E-05
		5.2	0.5	90.4	4.7	1.18E-04
		4.2	0.1	98.1	4.12	1.03E-04
		3.14	0.04	98.7	3.1	7.75E-05
GAC	Al	1.04	0.278	73.3	0.762	1.91E-02
		0.452	0.1	77.9	0.352	8.80E-03
		0.339	22	93.5	0.317	7.93E-03
	PO4P	30.2	25.5	15.6	4.7	1.18E-04
		20.1	14.9	25.9	5.2	1.30E-04
		9.7	5.3	45.4	4.4	1.10E-04
		30.2	25.3	16.2	4.9	1.23E-04
		20.1	14.9	25.9	5.2	1.30E-04
		9.7	5.2	46.4	4.5	1.13E-04
	Cu	4.78	1.26	73.6	3.52	8.80E-05
		3.82	0.93	75.7	2.89	7.23E-05
		3.08	0.5	83.8	2.58	6.45E-05
		4.78	0.84	82.4	3.94	9.85E-05
		3.82	0.17	95.6	3.65	9.13E-05
		3.08	0.17	94.5	2.91	7.28E-05
Pyritic fill	Al	1.040	0.03	97.1	1.01	2.53E-02
		0.452	0.029	93.6	0.423	1.06E-02
		0.339	0.025	92.6	0.314	7.85E-03
	PO4P	30.2	0.14	99.5	30.1	7.52E-04
		20.1	0.13	99.4	19.9	4.99E-04
		9.7	0.1	98.9	9.6	2.40E-04
		30.2	0.09	99.7	30.1	7.53E-04
		20.1	0.08	99.6	20	5.01E-04
		9.7	0.1	99	9.6	2.40E-04
	Cu	4.78	1.26	73.6	3.52	8.80E-05
		3.82	0.93	75.7	2.89	7.23E-05
		3.08	0.5	83.8	2.58	6.45E-05
		4.78	0.84	82.4	3.94	9.85E-05
		3.82	0.17	95.6	3.65	9.13E-05
		3.08	0.17	94.5	2.91	7.28E-05
Bayer residue	NH4N	36	14	61.1	22	5.50E-04
		21	11	47.6	10	2.50E-04
		11	6	45.5	5	1.25E-04
		18.9	7.2	31.9	11.7	2.93E-04
		8.5	2.9	65.9	5.6	1.40E-04
		4.9	1.3	73.5	36	9.00E-05
		18.9	7.1	62.4	11.8	2.95E-04
		9.5	2.9	69.5	6.6	1.65E-04
		4.9	1.3	73.5	3.6	9.00E-05
	PO4P	30.2	11.2	62.9	19	4.75E-04
		20.1	5.8	71.1	14.3	3.58E-04
		9.7	2.3	76.3	7.4	1.85E-04
		30.2	11.6	61.6	18.6	4.65E-04
		20.1	6.2	69.2	13.9	3.48E-04
		9.7	2.4	75.3	7.3	1.83E-04

Table B3: Results from 19°C adsorption isotherms

Media	Contaminant	Initial conc (mg/L)	Ce, Final Conc (mg/L)	% reduction	mg/L removed	x, mass removed (mg)
GAC	Al	1.040	0.108	89.5	0.932	932
		0.452	0.055	87.9	0.397	397
		0.339	0.022	93.5	0.317	317
		1.040	0.154	85.2	0.886	886
		0.452	0.175	61.3	0.277	277
		0.339	0.001	99.7	0.338	338
	PO4P	30.4	17.5	42.43	12.90	3.23E-04
		21.1	13.8	34.6	7.30	1.83E-04
		9.9	2.9	70.7	7.00	1.75E-04
		30.4	17.4	42.7	13.00	3.25E-04

		21.1	13.8	34.6	7.30	1.83E-04
		9.9	2.9	70.7	7.00	1.75E-04
Pyritic fill	Al	1.040	0.016	98.5	1.024	1024.10
		0.452	0.006	98.7	0.446	446
		0.339	0.001	99.7	0.339	339
		1.040	0.001	99.9	1.039	1039
		0.452	0.007	99.8	0.445	445
		0.339	0.002	99.9	0.337	337
	Cu	5.29	0.03	99.4	5.26	1.32E-04
		4.22	0.02	99.5	4.20	1.05E-04
		3.18	0.01	99.7	3.17	7.93E-05
Bayer residue	NH4N	39.8	15.6	60.8	24.2	6.05E-04
		18.6	8.4	54.8	10.2	2.55E-04
		9.6	6.1	36.5	3.5	8.75E-05
		39.8	16.6	58.3	23.2	5.80E-04
		18.6	8.8	52.7	9.8	2.45E-04
		9.6	5.9	38.5	3.7	9.25E-05
		176.6	93.3	47.1	83.8	2.08E-03
		95.9	49.2	48.7	46.7	1.17E-03
		176.6	93.5	47.1	83.1	2.08E-03
		95.9	49.6	48.3	46.3	1.16E-03
	PO4P	30.4	10.8	64.5	19.60	4.90E-04
		21.4	6.9	67.8	14.50	3.63E-04
		9.9	3.2	68.2	6.75	1.69E-04
		30.4	11.1	63.5	19.31	4.83E-04
		21.1	7.3	65.6	13.83	3.46E-04
		9.9	3.1	68.9	6.82	1.71E-04
	Cu	5.29	1.08	79.6	4.21	1.05E-04
		4.22	1.1	74	3.12	7.80E-05
		3.18	0.6	81.76	2.60	6.50E-05

Table B4: Results from pH adjusted adsorption isotherms

Contaminant	Media	Initial conc (mg/L)	Ce, Final Conc (mg/L)	% reduction	mg/L removed	x, mass removed (mg)
Copper	Coarse sand	10.5	2	80.9	8.50	2.13E-04
		8	1.5	81.2	6.50	1.63E-04
		2.6	0	100	2.62	6.55E-05
	GAC	20.4	3.5	82.6	16.85	4.21E-04
		10.2	1.5	85.3	8.70	2.18E-04
		2.62	0	100	2.62	6.55E-05
	Zeolite	20.4	2.4	88.2	18.00	4.50E-04
		10.2	1	90.2	9.20	2.30E-04
		2.6	0.03	98	2.59	6.48E-05
	Bottom ash	4.25	2.27	46.6	1.98	4.95E-05
		3.5	1.8	47.7	1.67	4.18E-05
		2.6	1	64	1.68	4.20E-05
PO4P	Zeolite	33.8	24.9	26.3	8.90	2.23E-04
		24.8	18.5	25.4	6.30	1.58E-04
		9.5	3.3	65.3	6.20	1.55E-04
		33.8	25	26.1	8.80	2.20E-04
		24.8	18.4	25.8	6.40	1.60E-04
		9.5	5.5	42.11	4.00	1.00E-04

	GAC	33.8	23.8	29.6	10.00	2.50E-04
		24.8	0.8	16.1	4.00	1.00E-04
		9.5	5.5	42.1	4.00	1.00E-04
		33.8	22.6	33.1	11.20	2.80E-04
		24.8	18.4	25.8	6.40	1.60E-04
		9.5	4.1	56.9	5.40	1.35E-04
	Bayer residue	98.5	5.4	94.5	93.10	2.33E-03
		50.3	2.5	95	47.80	1.20E-03
		10.9	0.1	99.1	10.8	2.70E-04
		29.6	0.1	99.6	29.5	7.38E-04
		19.6	0.1	99.5	19.5	4.88E-04
		10.09	0.1	99	10.8	2.70E-04
DOC	Fly ash	5	1.077	78.5	3.923	0.1471125
		5	0.84	83.2	4.16	0.156
		10	0.809	91.9	9.191	0.3446625
		10	0.566	94.3	9.434	0.353775
		20	0.794	96.0	19.206	0.720225
		20	1.052	94.7	18.948	0.71055
		50	2.064	95.9	47.936	1.7976
		50	1.434	97.1	48.566	1.821225
		100	4.16	95.8	95.84	3.594
		100	2.791	97.2	97.209	3.6453375
	Bauxite Residue	5	0.882	82.4	4.118	0.154425
		5	1.126	77.5	3.874	0.145275
		10	1.841	81.6	8.159	0.3059625
		10	1.038	89.6	8.962	0.336075
		20	2.243	88.8	17.757	0.6658875
		20	1.596	92.0	18.404	0.69015
		50	4.109	91.8	45.891	1.7209125
		50	2.921	94.2	47.079	1.7654625
		100	6.163	93.8	93.837	3.5188875
		100	4.902	95.1	95.098	3.566175
	Pyritic fill	2.5	0.828	66.9	1.672	0.0627
		2.5	0.961	61.6	1.539	0.0577125
		10	0.692	93.1	9.308	0.34905
		10	1.149	88.5	8.851	0.3319125
		20	1.736	91.3	18.264	0.6849
		20	0.978	95.1	19.022	0.713325
		50	2.415	95.2	47.585	1.7844375
		25	1.355	94.6	23.645	0.8866875
		100	3.982	96.0	96.018	3.600675
		100	3.963	96.0	96.037	3.6013875
	GAC	5	3.5	30.0	1.5	0.05625
		10	6.38	36.2	3.62	0.13575
		20	11.041	44.8	8.959	0.3359625
		20	11.978	40.1	8.022	0.300825
		50	40.711	18.6	9.289	0.3483375
		50	41.436	17.1	8.564	0.32115
		100	86.863	13.1	13.137	0.4926375
		100	91.19	8.8	8.81	0.330375
	GBS	5	1.886	62.3	3.114	0.116775
		10	2.584	74.2	7.416	0.2781
		10	1.944	80.6	8.056	0.3021

		20	4.044	79.8	15.956	0.59835
		20	1.857	90.7	18.143	0.6803625
		50	7.237	85.5	42.763	1.6036125
		50	6.563	86.9	43.437	1.6288875
		100	13.766	86.2	86.234	3.233775
		100	12.458	87.5	87.542	3.282825
	Zeolite	5	3.037	39.3	1.963	0.0736125
		10	4.602	54.0	5.398	0.202425
		10	1.366	86.3	8.634	0.323775
		20	13.465	32.7	6.535	0.2450625
		20	3.372	83.1	16.628	0.62355
		50	47.343	5.3	2.657	0.0996375
		25	11.741	53.0	13.259	0.4972125
		100	42.44	57.6	57.56	2.1585
		100	36.865	63.1	63.135	2.3675625
Al	Pyritic fill	0.452	0.123	72.8	0.329	0.008225
		0.339	0.085	74.9	0.254	0.00635
		1.045	0.04	96.2	1.005	0.025125
		0.452	0.173	61.7	0.279	0.006975
		0.339	0.061	82.0	0.278	0.00695
	Coarse sand	0.78	0.015	98.1	0.765	0.019125
		0.37	0.022	94.1	0.348	0.0087
		0.25	0.01	96.0	0.24	0.006
		0.2	0.006	97.0	0.194	0.00485
	GAC	1.045	0.0705	93.3	0.9745	0.0243625
		0.452	0.008	98.2	0.444	0.0111
		0.339	0.079	76.7	0.26	0.0065
		1.045	0.006	99.4	1.039	0.025975
		0.452	0.017	96.2	0.435	0.010875
		0.339	0.009	97.3	0.33	0.00825
	Zeolite	1.045	0.01	99.0	1.035	0.025875
		0.452	0.021	95.4	0.431	0.010775
		0.339	0.009	97.3	0.33	0.00825
		1.045	0.015	98.6	1.03	0.02575
		0.452	0.002	99.6	0.45	0.01125
		0.339	0.011	96.8	0.328	0.0082
	Bottom ash	1.045	0.018	98.3	1.027	0.025675
		0.452	0.108	76.1	0.344	0.0086
		0.339	0.138	59.3	0.201	0.005025
		1.045	0.01	99.0	1.035	0.025875
		0.452	0.051	88.7	0.401	0.010025
		0.339	0.01	97.1	0.329	0.008225
NO3-N	Bauxite Residue	27.8	3.3	88.1	24.5	0.6125
		17.6	2.4	86.4	15.2	0.38
		8.9	1.2	86.5	7.7	0.1925
		27.8	3.4	87.8	24.4	0.61
		17.6	2.5	85.8	15.1	0.3775
		8.9	1.1	87.6	7.8	0.195
	Pyritic fill	27.8	2	92.8	25.8	0.645
		17.6	0.5	97.2	17.1	0.4275
		8.9	0.1	98.9	8.8	0.22
		27.8	3	89.2	24.8	0.62
		17.6	1	94.3	16.6	0.415

		8.9	0.1	98.9	8.8	0.22
NH4-N	Fly ash	27.8	3.9	86.0	23.9	0.5975
		17.6	3.1	82.4	14.5	0.3625
		8.9	2.2	75.3	6.7	0.1675
		27.8	4	85.6	23.8	0.595
		17.6	3.2	81.8	14.4	0.36
		8.9	2	77.5	6.9	0.1725
	Pyritic fill	27.8	2	92.8	25.8	0.645
		17.6	0.5	97.2	17.1	0.4275
		8.9	0.1	98.9	8.8	0.22
		27.8	3	89.2	24.8	0.62
		17.6	1	94.3	16.6	0.415
		8.9	0.1	98.9	8.8	0.22
	Coarse sand	23	5	78.3	18	0.45
		9	6	33.3	3	0.075
		6	3	50.0	3	0.075
	GBS	27.8	3.5	87.4	24.3	0.6075
		17.6	4.3	75.6	13.3	0.3325
		8.9	3.8	57.3	5.1	0.1275
		27.8	3.5	87.4	24.3	0.6075
		17.6	3.7	79.0	13.9	0.3475
		8.9	3.5	60.7	5.4	0.135
	Zeolite	27.8	26.2	5.8	1.6	0.04
		17.6	5.5	68.8	12.1	0.3025
		8.9	7.3	18.0	1.6	0.04
		27.8	27.1	2.5	0.7	0.0175
		17.6	5.9	66.5	11.7	0.2925
		8.9	6.9	22.5	2	0.05

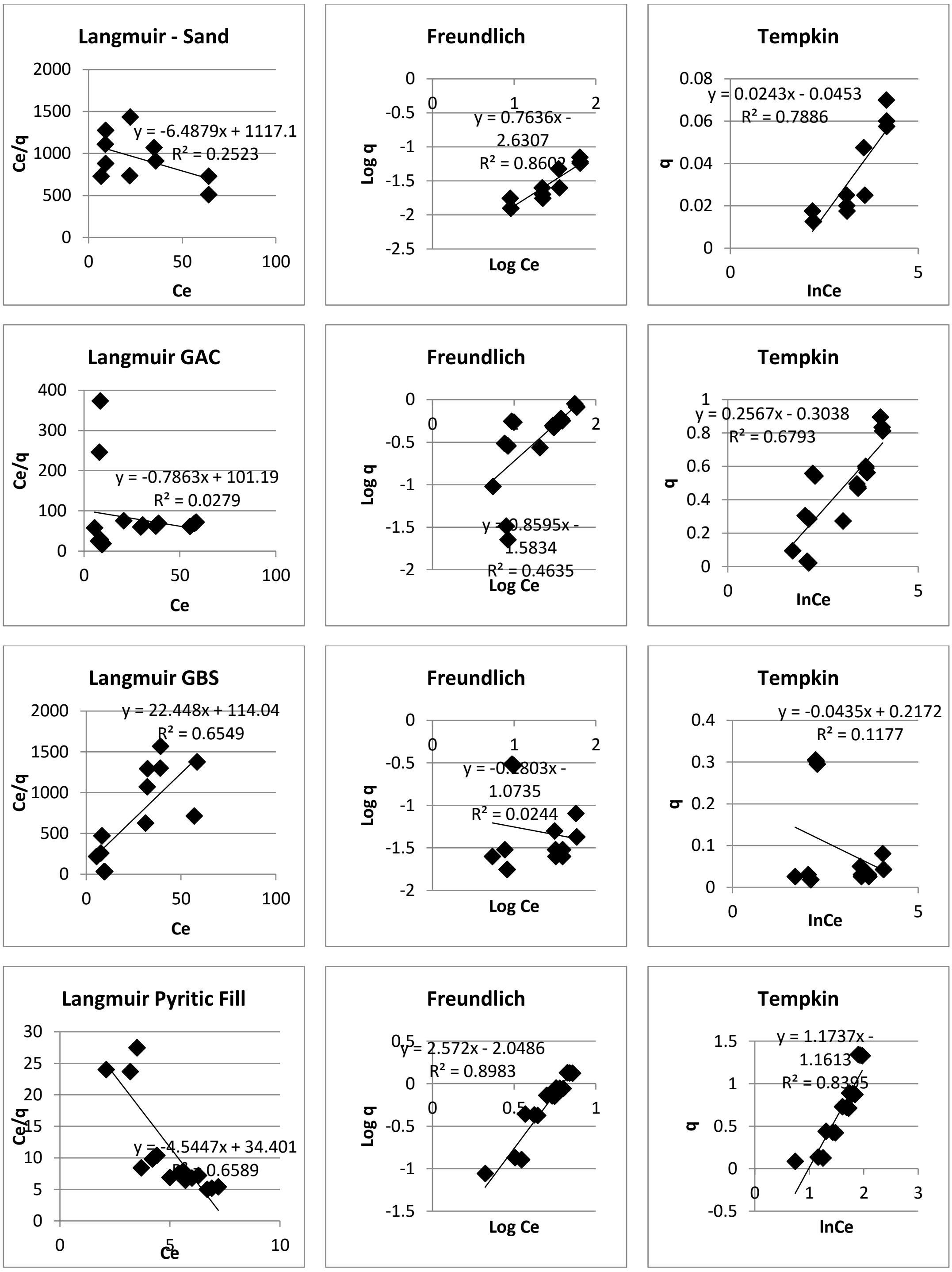
Table B5: Results from kinetic testing of adsorption

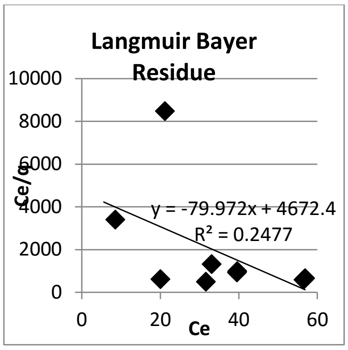
Contaminant	Media	Initial Conc (mg L^{-1})	1 h Conc (mg L^{-1})	4 h Conc (mg L^{-1})	8 h Conc (mg L^{-1})	12 h Conc (mg L^{-1})	24 h Conc (mg L^{-1})
Nitrate	Coarse sand	25.4	16.06	15.8	13.8	15.4	14.8
	Fine sand	25.4	16.8	16.4	17.1	17.6	16.9
	GAC	25.4	17.4	16.4	15.6	16.6	17.1
	Pyritic fill	67.5	14.8	14.3	14.9	14.8	14.7
	Zeolite	65.2	6.0	5.4	5.3	5.3	4.9
	Bottom ash	25.4	20.2	22.2	22.6	21.4	22.8
	Fly ash	18	16.3	8.5	6.1	5.4	6.3
	Bayer residue	18	15.6	17.3	16.9	16.9	16.9
	GBS	18	16.6	15.9	9.3	12.3	8.9
Ammonium	Coarse sand	19.8	13.9	12.4	11.9	11.7	10.9
	Fine sand	19.8	16.9	16.4	15.9	16.9	16.1
	GAC	19.8	18.2	18.1	17.6	17.7	17.6
	Pyritic fill	19.8	14.4	14.2	14.2	13.9	14
	Zeolite	19.8	3.5	2.7	2.5	2.5	2.5
	Bottom ash	18.3	17.4	16.9	16.5	16.1	16.1
	Fly ash	18.3	13.8	7.4	7.3	6.9	7.5
	Bayer residue	18.3	10.1	9.9	9.9	9.1	9.7
	GBS	18.3	14.2	14.1	14.1	14.3	12.6
Aluminium	Coarse sand	0.293	0.264	0.237	0.125	0.134	0.112
	Fine Sand	0.293	0.119	0.072	0.132	0.119	0.192

	GAC	0.293	0.012	0.015	0.057	0.062	0.208
	Pyritic Fill	0.293	0.053	0.212	0.1435	0.1135	0.265
	Zeolite	0.293	0.0315	0.061	0.1175	0.082	0.195
	Bottom ash	0.444	0.272	0.282	0.2845	0.3045	0.24
Phosphate	Coarse sand	24.9	23.95	22.55	21.2	20.8	17.15
	Fine sand	24.9	24.8	24.6	24.6	24.1	23.6
	GAC	24.9	18.7	23.7	24.3	23.5	26.3
	Pyritic fill	24.9	1.45	1.25	1.25	1.45	1.6
	Zeolite	24.9	19.9	21.9	21.6	21.4	20.2
	Bottom ash	20	19.2	18.8	18.1	17.6	15.6
	Fly ash	20	0.2	0.4	0.2	0.2	0.1
	Bayer residue	20	9.1	5.9	2.6	1.8	2.3
	GBS	20	0.1	0.1	0.1	0.1	0.1
DOC	Coarse sand	23.9	12.8	24.2	16.4	8.7	11.1
	Fine sand	23.9	14.6	23.4	15.9	8.5	24.7
	GAC	23.9	8.9	17.5	12.6	7.8	15.6
	Pyritic fill	23.9	2.4	9.7	2.5	1	1.5
	Zeolite	23.9	19.7	16.9	11.6	6.2	4.7
	Bottom ash	23.9	6.2	10.9	8.2	7	15.5
	Fly ash	23.9	0.9	7.3	2.1	1.2	0.8
	Bayer residue	23.9	14.3	12.4	6.7	5.6	7.3
	GBS	23.9	8.3	7.6	7.4	7.3	2
Copper	Coarse sand	10.6	8.6	13.2	8.5	3.4	1.8
	Fine sand	10.6	13.1	13.1	10.5	7.8	8.4
	GAC	10.6	7.4	7.1	6	5.1	3.1
	Pyritic fill	10.9	4.2	0.2	0.2	0.2	0.1
	Zeolite	10.9	1.3	1.7	1	0.2	0.1
	Bottom ash	10.9	5.6	4.6	5.4	7.3	4.1
	Fly ash	10.9	0.1	0.2	0.3	0.7	0.1
	Bayer residue	10.9	0.2	0.4	0.3	0.6	0.1
	GBS	10.9	0.7	1.8	0.7	0.2	0.1

Figure B1: Adsorption Isotherm Plots for all contaminants at room temperature

Nitrate Adsorption Plots




Langmuir Bayer Residue
Ce/q
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6000
4000
2000
0
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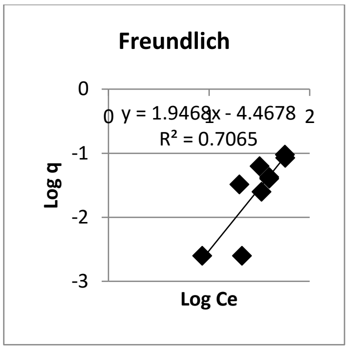
R² = 0.2477
0
20
40
60
Ce


Freundlich
Log q
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-2
-3
0
1
2
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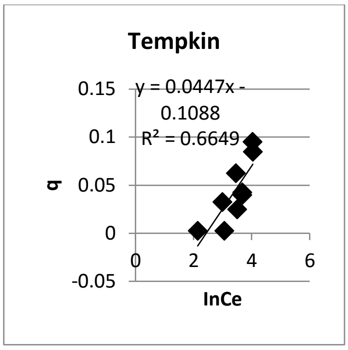
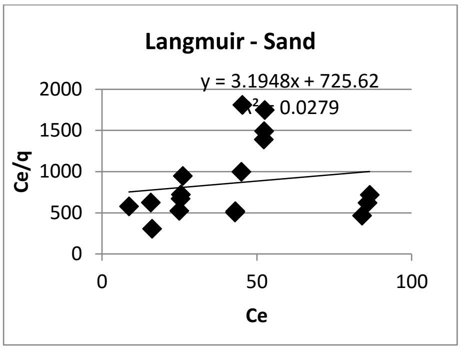
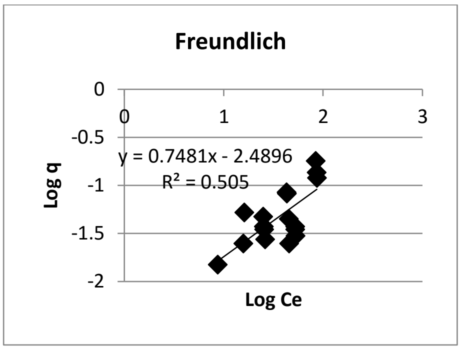
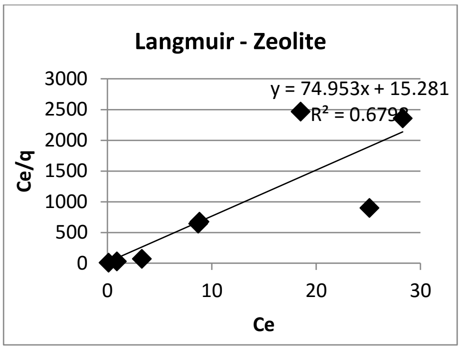
R² = 0.7065
Log Ce

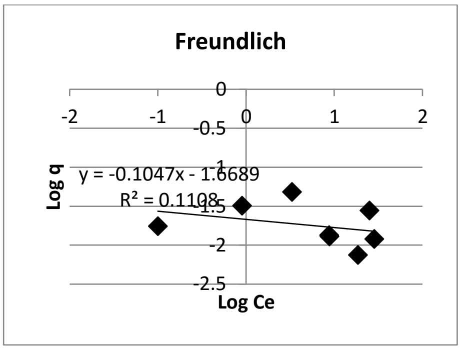

Tempkin
q
0.15
0.1
0.05
0
-0.05
y = 0.0447x - 0.1088
R² = 0.6649
0
2
4
6
lnCe

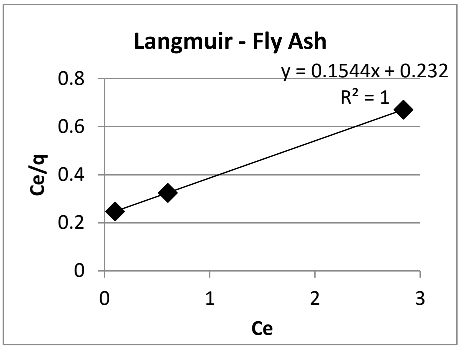
Phosphate Adsorption Plots

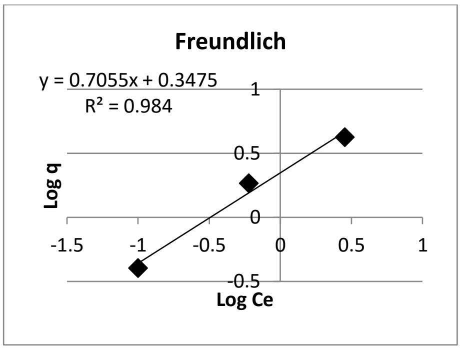

Langmuir - Sand

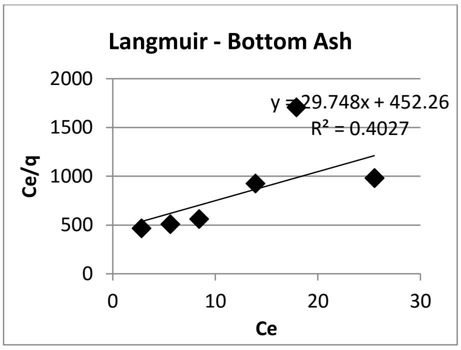

Freundlich

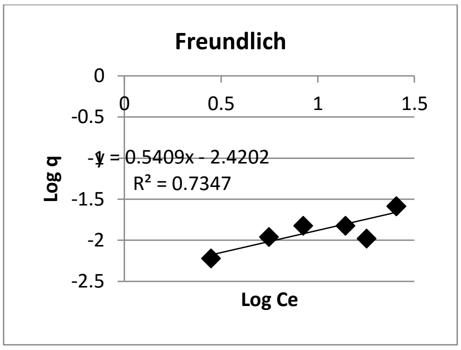

Langmuir - Zeolite

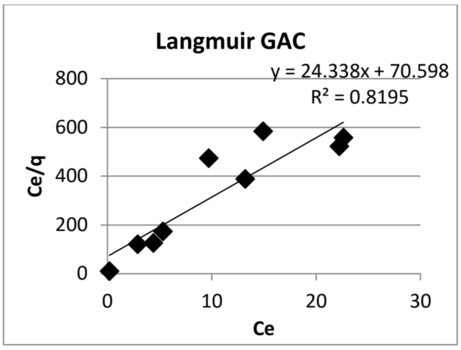

Freundlich

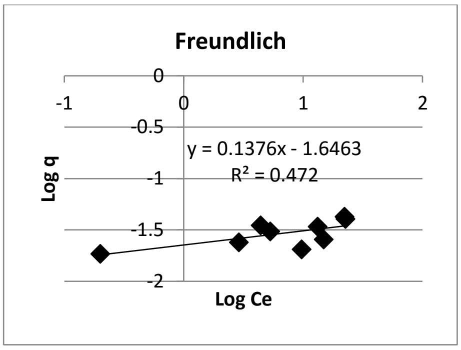

Langmuir - Fly Ash

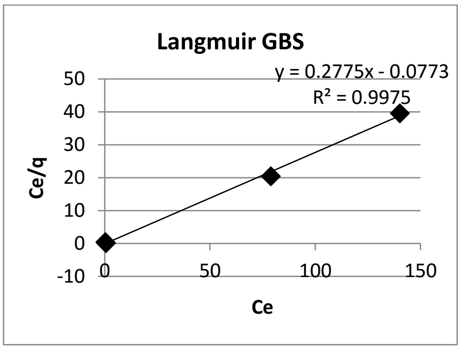

Freundlich

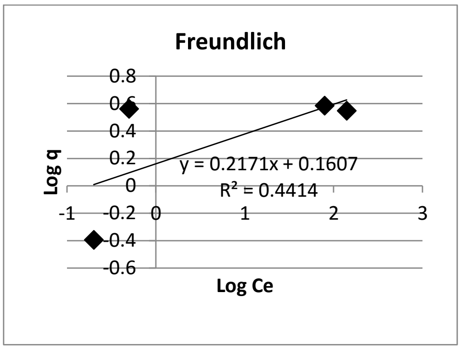

Langmuir - Bottom Ash

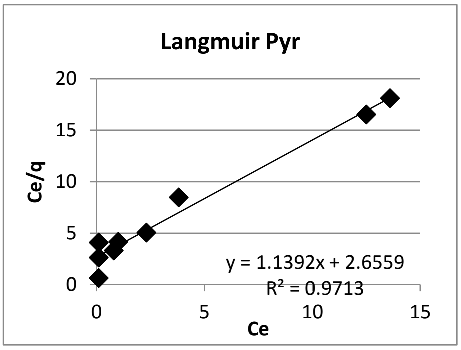

Freundlich

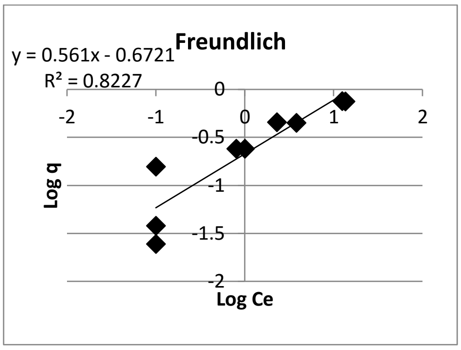

Langmuir GAC
y = 24.338x + 70.598
R² = 0.8195
800
600
400
200
0
0
10
20
30
Ce/q
Ce


Freundlich
0
-1
0
1
2
-0.5
y = 0.1376x - 1.6463
R² = 0.472
-1
-1.5
-2
Log q
Log Ce

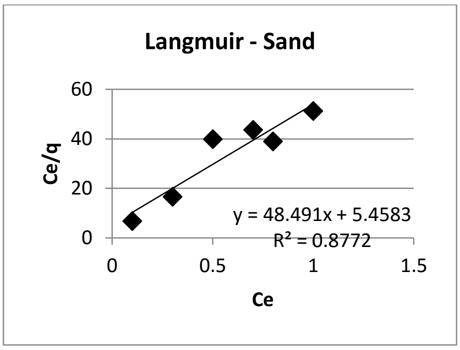

Langmuir GBS
y = 0.2775x - 0.0773
R² = 0.9975
50
40
30
20
10
0
-10
0
50
100
150
Ce/q
Ce

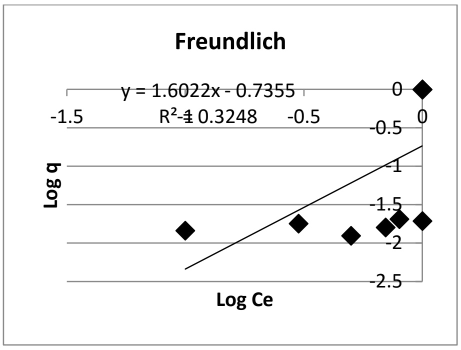

Freundlich
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-1
0
1
2
3
y = 0.2171x + 0.1607
R² = 0.4414
Log q
Log Ce

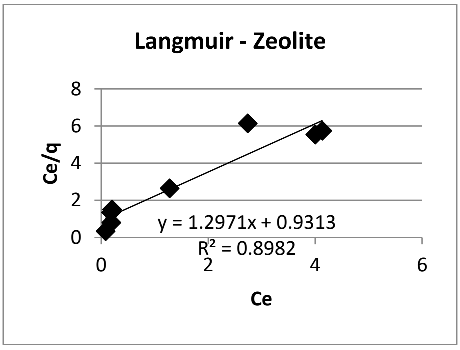

Langmuir Pyr
20
15
10
5
0
0
5
10
15
y = 1.1392x + 2.6559
R² = 0.9713
Ce/q
Ce

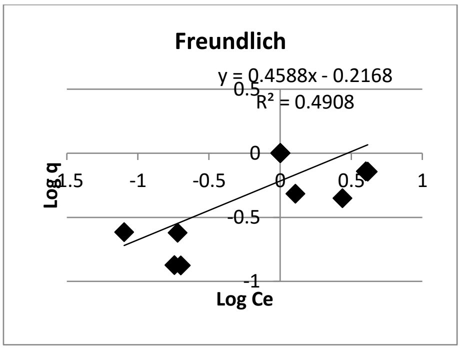

Freundlich
y = 0.561x - 0.6721
R² = 0.8227
0
-2
-1
0
1
2
-0.5
-1
-1.5
-2
Log q
Log Ce

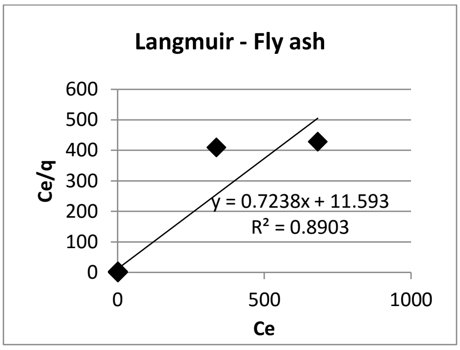
Copper Adsorption Plots

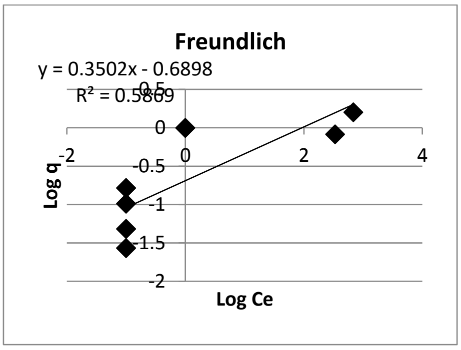


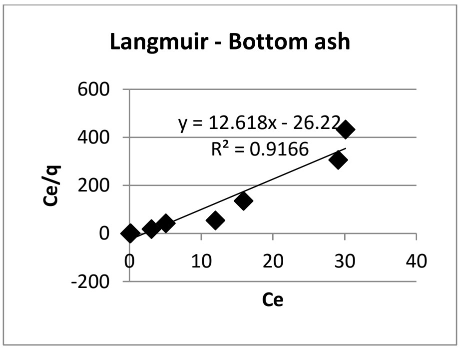


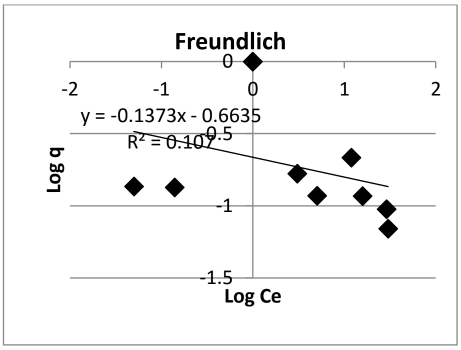


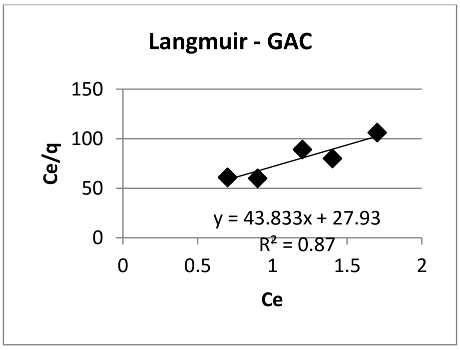


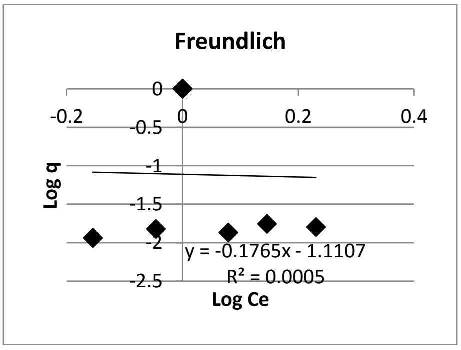


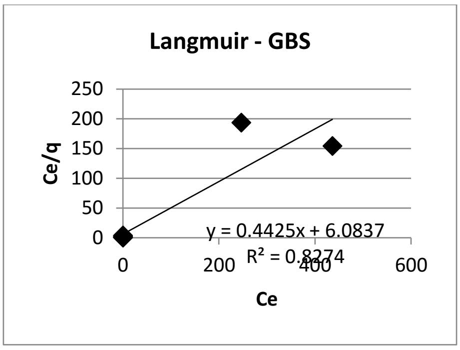


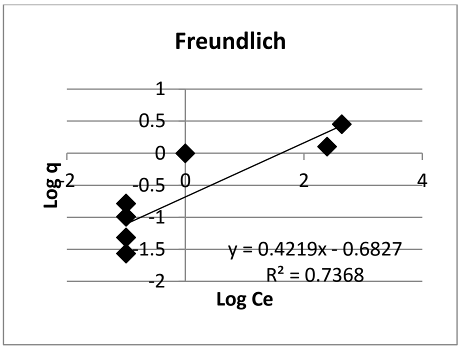


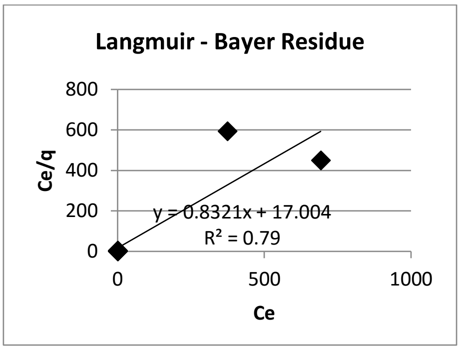


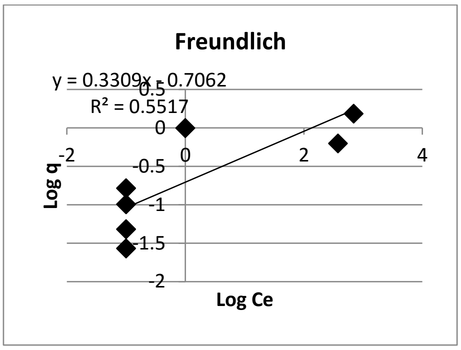


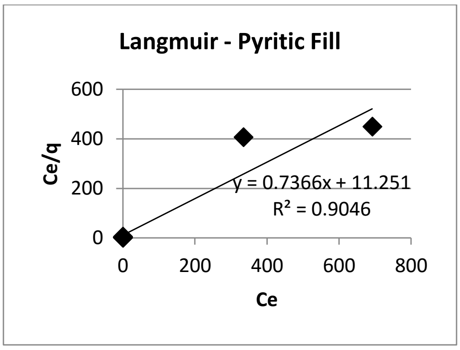


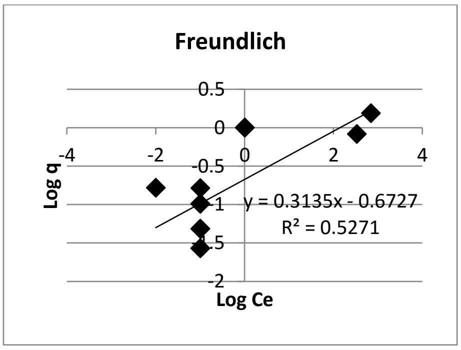

Langmuir - GBS
250
200
150
100
50
0
Ce/q
0
200
400
600
Ce
y = 0.4425x + 6.0837
R² = 0.8274


Freundlich
1
0.5
0
-0.5
-1
-1.5
-2
Log q
-2
0
2
4
Log Ce
y = 0.4219x - 0.6827
R² = 0.7368

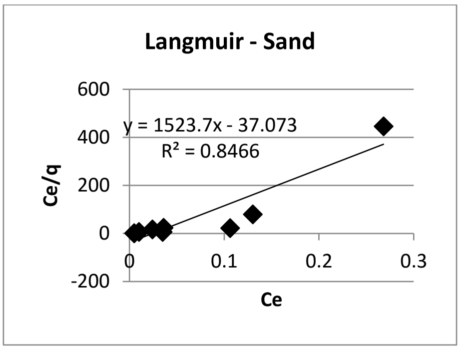

Langmuir - Bayer Residue
800
600
400
200
0
Ce/q
0
500
1000
Ce
y = 0.8321x + 17.004
R² = 0.79

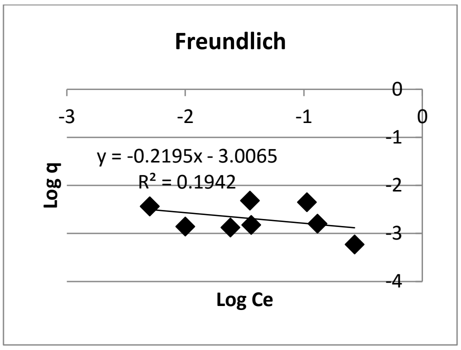

Freundlich
y = 0.3309x - 0.7062
R² = 0.5517
0.5
0
-0.5
-1
-1.5
-2
Log q
-2
0
2
4
Log Ce

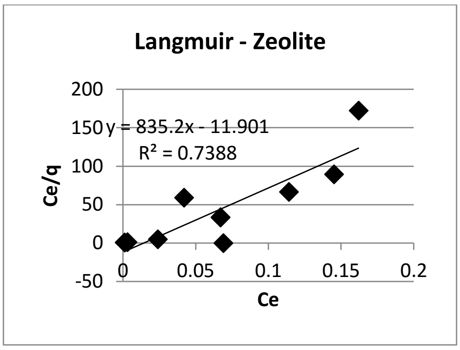

Langmuir - Pyritic Fill
600
400
200
0
Ce/q
0
200
400
600
800
Ce
y = 0.7366x + 11.251
R² = 0.9046

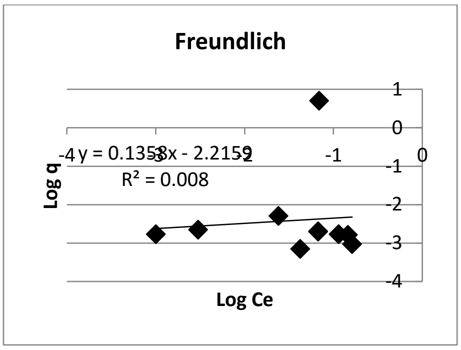

Freundlich
0.5
0
-0.5
-1
-1.5
-2
Log q
-4
-2
0
2
4
Log Ce
y = 0.3135x - 0.6727
R² = 0.5271

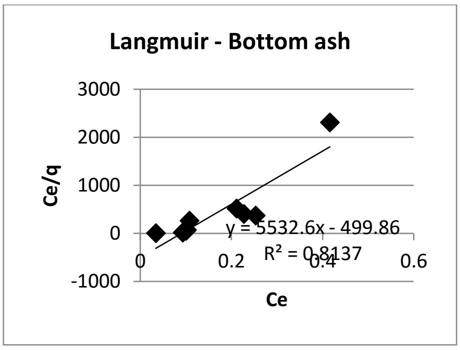
Aluminium Adsorption Plots

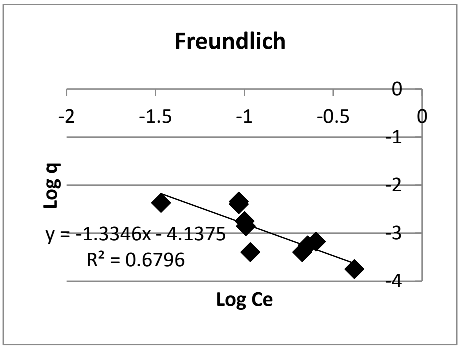


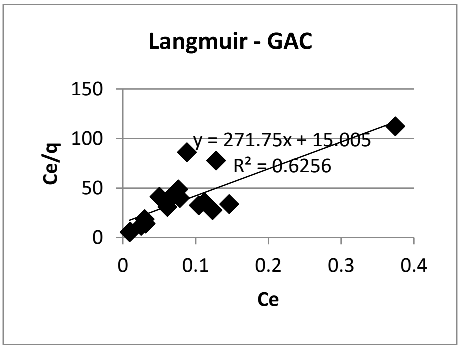


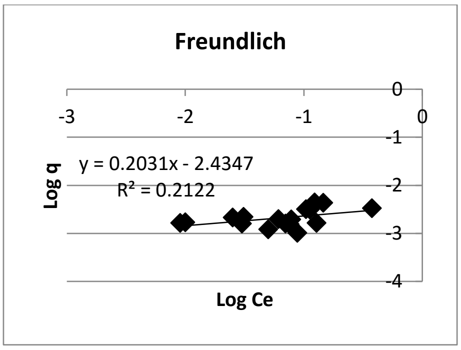


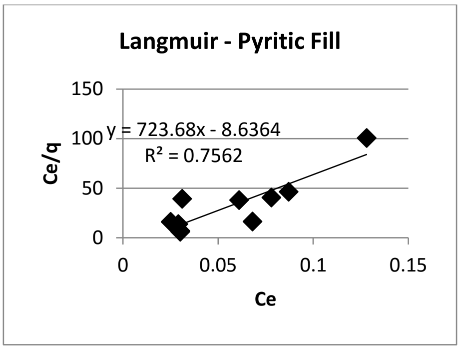


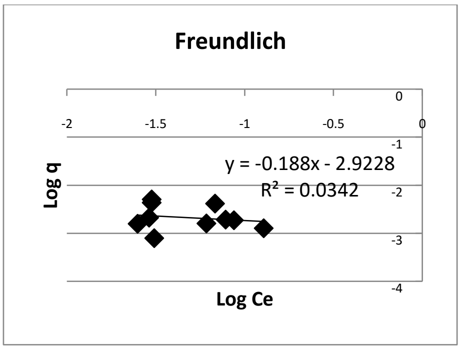




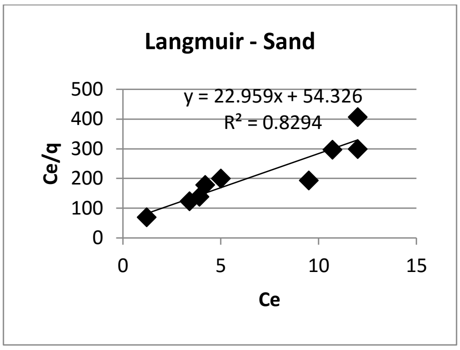


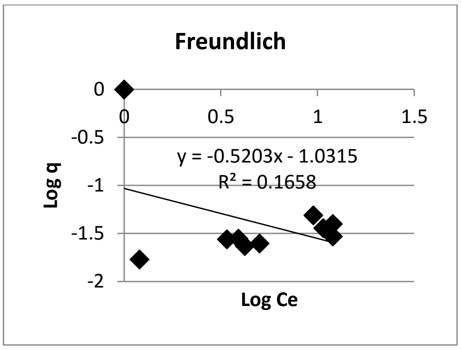


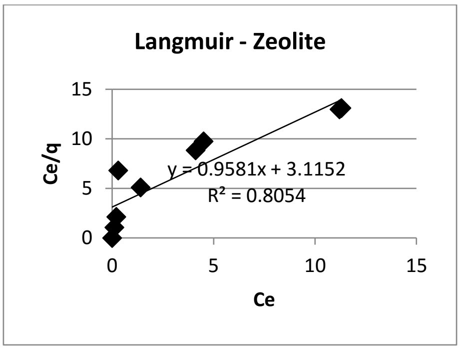

Langmuir - Pyritic Fill
y = 723.68x - 8.6364
R² = 0.7562
Ce/q
150
100
50
0
0
0.05
0.1
0.15
Ce

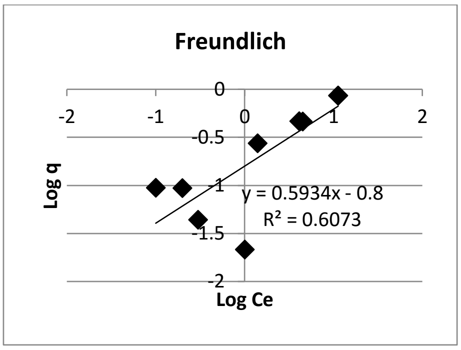

Freundlich
-2
-1.5
-1
-0.5
0
0
-1
-2
-3
-4
y = -0.188x - 2.9228
R² = 0.0342
Log q
Log Ce

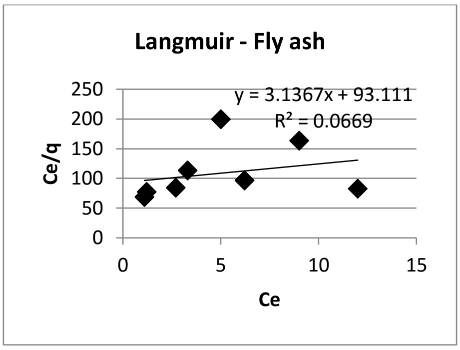
Ammonium Adsorption Plots

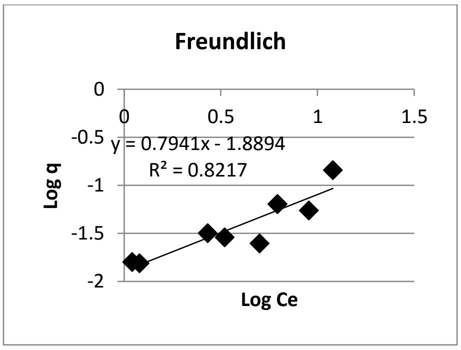


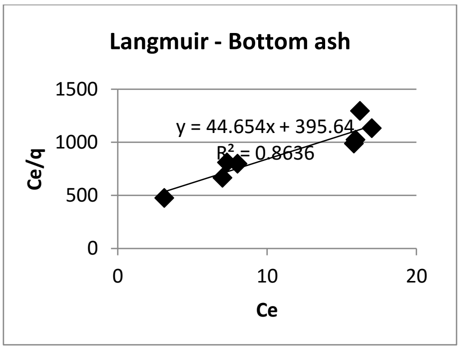


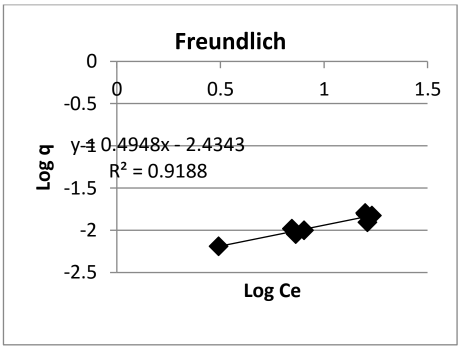


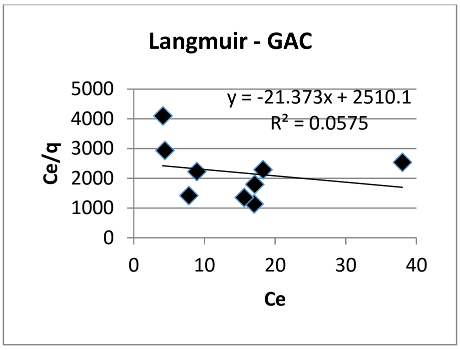


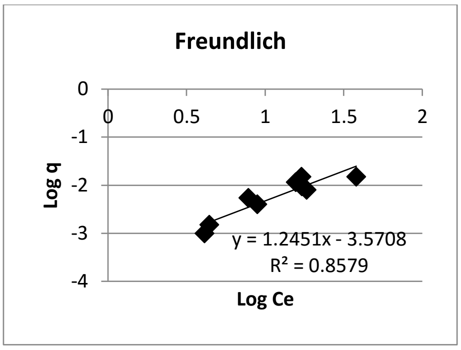


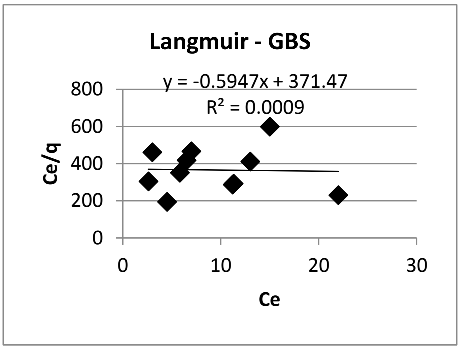


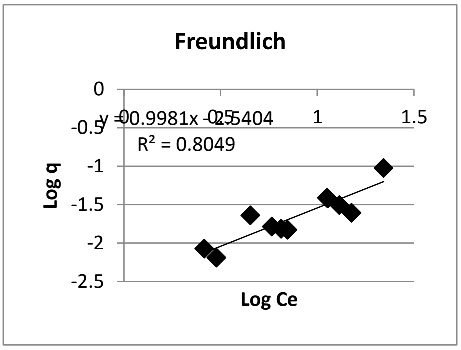


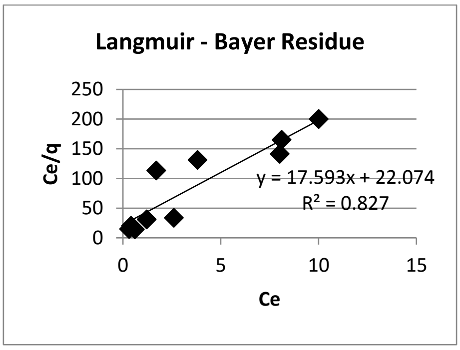


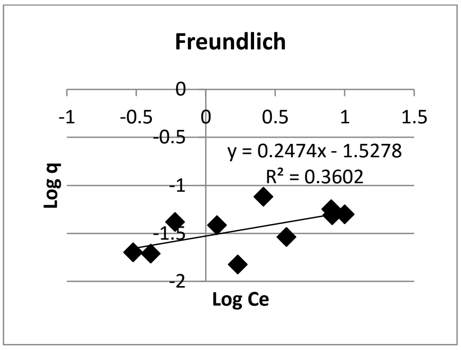

Langmuir - GAC
y = -21.373x + 2510.1
R² = 0.0575
Ce/q
5000
4000
3000
2000
1000
0
0
10
20
30
40
Ce

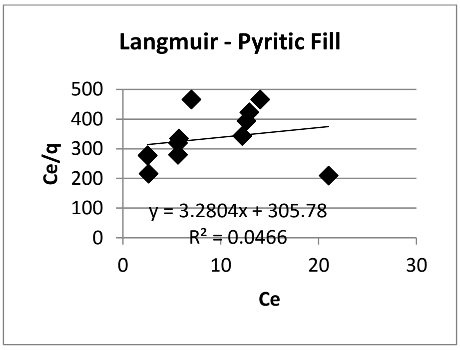

Freundlich
0
-1
-2
-3
-4
0
0.5
1
1.5
2
Log q
y = 1.2451x - 3.5708
R² = 0.8579
Log Ce

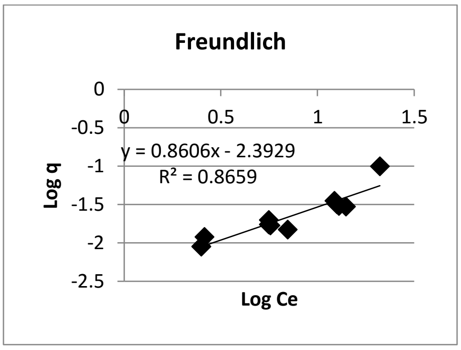

Langmuir - GBS
y = -0.5947x + 371.47
R² = 0.0009
Ce/q
800
600
400
200
0
0
10
20
30
Ce


Freundlich
0
-0.5
-1
-1.5
-2
-2.5
0
0.5
1
1.5
y = 0.9981x - 2.5404
R² = 0.8049
Log q
Log Ce

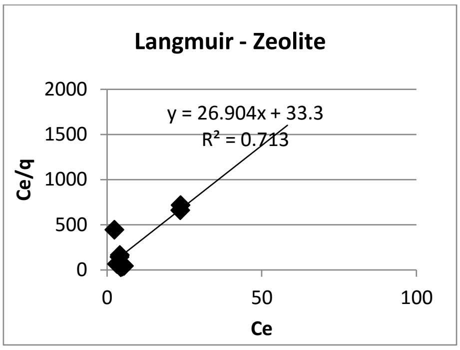

Langmuir - Bayer Residue
250
200
150
100
50
0
Ce/q
y = 17.593x + 22.074
R² = 0.827
0
5
10
15
Ce

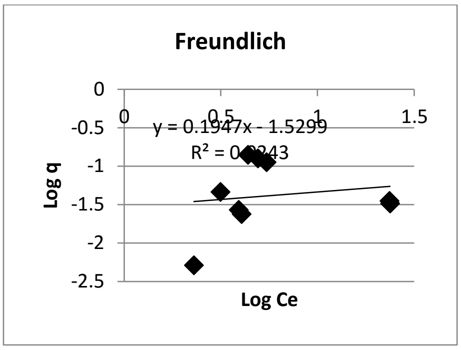

Freundlich
0
-1
-0.5
0
0.5
1
1.5
-0.5
y = 0.2474x - 1.5278
R² = 0.3602
-1
-1.5
-2
Log q
Log Ce

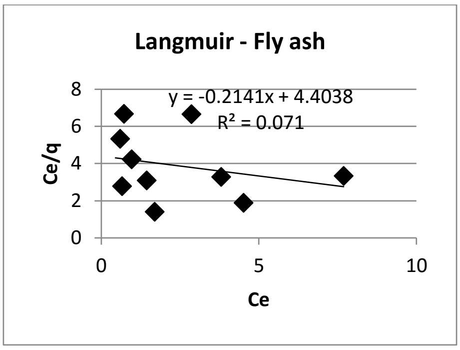

Langmuir - Pyritic Fill
500
400
300
200
100
0
Ce/q
y = 3.2804x + 305.78
R² = 0.0466
0
10
20
30
Ce

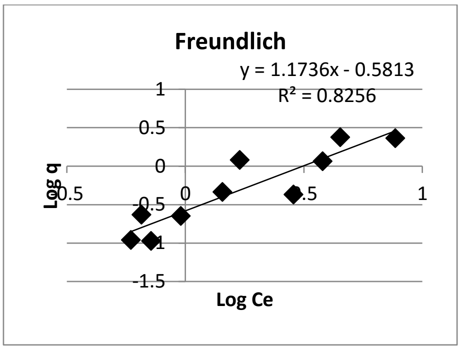

Freundlich
0
-0.5
-1
-1.5
-2
-2.5
0
0.5
1
1.5
y = 0.8606x - 2.3929
R² = 0.8659
Log q
Log Ce

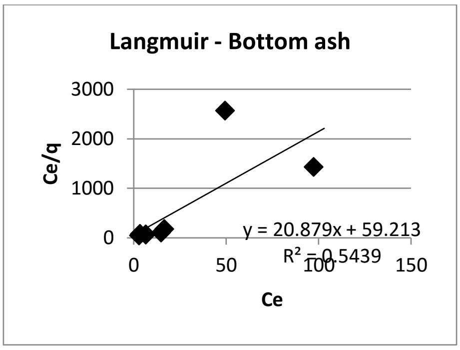
DOC Adsorption Plots

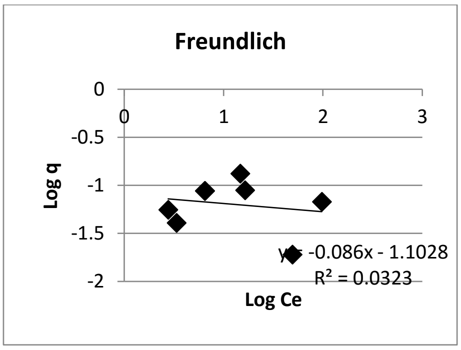


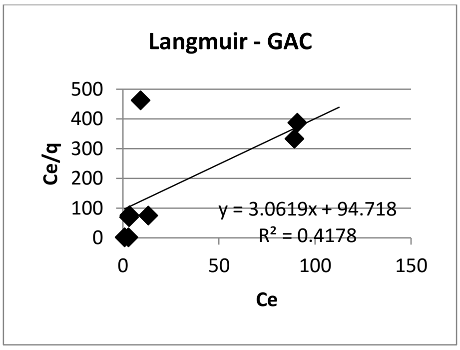


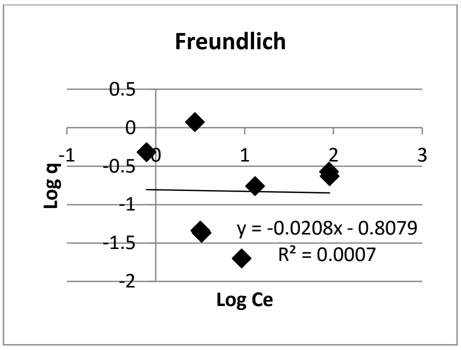


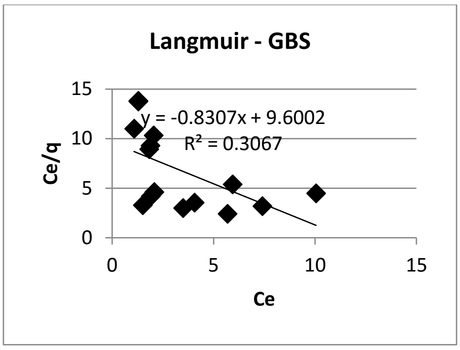


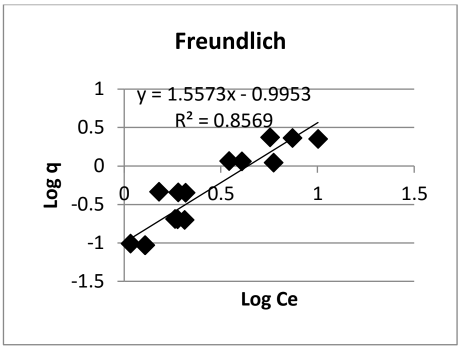


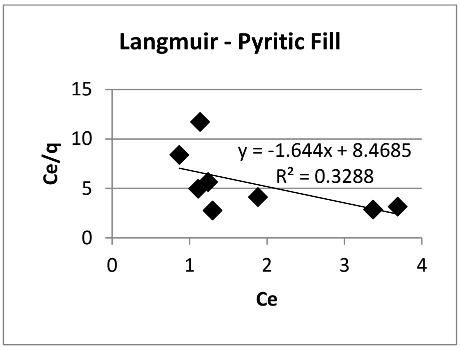


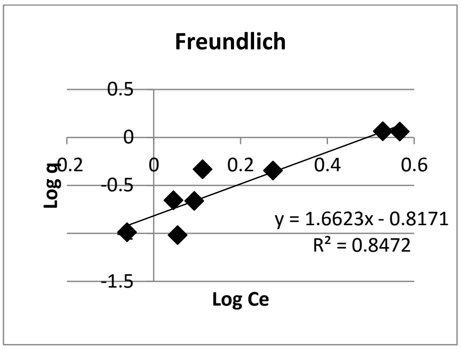


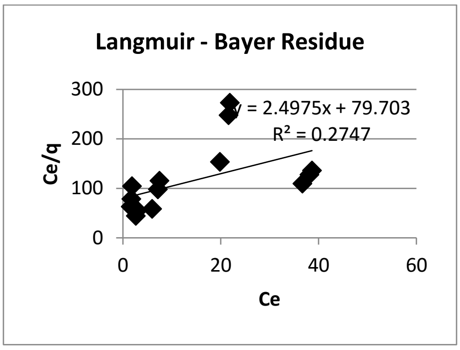


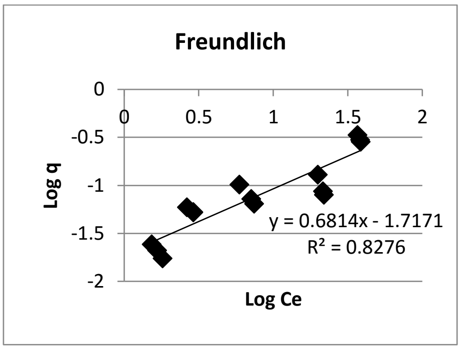

Langmuir - GBS
y = -0.8307x + 9.6002
R² = 0.3067
Ce/q
Ce
0
5
10
15
0
5
10
15


Freundlich
y = 1.5573x - 0.9953
R² = 0.8569
Log q
Log Ce
1
0.5
0
-0.5
-1
-1.5
0
0.5
1
1.5


Langmuir - Pyritic Fill
y = -1.644x + 8.4685
R² = 0.3288
Ce/q
Ce
15
10
5
0
0
1
2
3
4


Freundlich
y = 1.6623x - 0.8171
R² = 0.8472
Log q
Log Ce
0.5
0
-0.5
-1
-1.5
-0.2
0
0.2
0.4
0.6


Langmuir - Bayer Residue
y = 2.4975x + 79.703
R² = 0.2747
Ce/q
Ce
300
200
100
0
0
20
40
60


Freundlich
y = 0.6814x - 1.7171
R² = 0.8276
Log q
Log Ce
0
-0.5
-1
-1.5
-2
0
0.5
1
1.5
2

Appendix C

Notation used in Appendix C

Days: Days of operation of filters
Ref: Column Reference
Inf: Influent data
S: Slow loaded columns
I: Intermittently loaded columns
A: Port samples taken from the middle of the filter (i.e. at the base of the top layer)
B: Port samples taken from the middle of the filter (i.e. at the base of the second layer)
C: Port samples taken from the middle of the filter (i.e. at the base of the third layer)
Ref numbers 1,2,3: Control
Ref numbers 4,5,6: Configuration 1
Ref numbers 7,8,9: Configuration 2

S: Sulphur
P: Phosphorus
Ca: Calcium
Mg: Magnesium
K: Potassium
H: Hydrogen
B: Boron
Fe: Iron
Mn: Managenese
Cu: Copper
Zn: Zinc
Al: Aluminium
NO_3-N: Nitrate-nitrogen
NH_4-N: Ammonium-nitrate

Table C1: Results from continuously loaded laboratory-scale filter columns

Days	**Ref**	**Al µg L-1**	**NO3--N mg L-1**	**NH4+-N mg L-1**	**DOC mg L-1**
2	Inf	1450	57.3	12.5	6.6
2	S1A	29	65.7	10.8	3.9
2	S1B	17	18.4	5.1	
2	S1	0	17.4	3.8	3.1
2	S2	0	95	13.1	2.9
2	S3A	8.9	19.6	4.2	
2	S3B	9.2	20.7	8.1	4.2
2	S3	0	102	16.7	4
2	S4A	82.5	20	3.6	7.8
2	S4B	2.3	12.3	0	0
2	S4	0	87.5	0.7	2.8
2	S5A	813	17.3	0	2.4
2	S5B	12.7	20.4	0.7	0.2
2	S5	0	64.5	1.1	4
2	S6A	416	17.1	1.9	2.1
2	S6B	10.8	18.5	0.4	0
2	S6	0	64.5	0.6	4.6
2	S7A	117.3	19.7	6.9	2.2
2	S7B	166.2	12.2	3.6	0
2	S7C	9.9	8.8	1.3	0.8

2	S7	0	23.6	0.6	2
2	S8A	243.5	18.3	4.9	1.8
2	S8B	210.6	9.3	4.6	1
2	S8C	3.3	7.03	0	0.3
2	S8	0	8.5	0.7	0.9
2	S9A	162.1	20.2	6.4	1.5
2	S9B	197	5.3	2.3	0.7
2	S9C	17	6.6	0.05	0.8
2	S9	0	4.9	1.2	0.5
4	Inf	1540	24	6.2	4.34
4	S1	0	29	5.9	5.3
4	S2	0	31.6	5.5	3.1
4	S3	0	39.9	7.2	5
4	S4	0	32.4	1.4	2.6
4	S5	0	28.9	1.8	4.3
4	S6	0	34.4	1.6	5.4
4	S7	0	20.4	1.4	2.1
4	S8	0	18.4	1.4	0.7
4	S9	0	24.8	1.4	1.8
7	Inf	1650	22.7	6.4	8.4
7	S1	0	27.4	6.2	6.6
7	S2	0	35.5	2.9	5.3
7	S3	0	36.2	6.4	5.4
7	S4	0	292	1.5	5.3
7	S5	0	27.2	2.6	5.9
7	S6	0	37	2.2	6
7	S7	0	31	1.4	2.6
7	S8	0	31.5	1.4	1.9
7	S9	0	24.1	1.4	1.7
8	S1A	10.5	19.7	3.8	
8	S1B	26.7	24.7	3.9	
8	S3A	34.2	24.8	7.4	
8	S3B	3.5	26.2	4.6	
8	S4A	50.4	23.2	3.6	2.7
8	S4B	2.2	26.4	3.7	0.9
8	S5A	385	24.5	0	1.6
8	S5B	28.5	25.4	0.1	1.4
8	S6A	512.7	24.2	0.34	
8	S6B	3	22.9	0	0.1
8	S7A	94.7	29.5	2.6	1.7
8	S7B	67.3	20.7	1.7	1.4
8	S7C	2.7	20.9	0.8	0.6
8	S8A	100	28.1	5.6	1.5
8	S8B	85	22.6	10.6	1.2
8	S8C	8	23.5	0	0.2
8	S9A	72	27.7	4.3	2
8	S9B	103	20.6	1.4	0.6
8	S9C	2	18.1	2.1	1
10	Inf	1665	20.2	5.7	7.6
10	S1	0	52.2	6.6	4.7
10	S2	0	36.5	0.6	6.5
10	S3	0	59.6	4.7	7.2
10	S4	0	59.8	0.6	6.6
10	S5	0	46.9	3.8	6.6

10	S6	0	42.4	1.7	7
10	S7	0	31.6	0.5	6
10	S8	0	41	0.5	7.5
10	S9	0	40	1.4	5.9
14	Inf	1750	16.3	4.9	6.2
14	S1	0	39.8	2.9	6
14	S2	0	39.9	1.3	6.3
14	S3	0	40.1	3.9	7
14	S4	0	32.8	1.2	6.5
14	S5	0.4	36.2	4.6	6.1
14	S6	0	45.4	3.6	7.1
14	S7	0	46.9	1.4	5
14	S8	0	35.6	1.4	5.7
14	S9	0	28.7	1.3	5.2
16	S1A	5.7	16.4	2.4	
16	S1B	2.4	23.8	3.4	
16	S3A	2.9	15.1	2.9	
16	S3B	7.6	18.5	3.1	6.6
16	S4A	69.9	18.7	2.2	2.4
16	S4B	4.6	20.7	0.3	2
16	S5A	401	16.4	0.3	1.4
16	S5B	31.5	12.9	0.6	1.7
16	S6A	566	11.3	2.3	1
16	S6B	7	14.4	0.23	1.1
16	S7A	116.9	22.1	2.9	1.1
16	S7B	34.9	18.8	1.5	
16	S7C	6	24.3	0	0.8
16	S8A	88.6	24.1	0.11	1.3
16	S8B	44.2	15.8	0	0.7
16	S8C	5	22.5	0	0.5
16	S9A	96.1	18.2	0	1.2
16	S9B	40.6	12.9	0	
16	S9C	4.9	17.8	0	3.9
17	Inf	1679	16	3.1	4.2
17	S1	0	7.8	2	4
17	S2	0	11.6	1.2	2.4
17	S3	0	11.5	2.3	4.6
17	S4	0	15.5	1.2	4
17	S5	0	13.3	2.4	0.4
17	S6	0	23.2	2.7	0.5
17	S7	0	14.6	1.2	2
17	S8	0	11.4	1.2	0.6
17	S9	0	18.4	1.2	1
21	Inf	1740	15.5	3.8	8.8
21	S1	2.3	7.6	0.8	8.3
21	S2	0	14.6	0.7	7.2
21	S3	3.2	14.7	0.5	8.7
21	S4	0	17.9	0.7	7.4
21	S5	2.7	14.5	0	7.4
21	S6	2.3	12.5	0.8	8.3
21	S7	0	21	0.8	4.9
21	S8	0	23.9	4.3	5.2
21	S9	0	24.8	1.4	5.3
22	S1A	6.8	13.3	0.9	3.9

22	S1B	5.8	13.7	0	4.6
22	S3B	9	14.2	0.9	2.8
22	S4A	127	13.7	1.8	2.4
22	S4B	9.8	16.6	1.6	2.3
22	S5A	376	13.1	0.33	2.8
22	S5B	45.2	13.5	0.4	
22	S6A	264.7	11.7	5.2	4.2
22	S6B	0	12.8	1.5	1.7
22	S7A	352.9	12.1	1.8	2.6
22	S7B	67.4	14.9	6.25	
22	S7C	6.6	19.1	0.7	2.7
22	S8A	60.3	14.1	1.04	1.8
22	S8B	19	21.3	2	1.1
22	S8C	5	21.6	0	1.3
22	S9A	108.7	14.1	0.34	3.5
22	S9B	10.4	15.5	0.36	1.1
22	S9C	43	20.3	0.54	1.5
24	Inf	1580	18	5	7
24	S1	17.2	14.4	0	52
24	S2	0	14.4	0	5
24	S3	10.4	14.8	0.3	6.4
24	S4	0	17.2	1.3	3.4
24	S5	11.3	15	2	5.2
24	S6	4.9	2.4	1.4	6.8
24	S7	0	16.9	1.4	2
24	S8	0	22.2	1.3	2.1
24	S9	0	17.6	1.3	1.8
28	Inf	1240	16.6	6.6	4.6
28	S1	0	9.4	1.7	3.8
28	S2	0	7.7	1.3	1
28	S3	0	9.5	1.3	1
28	S4	0	6.4	1.3	0.6
28	S5	0	8	1.7	0.6
28	S6	0	7.8	1.7	0.8
28	S7				0.4
28	S8				0.2
28	S9				0.2
29	S1A	0	20.1	3.9	
29	S1B	55.6	20.2	5.4	
29	S3A	0	20.2	3.5	
29	S3B	10	21.2	0	
29	S4A	126.6	20.9	3.1	
29	S4B	4	22.5	1.9	
29	S5A	236.8	21.7	1.5	
29	S5B	193.7	21.7	3.4	
29	S6A	492.3	19.9	3	
29	S6B	29.6	21.2	2.1	
29	S7A	65.9	19.9	2.8	
29	S7B	0	8.3	4.7	
29	S7C	5.1	15.5	1.8	
29	S8A	73.1	20.7	2.5	
29	S8B	121.2	19.2	3.8	
29	S8C	19.7	20	1.3	
29	S9A	57.4	21	1.3	

29	S9B	19.1	9.5	1.5	
29	S9C	0	9.1	1.4	
31	Inf	1720	14	5.8	4.5
31	S1	31	21.2	1.2	4.2
31	S2	0	22.4	0.5	2.5
31	S3	0	22.6	1.2	4.3
31	S4	0	21.2	0.5	2.9
31	S5	19.6	7.7	1	2.4
31	S6	0	27.2	1.1	4.3
31	S7	0	10	0.5	1.3
31	S8	0	6.4	0.5	0.6
31	S9	0	9.4	1.3	0.9
35	Inf	1440	121.2	5	5
35	S1	2.7	20	2.6	3.7
35	S2	0	18.5	2.5	3.1
35	S4	0	23.2	1.3	3
35	S5	20.1	9.5	1.8	0.4
35	S7	0	15.4	1.3	1.1
35	S8	0	20	1.2	1
35	S9	0	14.9	1.2	1
37	S1A	6.1	22.6	3.1	2.6
37	S1B	4	23.2	2.7	2.3
37	S3A	2.7	22.2	3	1.6
37	S3B	4.8	24.9	0.8	
37	S4A	151.8	23.4	1.5	1.3
37	S4B	19.6	19.1	0	
37	S5A	467	23.3	1	2
37	S5B	44.9	23.8	0	
37	S6A	506.7	22.4	2.5	1.9
37	S6B	10.6	23.4	0.8	
l37	S7A	252.6	23.1	2.6	0.6
37	S7B	22	9.3	0	
37	S7C	9	9.3	0	0.1
37	S8A	179	23.5	1.8	0.6
37	S8B	39	22.2	1	0.2
37	S8C	7	22.8	0	0
37	S9A	143.9	24.4	0	0.9
37	S9B	20.8	17.1	0	0.5
37	S9C	17.8	9.7	0	0.3
38	Inf	1820	16.4	6.6	4.5
38	S1	0	23.9	2.6	3.3
38	S2	0	23.8	1.3	1.9
38	S3	0	22.1	2.2	3.7
38	S4	0	22.5	1.3	2.4
38	S5	2.9	30.6	2.4	2.8
38	S6	0	30.2	1.9	3.6
38	S7	0	9..8	1.2	0.8
38	S8	0	20.6	1.3	1.1
38	S9	0	9.9	1.3	1
42	Inf	1670	23.3	6.3	3.6
42	S1	179	14.1	2.8	2.1
42	S2	26.1	27.2	1.7	2.2
42	S3	52.5	23.5	3.5	3.1
42	S4	13.2	29.3	1.6	0.2

42	S5	27.8	19.5	2.3	2.2
42	S6	44.5	28.8	2.	2.4
42	S7	11.2	9.4	0	1
42	S8	21.4	23	0.4	0.4
42	S9	17	17.7	0	0.8
43	S1A	1.5	23.9	3.3	3.2
43	S1B	0.4	25.1	2.8	2.5
43	S3A	0.7	24	3.7	
43	S3B	0.7	25.4	2.4	2
43	S3				
43	S4A	61.4	25.4	1.2	2.9
43	S5A	434	25.7	0.6	3.3
43	S6A	39.2	22.9	3.5	
43	S7A	121.6	24.6	2.3	2.4
43	S8A	62.3	23.8	1.6	
43	S8B	9.7	22.4	0.6	
43	S8C	4.1	22.9	0	1.2
43	S9A	41.7	27.3	0	2.4
43	S9B	6.1	16.9	0	
43	S9C	4.9	15.7	0	
45	Inf	1308	14.8	7.2	3.8
45	S1	15.8	27.4	0.8	3.09
45	S2	0.	25.2	0.7	3.7
45	S3	13.9	28.8	0.9	3.3
45	S4	12.2	26.8	0.6	3.4
45	S5	0	23.2	2.4	3.5
45	S6	73.5	25.7	1.1	3.2
45	S7	2.4	9.7	0.6	1.2
45	S8	17.9	21.5	0.6	0.6
45	S9	9.9	9.7	1.3	0.6
49	Inf	1422	16.3	7.8	7.5
49	S1	0	25.1	2.8	8.1
49	S2	0	27.1	0.9	4.4
49	S3	0	24.2	2.6	8.5
49	S4	2	24.9	2.6	3.1
49	S5	114	26	1.6	3.9
49	S6	68.9	24	2.8	3.8
49	S7	4.7	9.5	0.9	2.2
49	S8	4.6	24.66	0.9	
49	S9	0	21.4	1.5	1.2
50	S1A	21	19.7	3.1	
50	S1B	17	19.5	3.1	0.6
50	S3A	15	19.2	2.9	
50	S3B	22	19.1	20.9	
50	S4A	94	18.7	1.4	0.5
50	S5A	881	20	1.4	1.8
50	S6A	707	19.4	1.6	
50	S7A	369	18.9	2.8	1.5
50	S7C	49	15.6	0.2	
50	S8C	24	18.8	0.1	0.6
50	S9A	99.8	18.2	0.1	
50	S9C	146	15.8	0.1	
52	Inf	1569	22.9	5.3	5
52	S1	44	26.4	3.4	5

52	S2	4	28.6	0	2
52	S3	164	40.7	1.9	3.7
52	S4	9	26.5	0	2.5
52	S5	171	26.4	1	4.3
52	S6	132	24.9	2.4	3.3
52	S7	29	26.3	0	3.3
52	S8	17	24.9	0.3	0.7
52	S9	16	9.9	0.4	0.9
56	Inf	1506	20.2	5.8	4.2
56	S1	50.8	25.8	1.9	5.3
56	S2	28.4	26.8	0.5	0.4
56	S3	66.4	24.6	2.3	3.7
56	S4	20.8	23.3	0.3	0.7
56	S5	130.5	26.3	1.2	3.2
56	S6	155.2	25.6	1.8	3.6
56	S7	24	18.3	0.3	0.8
56	S8	19.3	20.3	0.5	0.6
56	S9	0	20.5	0.4	0.5
57	S1A	18.7	22.1	3.	2.4
57	S1B	20.7	23.5	2.6	2.4
57	S3A	17.5	22.5	3.7	2.4
57	S3B	17.9	23.7	2.2	2.1
57	S4A	161.5	23.5	1.7	2.3
57	S4B	28.2	28.5	0.2	
57	S5B	23.9	24.5	0.4	
57	S6A	152.9	24.9	1.6	2.8
57	S6B	21.5	26.2	1.4	
57	S7A				1.5
57	S7C	23.4	8.6	0.2	1.8
57	S8A	189.5	24.8	2.5	
57	S8B	41.9	26.7	1.9	
57	S8C	21	26.6	0.2	0.6
57	S9A	76.8	28.3	0.2	1.8
57	S9B	23.3	21.1	0.2	
57	S9C	22.4	9.7	0.2	1.2
59	Inf	1330	18	11	13
59	S1	219.5	24.6	0.2	4.2
59	S2	58	24.8	0.1	1.6
59	S3	283.7	23.8	1.2	4.1
59	S4	54.6	23.9	0.1	2.7
59	S5	265.3	25.2	0.6	5.8
59	S6	521.8	22.1	1.3	4
59	S7	77.4	9.3	0.05	2
59	S8	71.1	22.9	0.06	0.8
59	S9	64	9.4	0.13	0.7
63	Inf	1626	14	5.1	5.8
63	S1A				0.6
63	S1B				2.1
63	S1	28.8	21.6	1.5	3.4
63	S2	24.7	22.7	0.5	2.1
63	S3A				0.75
63	S3B				1.5
63	S3	27.2	21.4	1.7	3.7
63	S4A				0.75

63	S4	21.6	9.9	0.36	2.2
63	S5A				2.25
63	S5	48	22.8	0.6	3.7
63	S6	48.6	21.2	1.8	3.8
63	S7A				1.05
63	S7	30.5	7.8	0.05	0.9
63	S8C				0
63	S8	23	22.5	0	0.8
63	S9A				1.8
63	S9	27.5	7.8	0.1	1.6
70	Inf	1500	19.8	4.9	6
70	S1	111	25.1	1.5	3.5
70	S2	6	27.4	0	2.8
70	S3	19	23.3	2.4	3.4
70	S4	10	24.6	0	2.2
70	S5	12	22.9	0.5	3.7
70	S6	84	23.8	1.8	4.8
70	S7	4	8.9	0	1.3
70	S8	61	22.5	1.8	3.1
70	S9	8.7	9	0	1.3
72	S1A	11	19.7	3.4	2.3
72	S1B	4	25.2	1.1	2.8
72	S3A	5	19.7	3.4	2.4
72	S3B	3	24.5	1.7	1.7
72	S4A	176.7	22.4	0.13	1.7
72	S5A	303.4	22.4	0	1.9
72	S6A	73.9	21.5	0.99	2.5
72	S6B	2.5	5.1	23.8	0.94
72	S7A	248	221	00.92	0.9
72	S7B	10.5	13.7	0	
72	S7C	8.6	14.5	0	
72	S8A	69.5	20.6	1.2	
72	S8B	10.5	20.6	0.2	
72	S8C	3.6	15	0	0
72	S9A	38.8	24.4	0	1.2
72	S9B	6.5	17.4	0	
72	S9C	11.2	15.9	0	
73	Inf	1441	18.08	4.45	3.8
73	S1	946	17.1	0.77	3.3
73	S2	247	17.14	0	0
73	S3	212	18.2	1.98	2.5
73	S4	542	17.75	0.32	3
73	S5	173	19.2	0.53	2
73	S6	324	17.8	1.7	1.8
73	S7	143	15.38	0	1.1
73	S8				1.5
73	S9	333	15.6	0.	07
76	Inf	1470	22.7	5.3	3.8
76	S1	16	28.3	0.65	3.1
76	S2	6	28.8	0.57	3.8
76	S3	10	24.1	0.69	3.3
76	S4	8	27.3	0.42	3.4
76	S5	97.8	25.1	2.1	3.6
76	S6	23	28.2	1.06	3.2

76	S7	6.8	9.7	0.43	1.2
76	S8	6	24.8	0.37	0.6
76	S9	8	20.1	0.31	0.6
79	S1A	19	18.8	2.6	1.2
79	S1B	20.9	19.6	1.6	1.2
79	S3A	18	18.5	3.2	1.4
79	S3B	15	19.8	1.4	1.2
79	S4A	311	19.9	1.11	1
79	S4B	25	18.34	0	
79	S5A	854	17.01	0.94	1.4
79	S5B	30	16.5	0	
79	S6A	406	24.9	0	
79	S6B	11	17.9	1.39	1.8
79	S7A	585	17.9	1.26	1.2
79	S7C	43	14.8	0	1
79	S8A	115	18.8	1.26	1.8
79	S8B	169	17.11	0.37	1
79	S8C	31	17.1	0	
79	S9A	94	17.17	0	0.6
79	S9B	28	16.36	0	
79	S9C	34	14.38	0	0.4
80	Inf	1520	21.6	5.25	4.7
80	S1	11.5	25.04	3.9	4.1
80	S2	2	27.2	0	3.8
80	S3	3	24.7	1.67	1.4
80	S4	2	25.6	0	3.4
80	S5	20.8	26.9	0.48	3.6
80	S6	17	24.2	1.78	4.5
80	S7	2	9.33	0	1.3
80	S8	3	24.4	0	1.7
80	S9	6	9.5	0	1
84	Inf	1138	18.6	4.5	3.6
84	S1	784	19.2	2.8	4.67
84	S2	64.5	19.5	0.07	1.2
84	S3	140	19.1	1.6	3.2
84	S4	75	19.1	0	1.9
84	S5	635	19.9	0.03	3.8
84	S6	453	18.9	2.01	4.6
84	S7	96.2	17	0.03	0.8
85	S1A	47	19.4	4.2	3.2
85	S1B	75	19.4	3.3	2.4
85	S3A	78	19.5	4.5	2.8
85	S3B	54	19.6	4.2	2
85	S4A	414	19.1	1.6	0.5
85	S4B		18.3	0	
85	S5A	735	19.3	1.5	0.6
85	S5B	150	19.5	0.04	
85	S6A	574	21.3	0.94	
85	S6B	45	19.2	2.2	2.4
85	S7A	715	19	2.8	0.5
85	S7B		12.5	0.1	
85	S7C				0.7
85	S8A	721	16.6	0	
85	S8B	241	19.8	1.1	

85	S8C	43	17.2	0.26	
85	S9A	465	18.8	0	1.2
85	S9B	42	17.2	0.03	
85	S9C	21	16.2	0	
87	Inf	1580	18.6	4.2	8.7
87	S1	491	18.6	1.79	9.1
87	S2	321	17.6	0.1	2.8
87	S3	325	18.6	1.6	5.1
87	S4	316	18.5	0	1.1
87	S5	325	18.7	0	3.5
87	S6	469	18.1	1.9	4
87	S7	154	14.9	0	0.8
87	S8	268	16.4	0	1.1
87	S9	207	14.8	0	0.7
91	Inf	1356	18.7	5.2	5
91	S1	0	18.7	2.2	6.9
91	S2	43	18.3	0	4.4
91	S3	0	18.8	2	6.8
91	S4	64	18.3	0	2.7
91	S5	351	18.7	0.1	4.2
91	S6	716	17.4	2.6	5.5
91	S7	80	15.9	0	1.1
91	S8	266	18.7	0	1.3
91	S9	115	15.9	0.075	1.3
92	S1A	13.3	19	5.3	3.5
92	S1B	15.7	20	4.4	2.4
92	S3A	89	18.1	6.7	4.3
92	S3B	13.8	19.8	4.7	2.5
92	S4A	204.5	20.5	2.05	3.8
92	S4B	5.5	21.2	0	
92	S5A	410.2	20.2	2.02	
92	S5B	24.1	29.3	0	
92	S6A	59.4	20.05	3.2	3.8
92	S6B	6.4	19.7	2.8	3.4
92	S7A	230	19.3	3.9	2.2
92	S7C	9.1	18.9	0	1.6
92	S8A	472	19.8	4.3	3.2
92	S8B	276	15.9	2.3	0.9
92	S8C	41	15.04	0	
92	S9A	134	14.2	0	1.8
94	Inf	1580	20	4.7	8.5
94	S1	236.9	28	0.8	5.8
94	S2	113	30.3	0	0.99
94	S3	280	29	0.79	7.8
94	S4	76	29.6	0	2.4
94	S5	189	28.8	0	4.3
94	S6	282	28.3	1.5	5.8
94	S7	214	16.4	0	1.2
94	S8	37.1	33.7	0	2.1
94	S9	214	17.7	0	1.6

Table C2: Results from intermittently loaded laboratory-scale filter columns

Days	Ref	Al µg L-1	NO3--N mg L-1	NH4+-N mg L-1	DOC mg L-1
2	Inf	1560	33.5	8.2	6.4
2	I1A	8.4	16.6	3.9	7.1
2	I1B	11	12.5	3.9	0.3
2	I1	0	38.8	7.6	3.5
2	I2A	4.5	17.9	4.6	5.2
2	I2B	14.8	18.1	4.3	5.8
2	I2	0	72.4	13	4.6
2	I3A	6.2	14.7	5.3	6.5
2	I3	0	24.6	1.2	5
2	I4A	477	18.2	4.07	3.9
2	I4B	50.9	18.3	0.11	0.3
2	I4	0	35.8	1.3	4.8
2	I5A	175.6	13.2	3.2	1.4
2	I5B	0	8.5	0.11	0.1
2	I5	0	44.4	1.3	2.8
2	I6A	84.1	18.3	3.33	0.57
2	I6B	0	17.5	0.2	8
2	I6	0	33.3	1.2	3.1
2	I7A	37.5	17.8	6.11	1.4
2	I7	0	5.7	1.2	0.5
2	I8A	15.5	17.8	3.9	1.7
2	I8	0	23.6	1.3	1.3
2	I9A	120	19.5	4.1	1.2
2	I9B	4.8	4.3	1.4	
2	I9C	6.4	7.8	0	0.3
2	I9	0	43	1.3	1.5
4	Inf	1226	16	4.8	6.7
4	I1	0	27.1	6.2	4
4	I2	0	59.6	11.9	3.9
4	I3	0	24.9	6.2	4.8
4	I4	0	28	1.3	5.9
4	I5	0	16.8	1.7	1.6
4	I6	0	46.2	1.5	0.7
4	I7	0	9.2	1.3	1.6
4	I8	0	18.8	1.4	1.7
4	I9	0	32.8	1.6	1.5
7	Inf	1910	22.7	7.3	8.4
7	I1	8.7	23.8	6.3	8
7	I2	0	25.6	6.6	5.6
7	I3	0	24.7	7.1	6.9
7	I4	0	22	1.5	6.2
7	I5	0	20.2	2.1	6.2
7	I6	0	22.8	1.4	6.8
7	I7	0	25.7	1.5	4.2
7	I8	0	21.9	1.8	4.7
7	I9	0	26.1	1.4	1.7
8	I1B	1	18.04	4.9	5.9
8	I2A	2.9	20.7	5.36	7.6

8	I2B	8	19.3	5.4	6.3
8	I3A	4.3	17.6	1.9	8.6
8	I3B	4.2	17.6	4.6	7.2
8	I4A	31.9	18.4	4.8	3.5
8	I4B	6.3	18.3	0.02	5.9
8	I5A	25.4	19.8	3.2	5.2
8	I5B	6.2	18.3	0.02	6.2
8	I6A	31.9	19.9	3.8	4.4
8	I6B	5.7	21	1.12	8.6
8	I7A	34	20.7	2.5	3.9
8	I8A	53	20.9	4.7	3.7
8	I9A	377.8	20.5	5.4	3.7
8	I9C	0	9.1	3.02	
10	Inf	1397	19.8	5.2	8.5
10	I1	0	29.7	7.3	7.6
10	I2	0	31.8	6.2	6.2
10	I3	0	30.6	7.8	6.6
10	I4	0	41.7	1.4	4.9
10	I5	0	18.6	2.5	4.8
10	I6	0	24.8	1.1	7.2
10	I7	0	32.2	1.2	6.5
10	I8	1.1	38.1	3.4	8
10	I9	0	25.6	1.4	5.8
14	Inf	1398	15.4	5.2	6.5
14	I1	0.1	21	4.9	8.5
14	I2	0	29.8	4.6	7
14	I3	2.4	20.3	5.3	6.8
14	I4	0	14.5	1.6	5.5
14	I5	0	23.1	2.6	6.6
14	I6	0	37.9	1.3	6.3
14	I7	0	34.6	1.2	4.5
14	I8	0	36.1	3.5	5.8
14	I9	0	23.6	1.2	5
16	I1B	0.4	16.6	0.62	
16	I2A	0	21.6	2.3	8.4
16	I2B	0	23.5	1.76	5
16	I3A	2	18.8	0.99	8.4
16	I4A	18	22.3	1.02	2.6
16	I4B	3.8	21.1	0	7.2
16	I5A	18.2	14.4	0.17	2.4
16	I5B	3	21.4	0	8.3
16	I6A	9.9	23.5	1.4	8.1
16	I6B	3	24.1	0	
16	I7A	6	22.8	0.3	6
16	I8A	11.8	21.9	0	4.5
16	I9A	139	23.6	0.3	1.8
17	Inf	1672	16	3	5.1
17	I1	7.5	9.5	3.4	4.2
17	I2	0	10.6	2.3	6.6
17	I3	32.4	5.7	2.6	6.8
17	I4	0	9.5	1.6	6.2
17	I5	0	5.33	1.4	6.4
17	I6	0	22.9	1.2	4.6
17	I7	0	21.8	1.2	2

17	I8	0	26.7	1.9	2.8
17	I9	0	26.5	1.3	1.4
21	Inf	1856	15.5	3.8	8.7
21	I1	5	19.7	3.7	7.6
21	I2	5.2	12.9	1.6	8.7
21	I3	14.4	19	4.2	6.5
21	I4	0	24.7	2.3	5.9
21	I5	0	19.9	1.9	6.9
21	I6	0	25.7	1.4	6.2
21	I7	0	25.5	1.3	4.7
21	I8	0	22.7	1.4	5.5
21	I9	0	33.2	1.4	5.1
22	I1A	25.4	18.7	4.4	11.7
22	I1B	16.7	17.5	4.6	7.5
22	I2A	0	21.3	5.4	7
22	I2B	0	22.6	3.9	7.7
22	I3A	2	18.1	4.01	6.1
22	I3B	99	17.6	5.9	7.6
22	I4A	49.9	23	2.7	6.3
22	I4B	5	25.6	2.02	7.9
22	I5A	15	19.09	4.3	7.1
22	I5B	44	19.08	2.4	5.4
22	I6A	27.8	23.4	3.07	5.6
22	I6B	3.9	24.86	1.6	7.2
22	I7A	63.4	23.3	5.03	3.9
22	I8A	27	24.2	1.75	7
22	I9A	71.8	23.7	3.6	5.2
24	Inf	1380	18	7.6	5.6
24	I1	0	19.3	2.4	6.1
24	I2	0	25.6	1.4	5.8
24	I3	1.5	18.4	3.7	7.4
24	I4	0	26.8	2.3	5.4
24	I5	0	20.2	1.6	7.2
24	I6	0	27.8	1.4	4.2
24	I7	0	25.7	1.3	1
24	I8	0	23.8	1.3	3.8
24	I9	0	34.7	1.3	1.2
28	Inf	1200	17.2	6.8	8
28	I1	0	21.7	1.4	7.3
28	I2	0	26.7	1.4	7.8
28	I3	2.7	20.5	2.4	7.2
28	I4	2	82	1.3	7.8
28	I5	0	80	1.3	6.7
28	I6	0	27.9	1.3	7.1
28	I7	0	22.2	1.3	5.4
28	I8	0	25.1	1.3	5.7
28	I9	0	23.9	1.3	4.6
29	I1A	21	21	5	
29	I1B	9.9	20.4	5.2	
29	I2A	1.1	21.3	5.2	
29	I2B	95	22.6	6.3	
29	I3A	0	19.7	5.2	
29	I3B	14	19.3	5.5	
29	I4A	27.5	30.6	3.9	

29	I4B	3.5	39.5	4.1	
29	I5A	189	29	4.9	
29	I5B	0	42.3	1.9	
29	I6A	94.4	21.5	3.8	
29	I6B	0	24.3	1.8	
29	I7A	21	23.6	2.1	
29	I8A	0	24.7	1.7	
29	I9A	397	22.4	3.7	
31	Inf	1720	14	5.8	3.6
31	I1	112	6.6	1.2	2.3
31	I2	0.6	17.6	1.1	2.6
31	I3	12.8	34.8	2.8	3.4
31	I4	0	22.2	1.1	2
31	I5	0.5	8.3	1.1	2
31	I6	0	26.8	1.1	2.6
31	I7	0	16.4	1.1	1.5
31	I8	0	21.5	1.4	1.6
31	I9	0	17.9	1.3	0.7
35	Inf	1320	12.4	6.1	5.8
35	I1	0.7	23.2	2.2	6.2
35	I2	0	18.9	1.6	4
35	I3	3.8	22.3	2.1	6
35	I4	0	30	0.6	4.2
35	I5	0	20.1	0.6	
35	I6	0	26.6	0.6	4.6
35	I7	0	15.4	0.6	1.4
35	I8	0	14	1.3	2
35	I9	0	17.7	1.3	2.2
37	I1A	13	20.5	3.1	2.3
37	I1B	3	25.3	1.2	2.7
37	I2A	2.4	21.8	2.6	2.1
37	I2B	3.9	25.2	1.07	2.1
37	I3A	3.5	19.2	3.1	1.8
37	I3B	22.7	522.6	3.4	
37	I4A	71.5	22.3	2.5	1.6
37	I4B	6.6	26.4	0.9	2.02
37	I5A	34.5	24.8	1.9	1.7
37	I5B	14.7	27.9	0.8	1.8
37	I6A	34.8	21.6	2.7	1.9
37	I6B	4	26.5	0.7	2
37	I7A	18.7	22.9	1.2	0.7
37	I8A	6.4	23.9	0.8	1.5
37	I8B	7	7.4	0.8	
37	I9A	195.9	23	3	
38	Inf	1840	17	7.4	4.5
38	I1	0	26.1	1.3	3.4
38	I2	0	26.3	1.3	1.9
38	I3	0	22.6	1.4	3.7
38	I4	0	25.9	1.2	2.4
38	I5	0	22.1	1.2	2.8
38	I6	0	25.7	1.2	3.6
38	I7	0	8.47	1.3	0.9
38	I8	0	21.7	1.3	1.2
38	I9	0	17.4	1.3	1.4

42	Inf	1670	20.3	6.3	3.6
42	I1	171.6	21.9	1.7	2.5
42	I2	199	19.2	2.9	2.3
42	I3	269	29.7	1.8	2.7
42	I4	80.6	27.4	1.4	3
42	I5	112.8	37	1.4	0
42	I6	28.2	14.5	1.5	1.7
42	I7	139	23.4	1.6	0.6
42	I8	264	28.1	1.8	1.6
42	I9	81.1	17.8	1.6	1.1
43	I1A	2.4	20.8	2.3	5.7
43	I1B	21	23.4	0.32	3.1
43	I2A	19.09	25.3	2.87	5.8
43	I2B	0.9	27.9	1.5	4.8
43	I3A	0.9	22.2	2.2	4.3
43	I4A	14.6	23.9	1.4	4.8
43	I4B	3.7	26.4	0	6.1
43	I5A	2.3	28.1	0.9	5.7
43	I5B	1.5	29.6	0	4.5
43	I6A	9	23.9	1.6	7.2
43	I6B	5.4	25.9	0	7.2
43	I7A	5.6	24.7	0	3.2
43	I8A	2.9	29.9	0	2.7
43	I9A	38.9	23.6	2.55	
43	I9C		6.3	0.4	
45	Inf	1520	15.6	8	3.8
45	I1	20	20.8	1.2	3.7
45	I2	16.5	50.4	3.4	3
45	I3	62.5	28.9	1.3	4.3
45	I4	27.6	26.3	1.2	0
45	I5	89.9	39.2	1.2	3.3
45	I6	20.7	25.9	1.2	3.7
45	I7	11.3	8.6	1.5	2.6
45	I8	29.7	30.5	1.2	1.9
45	I9	3.3	9.6	1.3	1.6
49	Inf	1210	15.8	7.8	7.5
49	I1	4.7	22.6	1.3	2.7
49	I2	10.4	23.1	2.3	3.6
49	I3	11.6	21.9	1.3	2.8
49	I4	13.4	23.7	1.4	2.8
49	I5	45.7	25.9	1.4	3.1
49	I6	4.9	24.7	1.3	2.8
49	I7				0.9
49	I8	0	19.8	1.3	2.3
49	I9	1.4	25.2	1.3	0.9
50	I1A	16	19.5	1.7	2.4
50	I1B	18	19.7	0.33	0.6
50	I2A	10	18.6	2.3	2.1
50	I2B	13	19.4	1.1	
50	I3A	19.7	18.7	1.8	2.4
50	I3B	13	19.2	0.8	
50	I4A	98	15.6	1.34	2.1
50	I4B	23	19.7	0	
50	I5A	35	18.7	1.5	1.6

50	I5B	21	18.2	0.1	
50	I6B	21.7	18.7	0.06	
50	I7A	32	17.8	0.45	0.8
50	I8A	26	19.2	0.39	0.6
50	I9A	114	19.6	1.8	0.4
52	Inf	1569	22.5	6.1	5
52	I1	133	24.2	0.4	4.3
52	I2	194	25.5	0.5	3.7
52	I3	61.7	24.5	0.2	2.9
52	I4	18	27.2	0.1	3.6
52	I5	176.3	25.7	0.6	3.6
52	I6	63.3	26.5	0.3	3.1
52	I7	7	9.12	0.04	1.4
52	I8	359	25.3	0.09	2.8
52	I9	27	20.9	0.02	0.9
56	Inf	1500	15.2	6.6	7
56	I1	0	25.1	0.6	4.9
56	I2	0	25.6	0.4	3.4
56	I3	0	25.6	0.6	3.6
56	I4	0	25.8	0.4	2.8
56	I5	0	26.4	0.65	3.8
56	I6	0	23.7	0.75	4.4
56	I7	0	14.9	0.7	0.6
56	I8	0.8	26.6	0.8	2.4
56	I9	0	21	0.8	0.8
57	I1A	17.9	25.8	1.7	3.9
57	I1B	16.6	27.8	0.57	3.6
57	I2A	16.1	25.2	1.98	3.6
57	I2B	18.4	26.1	1.34	3.9
57	I3A	18.3	25.4	2.1	3.2
57	I3B	19.4	25	1.1	6.2
57	I4A	85.9	22.8	1.9	16.8
57	I4B	19.2	28.4	0.35	
57	I5A	19.2	25.9	2.05	4
57	I5B	16.6	26.9	0.37	3.4
57	I6A	84.4	25.2	1.9	3.2
57	I6B	18	26.3	0.3	
57	I7A	22.4	23.9	1.04	1.6
57	I8A	18.6	25.5	1.97	1.8
57	I8C	21.4	8	0.3	
57	I9A	200.7	23.7	2.3	2.1
57	I9C	29.5	6.2	0.7	
59	Inf	1670	18.9	5.07	7.5
59	I1	243.3	22.8	0.88	5.4
59	I2	197.5	23.3	0.19	4
59	I3	224.6	24.2	0.5	4
59	I4	165.7	25	0.1	3
59	I5	610.5	24.9	0.27	4.5
59	I6	46.9	22.2	0.46	4
59	I7	58.5	9.1	0.1	0.5
59	I8	294.7	23.6	0.2	2.7
59	I9	134.8	9.9	0.2	0.8
63	Inf	1260	14	5	7.4
63	I1	63.5	21.8	0.23	2.5

63	I2	56.6	21.3	0.89	5.2
63	I3	61.2	18.7	1.9	6
63	I4	27.4	22.6	0.07	3.4
63	I5	143.7	21.6	0.2	5.2
63	I6	46.9	22.2	0.46	4
63	I7	121.8	7.9	0	1.6
63	I8	168.1	22.4	0	3.7
63	I9	46.7	8.3	0	0.9
70	Inf	1840	19.3	5.2	6
70	I1	64	24.9	0	3.9
70	I2	61	23.3	1.2	4.4
70	I3	74	22.3	0	3
70	I4	60	17.7	0	4.3
70	I5	89.4	21.3	0.47	3.3
70	I6	10	24.7	0	3.2
70	I7	4.7	9.7	0	1.5
70	I8	81	24.6	0	2.8
70	I9	7.6	20.1	0	1.6
72	I1A	1.4	37.3	0	
72	I1B	3.7	27.1	0	
72	I2A	8.5	47.5	0	
72	I2B	4.9	32.2	0	
72	I3A	7.3	25.1	0	
72	I4A	14.6	24.5	0	
72	I4B	4.6	25.1	0	
72	I5A	8.2	23.1	0.6	
72	I5B	6.9	46.5	0	
72	I6A	39.4	22.2	0	
72	I8A	2.9	24.7	0	
72	I8C	5.4	22.3	0	
72	I9A	93.2	21.3	0.6	
73	Inf	1951	17.5	4.6	3.4
73	I1	418	17.3	0.07	2.7
73	I2	515	17.44	0.36	2.8
73	I3	556	17.9	0.14	2
73	I4	174	18.6	0	2.5
73	I5	675	17.7	0.7	3.1
73	I6	143	18.3	0.09	2.4
73	I7	119	15.6	0.02	1.7
73	I8	579	17.7	0	2.3
73	I9	55	16.1	0	
76	Inf	1470	23	4.9	3.8
76	I1	11	22.9	0.3	3.7
76	I2	9	18.8	2.3	3
76	I3	34	23	0.25	4.3
76	I4	12.8	32.3	0.2	0.1
76	I5	12	25.5	0.2	3.3
76	I6	9.5	29.9	0.24	3.7
76	I7	7.5	16.8	0.85	2.7
76	I8	12.9	26.5	0.5	1.9
76	I9	7.8	21.8	0.5	1.6
79	I1A	16	17.1	0	1.6
79	I1B	28	16.2	0	0.6
79	I2A	19	17.8	0	1.2

79	I2B	32	15.5	0	
79	I3A	33	16.2	0	1.8
79	I4A	58	19.4	0	2.4
79	I4B	28	19.1	0	2.8
79	I5A	8	19.2	1.8	3
79	I5B	18	18.5	0.2	0.6
79	I6A	5.3	26.8	1.2	1.2
79	I6B	26	18.5	0	0.4
79	I8A	17	18.9	0.6	1.5
79	I8C	13	17.4	0	0.3
79	I9A	274	18.9	1.7	1.6
79	I9B	36	18.8	2.4	
80	Inf	1520	20.5	4.9	4.7
80	I1	10	22.5	0	3.4
80	I2	14	27.7	0.65	3.5
80	I3	12	23.2	0	3.5
80	I4	5..9	25.3	0	2.9
80	I5	16.5	27.3	0	4
80	I6	5	24.9	0	3.2
80	I8	3	20.5	0	1.4
80	I9	5	25.2	0	2.3
84	Inf	1674	18.6	5.4	5.2
84	I1	590	8.4	0.03	3.5
84	I2	408	18.8	0.04	2.9
84	I3	159	19.1	0	3.8
84	I4	114.6	18.8	0	2.6
84	I5	719.9	18.8	0	4.5
84	I6	115	18.8	0	2.9
84	I7	98.5	18	0	0.6
84	I8	352.7	19.2	0.13	2.6
84	I9	108	16.8	0	0.8
85	I1A	38	18.6	0	5.2
85	I1B	37	19.3	0.1	2.4
85	I3A	53	17.1	0	
85	I4A	412	18.6	0	3.7
85	I4B	31	18.5	0.17	
85	I5A	61	19.6	2.2	5.3
85	I5B	35	19.4	0.1	4.8
85	I6A	323	18.8	1	2.2
85	I6B	62	19.5	0.6	0.2
85	I7A	53	19.6	2.7	2.1
85	I8A	36	19.4	2.5	4.3
85	I8C	32	17.9	0.17	0.3
85	I9A	950	18.9	1.7	2.1
85	I9B		10.1	1.79	
85	I9	67	15.8	1.24	
87	Inf	1535	18.8	5.06	8.7
87	I1	510	16.4	0	1.4
87	I2	417	17.7	0	3.7
87	I3	310	18.1	0	3.1
87	I4	169	18.9	0	2.7
87	I5	755	18.2	0	4.6
87	I6	149	18.4	0	2.4
87	I7	123	15.8	0	0.8

87	I8	340	17.8	0	2.5
87	I9	269	15.7	0	0.9
91	Inf	1356	18.7	4.8	5
91	I1	208	17.3	0.18	
91	I2	651	18.8	0	3.6
91	I3	269	19.6	1.2	2.9
91	I4	251	19	0	2.5
91	I5	669	18.7	0.1	4.6
91	I6	258	17.5	0	3.6
91	I7	82	17.4	0	0.8
91	I8	414	18.3	0.2	2.3
91	I9	63	16.2	0.02	1.3
92	I1A	13.9	17.4	0.5	
92	I1B	10	19.9	0	
92	I2A	40	21.3	0	4.7
92	I2B	11.6	20.3	0	4.8
92	I3A	8.4	18.7	0	
92	I3B	9	19.6	0.03	
92	I4A	126.5	29.7	0	3.6
92	I4B	6	20.3	0	
92	I5A	6.7	18.8	2.5	5.2
92	I5B	8.9	22.7	0	4.8
92	I6A	61.3	21.6	0	2.4
92	I6B	22	21.3	0	2.4
92	I7A	11	23	2.6	2.9
92	I8A	8.6	20.4	1.9	4.3
92	I8C	5.6	19.7	0	1.6
92	I9A	276.9	19.6	1.3	2.1
94	Inf	1580	20.5	5.03	8.5
94	I2	52.4	30.6	0	5.4
94	I3	33.6	28.5	0	4
94	I4	27	28.7	0	3.4
94	I5	312	30.8	0	5.4
94	I6	69.5	30.4	0	3.7
94	I7	25	30	0	1.5
94	I8	131	27.9	0	2.6
94	I9	31.3	21.	0	1.5

Table C3: Results from deconstruction of laboratory-scale filter columns

Ref	**Depth (mm)**	**Total Exchange Capacity (meq/100 g)**	**pH**	**Organic Matter (%)**	**Estimated Nitrogen Release (#'s N/acre)**	**S* (ppm)**
S1	0-20	2.67	7.2	0.52	21	15
S1	40-60	1.64	7.4	0.42	17	17
S1	80-100	3.09	6.5	0.39	16	15
S1	140-160	2.91	6.9	0.57	23	17
S1	220-240	2.97	6.8	0.4	16	17
S2	0-20	1.23	7.5	0.16	6	6
S2	40-60	1.34	7.8	0.11	4	5
S2	80-100	1.27	7.3	< 0.10	4	5
S2	140-160	1.07	7.1	< 0.10	4	4
S2	220-240	1.26	7.3	< 0.10	4	4
S3	0-20	2.99	7.4	0.72	29	21
S3	40-60	2.27	7.5	0.46	18	19

S3	80-100	2.64	6.9	0.52	21	17
S3	140-160	3.68	6.4	0.39	16	17
S3	220-240	2.59	6.4	0.31	12	13
S4	0-20	83.62	8.1	6.07	105	272
S4	40-60	83.06	8.4	5.72	104	270
S4	80-100	73.43	7.7	5.62	103	316
S4	140-160	80.99	7.7	5.16	101	361
S4	220-240	89.38	8.3	5.07	100	375
S5	0-20	78.65	8	5.98	105	351
S5	40-60	80.47	8.1	5.47	102	364
S5	80-100	81	8.3	5.31	102	398
S5	140-160	81.78	8.3	5.13	101	376
S5	220-240	83.77	8	5.21	101	380
S6	0-20	80.24	8.3	6.4	107	254
S6	40-60	82.8	8.5	5.74	104	269
S6	80-100	83.29	8.8	5.5	102	315
S6	140-160	81.91	8.7	5.6	103	309
S6	220-240	87.88	7.8	5.82	104	377
S7	0-20	13.23	8	0.91	36	44
S7	40-60	17.99	8.4	0.81	32	58
S7	80-100	22.56	8.2	0.65	26	88
S7	140-160	18.78	8.5	0.63	25	63
S7	220-240	21.04	8.5	0.55	22	84
S8	0-20	48.51	9.4	0.67	27	383
S8	40-60	46.43	9.7	0.56	22	627
S8	80-100	36.6	9.9	0.64	26	508
S8	140-160	24.56	8.9	0.84	34	65
S8	220-240	28.4	8.8	0.57	23	61
S9	0-20	13.33	8.2	1.23	45	48
S9	40-60	21.72	8.5	0.65	26	74
S9	80-100	24.47	8.5	0.57	23	89
S9	140-160	20.32	8.6	0.57	23	78
S9	220-240	20.6	8.4	0.47	19	70
I1	0-20	4.58	7.8	0.63	25	23
I1	40-60	2.36	8	0.38	15	16
I1	80-100	1.94	7.7	0.32	13	15
I1	140-160	1.83	7.5	0.3	12	15
I2	0-20	3.92	7.5	1.24	45	24
I2	40-60	2.14	7.6	0.41	16	17
I2	80-100	1.99	7.3	0.37	15	14
I2	140-160	1.74	7.2	0.22	9	11
I3	0-20	3.5	7.6	1.04	41	23
I3	40-60	2.05	7.6	0.39	16	16
I3	80-100	1.8	7.2	0.32	13	14
I3	140-160	1.64	7	0.29	12	9
I4	0-20	79.99	8.1	5.83	104	377
I4	40-60	82.33	8.2	5.3	102	349
I4	80-100	84.41	8	5.01	100	386
I4	140-160	86.08	8.3	5.12	101	395
I5	0-20	80.64	8.2	5.28	101	393
I5	40-60	77.12	8.3	5.18	101	392
I5	80-100	83.71	8.3	5.22	101	392
I5	140-160	87.1	7.9	5.23	101	392
I6	0-20	78.83	7.8	6.19	106	360

I6	40-60	74.87	8.1	5.36	102	353
I6	80-100	84.57	8.5	5.06	100	396
I6	140-160	87.3	8.5	5.1	100	417
I7	0-20	11.2	7.6	1.53	51	34
I7	40-60	20.66	8.3	0.7	28	39
I7	80-100	24.53	8.4	0.72	29	50
I7	140-160	28.94	8.4	0.62	25	49
I8	0-20	16.95	8	0.89	36	36
I8	40-60	20.75	8.4	0.73	29	43
I8	80-100	24.99	8.4	0.66	26	47
I8	140-160	25.92	8.3	0.64	26	50
I9	0-20	11.45	7.7	1.69	54	25
I9	40-60	25.61	8.4	0.65	26	47
I9	80-100	25.16	8.4	0.74	30	50
I9	140-160	25.85	8.4	0.58	23	45
Raw Sand		0.96	8	0.1	4	10
Raw Zeo		22.13	8.7	< 0.10	4	20
Raw Pyr		80.76	6.4	1.57	51	6241
Raw B Re		108.8	10.3	5.7	104	935
Raw F As		54.19	11.5	0.22	9	562
Raw GBS		80.42	10.6	0.62	25	741
Raw GAC		12.99	10.1	72.3	> 130	39

Table C4: Results from deconstruction of laboratory-scale filter columns

Ref	Depth (mm)	P* (mg/kg)	Bray II P (mg/kg)	Ca* (mg/kg)	Mg* (mg/kg)	K* (mg/kg)
S1	0-20	5	3	409	31	54
S1	40-60	4	3	243	20	40
S1	80-100	4	2	430	39	55
S1	140-160	4	5	443	33	55
S1	220-240	4	8	442	34	50
S2	0-20	4	3	158	19	53
S2	40-60	5	3	167	22	66
S2	80-100	3	2	159	23	55
S2	140-160	3	3	130	20	54
S2	220-240	4	3	161	22	58
S3	0-20	4	2	461	30	59
S3	40-60	4	2	338	27	47
S3	80-100	3	2	408	27	46
S3	140-160	4	4	476	32	66
S3	220-240	4	8	352	28	52
S4	0-20	7	< 1	8348	93	1998
S4	40-60	10	1	8468	88	1663
S4	80-100	12	3	6157	63	1676
S4	140-160	12	3	6830	69	1406
S4	220-240	14	4	7258	86	992
S5	0-20	9	2	5873	73	3720
S5	40-60	9	1	6523	67	3214
S5	80-100	10	4	5870	68	2870
S5	140-160	11	3	6461	71	2396

S5	220-240	10	8	6847	84	2243
S6	0-20	7	< 1	8490	83	1632
S6	40-60	10	< 1	7898	87	1475
S6	80-100	10	7	7103	90	1549
S6	140-160	11	7	6960	87	1451
S6	220-240	10	7	7260	132	1707
S7	0-20	66	257	1665	396	153
S7	40-60	75	251	2393	582	124
S7	80-100	110	75	2862	665	186
S7	140-160	109	94	2615	552	115
S7	220-240	135	83	2911	602	137
S8	0-20	824	817	6419	1795	111
S8	40-60	817	465	7046	1205	75
S8	80-100	967	518	5514	971	61
S8	140-160	75	85	3638	629	98
S8	220-240	51	45	4386	613	110
S9	0-20	83	264	1738	435	133
S9	40-60	96	231	2923	699	150
S9	80-100	122	66	3318	784	150
S9	140-160	144	84	2894	557	139
S9	220-240	141	68	3035	491	137
I1	0-20	13	20	694	72	59
I1	40-60	6	4	346	36	45
I1	80-100	3	51	276	26	48
I1	140-160	3	35	269	22	44
I2	0-20	4	< 1	611	43	68
I2	40-60	3	1	321	26	49
I2	80-100	2	19	295	23	47
I2	140-160	4	12	253	22	47
I3	0-20	3	2	548	36	66
I3	40-60	3	2	298	29	47
I3	80-100	3	11	267	22	41
I3	140-160	2	11	235	22	50
I4	0-20	13	2	6317	74	3384
I4	40-60	10	1	6431	72	2876
I4	80-100	10	10	6492	71	2529
I4	140-160	11	9	6591	79	2195
I5	0-20	12	1	5471	69	3090
I5	40-60	13	1	5243	62	2872
I5	80-100	13	8	6098	71	2686
I5	140-160	11	10	6929	85	2080
I6	0-20	11	2	5941	81	3748
I6	40-60	13	2	5532	67	2783
I6	80-100	9	6	6393	80	2243
I6	140-160	10	6	6220	84	1563
I7	0-20	46	201	1188	418	182
I7	40-60	57	199	2762	637	141
I7	80-100	67	66	3351	745	153
I7	140-160	96	73	3889	955	139
I8	0-20	40	231	2202	530	172
I8	40-60	62	230	2849	620	138
I8	80-100	86	65	3390	805	136
I8	140-160	90	68	3391	887	173
I9	0-20	41	212	1319	434	182

I9	40-60	57	192	3701	679	158
I9	80-100	82	58	3577	714	139
I9	140-160	89	65	3319	921	132
Raw Sand		4	5	120	26	16
Raw Zeo		3	3	1004	340	4224
Raw Pyr		3	7	12780	585	184
Raw B Re		10	2	5488	24	189
Raw F As		1044	751	9210	884	25
Raw GBS		4	< 1	12405	1967	234
Raw GAC		87	69	256	59	3938

Table C5: Results from deconstruction of laboratory-scale filter columns

Ref	Depth (mm)	Na (mg/kg)	Ca** (%)	Mg** (%)	K** (%)	Na** (%)
S1	0-20	27	76.59	9.68	5.19	4.4
S1	40-60	20	74.09	10.16	6.25	5.3
S1	80-100	20	69.58	10.52	4.56	2.81
S1	140-160	25	76.12	9.45	4.85	3.74
S1	220-240	29	74.41	9.54	4.32	4.25
S2	0-20	22	64.23	12.87	11.05	7.78
S2	40-60	25	62.31	13.68	12.63	8.11
S2	80-100	20	62.6	15.09	11.1	6.85
S2	140-160	16	60.75	15.58	12.94	6.5
S2	220-240	17	63.89	14.55	11.8	5.87
S3	0-20	37	77.09	8.36	5.06	5.38
S3	40-60	33	74.45	9.91	5.31	6.32
S3	80-100	23	77.27	8.52	4.47	3.79
S3	140-160	81	64.67	7.25	4.6	9.57
S3	220-240	24	67.95	9.01	5.15	4.03
S4	0-20	7641	49.92	0.93	6.13	39.73
S4	40-60	7642	50.98	0.88	5.13	40
S4	80-100	8075	41.92	0.71	5.85	47.81
S4	140-160	9122	42.17	0.71	4.45	48.97
S4	220-240	10824	40.6	0.8	2.85	52.65
S5	0-20	8387	37.34	0.77	12.13	46.36
S5	40-60	8373	40.53	0.69	10.24	45.24
S5	80-100	9479	36.23	0.7	9.09	50.88
S5	140-160	9248	39.5	0.72	7.51	49.17
S5	220-240	9255	40.87	0.84	6.87	48.04
S6	0-20	6998	52.9	0.86	5.22	37.92
S6	40-60	8373	47.69	0.88	4.57	43.97
S6	80-100	9404	42.64	0.9	4.77	49.09
S6	140-160	9304	42.49	0.89	4.54	49.39
S6	220-240	9877	41.31	1.25	4.98	48.87
S7	0-20	176	62.93	24.94	2.97	5.78
S7	40-60	72	66.51	26.96	1.77	1.74
S7	80-100	348	63.43	24.56	2.11	6.71
S7	140-160	62	69.62	24.49	1.57	1.44
S7	220-240	116	69.18	23.84	1.67	2.4
S8	0-20	47	66.16	30.84	0.59	0.42
S8	40-60	41	75.88	21.63	0.41	0.38
S8	80-100	54	75.33	22.11	0.43	0.64
S8	140-160	60	74.06	21.34	1.02	1.06

S8	220-240	79	77.22	17.99	0.99	1.21
S9	0-20	56	65.19	27.19	2.56	1.83
S9	40-60	62	67.29	26.82	1.77	1.24
S9	80-100	57	67.8	26.7	1.57	1.01
S9	140-160	65	71.21	22.84	1.75	1.39
S9	220-240	83	73.67	19.86	1.71	1.75
I1	0-20	44	75.76	13.1	3.3	4.18
I1	40-60	30	73.31	12.71	4.89	5.53
I1	80-100	35	71.13	11.17	6.34	7.84
I1	140-160	27	73.5	10.02	6.17	6.41
I2	0-20	42	77.93	9.14	4.45	4.66
I2	40-60	25	75	10.12	5.87	5.08
I2	80-100	27	74.12	9.63	6.06	5.9
I2	140-160	23	72.7	10.54	6.93	5.75
I3	0-20	36	78.29	8.57	4.84	4.47
I3	40-60	27	72.68	11.79	5.88	5.73
I3	80-100	24	74.17	10.19	5.84	5.8
I3	140-160	18	71.65	11.18	7.82	4.77
I4	0-20	8388	39.49	0.77	10.85	45.59
I4	40-60	9100	39.06	0.73	8.96	48.06
I4	80-100	9661	38.46	0.7	7.68	49.76
I4	140-160	10160	38.28	0.76	6.54	51.32
I5	0-20	9708	33.92	0.71	9.83	52.34
I5	40-60	9346	33.99	0.67	9.55	52.69
I5	80-100	9924	36.42	0.71	8.23	51.54
I5	140-160	9974	39.78	0.81	6.12	49.79
I6	0-20	8280	37.68	0.86	12.19	45.67
I6	40-60	8521	36.94	0.75	9.53	49.48
I6	80-100	10060	37.8	0.79	6.8	51.72
I6	140-160	11260	35.62	0.8	4.59	56.08
I7	0-20	203	53.04	31.1	4.17	7.88
I7	40-60	125	66.84	25.69	1.75	2.63
I7	80-100	100	68.3	25.31	1.6	1.77
I7	140-160	72	67.19	27.5	1.23	1.08
I8	0-20	117	64.96	26.06	2.6	3
I8	40-60	83	68.65	24.9	1.71	1.74
I8	80-100	53	67.83	26.84	1.4	0.92
I8	140-160	76	65.41	28.52	1.71	1.27
I9	0-20	81	57.6	31.59	4.08	3.08
I9	40-60	62	72.26	22.09	1.58	1.05
I9	80-100	50	71.09	23.65	1.42	0.86
I9	140-160	107	64.2	29.69	1.31	1.8
Raw Sand		15	62.5	22.57	4.27	6.79
Raw Zeo		655	22.68	12.8	48.94	12.87
Raw Pyr		48	79.12	6.04	0.58	0.26
Raw B Re		18280	25.22	0.18	0.45	73.05
Raw F As		175	84.98	13.59	0.12	1.4
Raw GBS		174	77.13	20.38	0.75	0.94
Raw GAC		219	9.85	3.78	77.73	7.33

Table C6: Results from deconstruction of laboratory-scale filter columns

Ref	Depth (mm)	Other Bases** (%)	H** (%)	B* (mg/kg)	Fe* (mg/kg)	Mn* (mg/kg)

S1	0-20	4.2	0	0.22	41	5
S1	40-60	4	0	< 0.20	28	3
S1	80-100	4.9	7.5	0.29	40	4
S1	140-160	4.5	1.5	< 0.20	43	3
S1	220-240	4.6	3	< 0.20	39	4
S2	0-20	3.9	0	< 0.20	35	4
S2	40-60	3.6	0	< 0.20	35	6
S2	80-100	4.1	0	< 0.20	42	5
S2	140-160	4.3	0	< 0.20	40	4
S2	220-240	4.1	0	< 0.20	36	5
S3	0-20	4	0	< 0.20	43	4
S3	40-60	3.9	0	< 0.20	38	3
S3	80-100	4.5	1.5	< 0.20	36	3
S3	140-160	5	9	0.42	54	4
S3	220-240	5	9	0.25	35	4
S4	0-20	3.3	0	0.95	18	< 1
S4	40-60	3	0	0.97	29	< 1
S4	80-100	3.7	0	0.76	57	< 1
S4	140-160	3.7	0	0.64	56	< 1
S4	220-240	3.1	0	0.77	60	< 1
S5	0-20	3.4	0	0.93	18	< 1
S5	40-60	3.3	0	0.87	13	< 1
S5	80-100	3.1	0	0.77	29	< 1
S5	140-160	3.1	0	0.71	17	< 1
S5	220-240	3.4	0	0.8	30	< 1
S6	0-20	3.1	0	0.94	27	< 1
S6	40-60	2.9	0	1.02	35	< 1
S6	80-100	2.6	0	0.84	55	< 1
S6	140-160	2.7	0	0.85	43	< 1
S6	220-240	3.6	0	0.9	61	< 1
S7	0-20	3.4	0	8.94	327	9
S7	40-60	3	0	10.1	297	11
S7	80-100	3.2	0	9.67	296	9
S7	140-160	2.9	0	9.99	351	9
S7	220-240	2.9	0	11.37	328	9
S8	0-20	2	0	40.33	196	23
S8	40-60	1.7	0	48.34	202	21
S8	80-100	1.5	0	37.86	202	20
S8	140-160	2.5	0	9.72	352	9
S8	220-240	2.6	0	8.53	318	9
S9	0-20	3.2	0	10.04	322	10
S9	40-60	2.9	0	12.02	326	11
S9	80-100	2.9	0	10.64	315	11
S9	140-160	2.8	0	11.97	331	10
S9	220-240	3	0	10.87	323	10
I1	0-20	3.6	0	0.85	82	8
I1	40-60	3.4	0	0.45	47	5
I1	80-100	3.7	0	< 0.20	43	3
I1	140-160	3.9	0	< 0.20	38	3
I2	0-20	3.9	0	0.28	38	5
I2	40-60	3.8	0	< 0.20	36	2
I2	80-100	4.1	0	< 0.20	34	2
I2	140-160	4.2	0	< 0.20	44	3
I3	0-20	3.8	0	< 0.20	36	5

I3	40-60	3.8	0	< 0.20	35	3
I3	80-100	4.2	0	< 0.20	38	2
I3	140-160	4.4	0	< 0.20	36	3
I4	0-20	3.3	0	0.92	113	< 1
I4	40-60	3.2	0	0.9	53	< 1
I4	80-100	3.4	0	0.9	16	< 1
I4	140-160	3.1	0	0.95	28	< 1
I5	0-20	3.2	0	0.96	64	< 1
I5	40-60	3.1	0	1	68	< 1
I5	80-100	3.1	0	0.88	28	< 1
I5	140-160	3.5	0	0.91	27	< 1
I6	0-20	3.6	0	0.92	72	< 1
I6	40-60	3.3	0	0.94	76	< 1
I6	80-100	2.9	0	0.93	91	< 1
I6	140-160	2.9	0	0.95	36	< 1
I7	0-20	3.8	0	6.1	335	8
I7	40-60	3.1	0	7.47	363	13
I7	80-100	3	0	8.83	347	11
I7	140-160	3	0	10.36	365	11
I8	0-20	3.4	0	7.43	329	11
I8	40-60	3	0	8.97	350	11
I8	80-100	3	0	8.84	339	11
I8	140-160	3.1	0	9.28	345	11
I9	0-20	3.7	0	6.43	322	8
I9	40-60	3	0	8.56	354	13
I9	80-100	3	0	8.41	357	11
I9	140-160	3	0	9.02	352	10
Raw Sand		3.4	0	< 0.20	39	3
Raw Zeo		2.7	0	< 0.20	23	15
Raw Pyr		5	9	0.68	687	64
Raw B Re		1.1	0	0.96	59	1
Raw F As		-0.1	0	50.65	189	22
Raw GBS		0.8	0	2.21	90	95
Raw GAC		1.3	0	0.78	14	2

Table C7: Results from deconstruction of laboratory-scale filter columns

Ref	Depth (mm)	Cu* (mg/kg)	Zn (mg/kg)	Al* (mg/kg)	NO3-N (ppm)	NH4-N (ppm)
S1	0-20	135.3	5.94	730	9.6	2.6
S1	40-60	74.49	4.47	602	6.2	2.9
S1	80-100	61.1	3.77	623	6.2	2.5
S1	140-160	48.47	2.85	685	7.6	2
S1	220-240	45.83	2.72	565	8.5	1.9
S2	0-20	92.35	3.04	249	2.2	7.7
S2	40-60	39.28	1.86	176	1.7	5.3
S2	80-100	28.89	1.35	127	1	2
S2	140-160	15.82	0.88	117	1.1	2.1
S2	220-240	7.72	0.63	108	0.9	1.3
S3	0-20	177.2	8.04	974	10.8	2
S3	40-60	104.9	5.55	860	5.5	1.8
S3	80-100	55.02	3.64	616	6.5	1
S3	140-160	57.56	10.14	629	8.4	1.1
S3	220-240	31.16	2.78	430	6.7	1

S4	0-20	11.48	0.83	8975	67.4	1
S4	40-60	9.63	0.41	9220	37.7	2.3
S4	80-100	45.26	1.29	9347	45.9	2.4
S4	140-160	8.54	< 0.4	9688	81	4.3
S4	220-240	3.42	< 0.4	10511	27.2	5.1
S5	0-20	24.89	0.82	11190	59.2	1.8
S5	40-60	26.6	0.84	11030	46.8	0.5
S5	80-100	12.06	< 0.4	11079	43.6	2.3
S5	140-160	6.87	< 0.4	10599	40.4	2.1
S5	220-240	4.98	< 0.4	9927	84	1.8
S6	0-20	7.95	0.47	8293	43	0.6
S6	40-60	8.28	0.46	9281	34.1	2.3
S6	80-100	6.7	< 0.4	9701	31	1.6
S6	140-160	4.51	< 0.4	9313	40.8	1.6
S6	220-240	4.87	< 0.4	9186	673.6	2
S7	0-20	63.49	9.8	1818	14.4	0.5
S7	40-60	82.16	9.41	1555	9.9	1.3
S7	80-100	40.95	8.73	1703	11	1.6
S7	140-160	10.06	5.24	1419	10.6	2
S7	220-240	15.71	6.89	1434	12.1	1.9
S8	0-20	10.3	6.18	1264	18.8	1.3
S8	40-60	9.06	5.66	1250	15	1.4
S8	80-100	6.32	6.07	1288	14.2	2
S8	140-160	6.92	5.86	1519	7.8	1.5
S8	220-240	7.05	5.28	1545	6.1	1.5
S9	0-20	65.59	9.28	1691	16	0.5
S9	40-60	46.25	7.37	1655	12.3	1.4
S9	80-100	19.52	8.42	1537	10.7	1.7
S9	140-160	16.46	7.51	1434	10	1.5
S9	220-240	11.51	6.33	1318	22.1	1.3
I1	0-20	256.4	8.06	1040	6.5	2.5
I1	40-60	125.6	5.4	628	2	1.8
I1	80-100	71.65	3.01	514	2.8	1.3
I1	140-160	47.01	1.89	499	2.5	1
I2	0-20	280.9	9.25	1233	18	1.1
I2	40-60	153.7	5.94	806	6.3	0.7
I2	80-100	80.35	3.15	565	4.4	2.1
I2	140-160	45.38	1.97	412	2.5	1.6
I3	0-20	238.5	8.34	1079	19.2	0.5
I3	40-60	133.8	5.12	710	4.7	1.4
I3	80-100	77.7	2.91	516	2.8	0.7
I3	140-160	45.85	1.78	423	5.1	2
I4	0-20	27.96	0.91	10710	70	2.4
I4	40-60	11.74	< 0.4	11310	54.2	1.1
I4	80-100	8.17	< 0.4	11420	48.2	1.7
I4	140-160	5.98	< 0.4	11680	43.1	1
I5	0-20	13.84	0.46	11980	45.4	0.8
I5	40-60	12.11	< 0.4	11660	45.7	1.6
I5	80-100	8.18	< 0.4	11790	37.7	2
I5	140-160	6.8	< 0.4	10960	203.4	1.7
I6	0-20	27.27	1.7	11380	98.1	2.3
I6	40-60	13.18	0.72	11290	55.3	0.6
I6	80-100	7.09	< 0.4	11410	41.8	0.6
I6	140-160	5.5	< 0.4	11970	38.5	1.3

I7	0-20	68.51	10.29	1916	38.9	1.4
I7	40-60	34.61	6.89	1798	10.5	1.1
I7	80-100	29.23	7.91	1839	12.4	3.3
I7	140-160	13.27	8.9	1817	9	1.8
I8	0-20	63.6	8.9	1888	25.7	1.1
I8	40-60	44.97	6.93	1773	14.6	0.7
I8	80-100	41.09	7.32	1816	12.5	3.2
I8	140-160	17.73	6.01	1737	44.3	1.6
I9	0-20	96.45	12.59	1957	29.6	4.4
I9	40-60	32.01	7.68	1845	15.7	2.6
I9	80-100	22.02	7.38	1742	11	1.7
I9	140-160	10.49	7.54	1798	9.2	2.5
Raw Sand		4.65	1.37	87	1.6	2.3
Raw Zeo		1.18	1.64	263	10.5	34.3
Raw Pyr		9.29	13.8	163	2.2	4.2
Raw B Re		4.17	< 0.4	8388	1.8	1.4
Raw F As		4.35	4.43	1223	0.8	5.6
Raw GBS		0.25	0.49	2083	1.3	3.3
Raw GAC		0.55	< 0.4	49	< 0.5	0.8

Table C8: Hydraulic conductivity results from deconstruction of laboratory-scale filter columns

Column ID	**Layer ID**	**dH/dz**	**A (m^2)**	**Q (m^3 s^{-1})**	**K (m s^{-1})**
I1	0-20	2.615384615	0.001963	5.42E-07	0.000105479
		2.833333333	0.001963	5E-07	8.98757E-05
	20-40	2.615384615	0.001963	1.67E-07	3.24551E-05
		3.090909091	0.001963	2E-07	3.29544E-05
	40-60	3.090909091	0.001963	3.33E-07	5.49241E-05
		2.615384615	0.001963	3.67E-07	7.14013E-05
	60-80	2.833333333	0.001963	3.33E-07	5.99172E-05
		3.090909091	0.001963	3.83E-07	6.31627E-05
	80-100	2.833333333	0.001963	8.33E-07	0.000149793
		2.615384615	0.001963	8.33E-07	0.000162276
	100-120	3.578947368	0.001963	3.33E-07	4.74344E-05
		2.833333333	0.001963	4.33E-07	7.78923E-05
	120-140	2.833333333	0.001963	1.01E-06	0.000181249
		2.615384615	0.001963	1.05E-06	0.000204467
	140-160	2.344827586	0.001963	8.42E-07	0.00018281
		2.833333333	0.001963	9E-07	0.000161776
	160-180	3.090909091	0.001963	1.13E-06	0.000186742
		2.615384615	0.001963	1.17E-06	0.000227186
	180-200	3.090909091	0.001963	1.21E-06	0.000199649
		2.833333333	0.001963	1.25E-06	0.000224689
I2	0-20	3.578947368	0.001963	5.22E-07	7.42349E-05
		3.578947368	0.001963	5.35E-07	7.61322E-05
	20-40	2.615384615	0.001963	4.63E-07	9.02252E-05

		2.615384615	0.001963	4.4E-07	8.56815E-05
	40-60	2.615384615	0.001963	5.97E-07	0.000116189
		2.615384615	0.001963	5.53E-07	0.000107751
	60-80	2.344827586	0.001963	5.08E-07	0.00011041
		2.344827586	0.001963	5.05E-07	0.000109686
	80-100	2.833333333	0.001963	7.55E-07	0.000135712
		2.833333333	0.001963	8.07E-07	0.000145
	100-120	3.090909091	0.001963	7.23E-07	0.000119185
		3.090909091	0.001963	6.23E-07	0.000102708
	120-140	3.090909091	0.001963	1.01E-06	0.000166695
		3.090909091	0.001963	1.11E-06	0.000182348
	140-160	3.090909091	0.001963	1.21E-06	0.000199374
		3.090909091	0.001963	1.32E-06	0.000217225
I3	0-20	2.428571429	0.001963	1.38E-07	2.90099E-05
		2.428571429	0.001963	1.47E-07	3.07575E-05
	20-40	3.777777778	0.001963	1.63E-07	2.20196E-05
		3.777777778	0.001963	1.67E-07	2.24689E-05
	40-60	2.344827586	0.001963	1.28E-07	2.7874E-05
		2.344827586	0.001963	1.15E-07	2.4978E-05
	60-80	2.833333333	0.001963	7.08E-07	0.000127324
		2.833333333	0.001963	7.48E-07	0.000134514
	80-100	3.578947368	0.001963	1.19E-06	0.000169341
		3.578947368	0.001963	1.25E-06	0.000178353
	100-120	2.956521739	0.001963	1.19E-06	0.000204992
		2.956521739	0.001963	1.25E-06	0.000215901
S1	0-20	2.344827586	0.001963	7.47E-07	0.000162176
		2.344827586	0.001963	7.12E-07	0.000154574
	20-40	2.615384615	0.001963	2.9E-07	5.64719E-05
		2.615384615	0.001963	2.77E-07	5.38755E-05
	40-60	2.615384615	0.001963	4.03E-07	7.85414E-05
		2.615384615	0.001963	3.97E-07	7.72432E-05
	60-80	3.578947368	0.001963	8.87E-07	0.000126176
		3.578947368	0.001963	8.77E-07	0.000124753
	80-100	3.578947368	0.001963	9.88E-07	0.000140643
		3.578947368	0.001963	9.73E-07	0.000138508
	100-120	3.090909091	0.001963	5.92E-07	9.74902E-05
		3.090909091	0.001963	5.05E-07	8.32099E-05
	120-140	3.090909091	0.001963	3.97E-07	6.53596E-05
		3.090909091	0.001963	3.68E-07	6.06911E-05
	140-160	2.615384615	0.001963	1.7E-07	3.31042E-05
		2.615384615	0.001963	1.45E-07	2.8236E-05
	160-180	2.615384615	0.001963	4.2E-07	8.17869E-05
		2.615384615	0.001963	4.12E-07	8.01642E-05
	180-200	2.344827586	0.001963	4.78E-07	0.000103894

		2.344827586	0.001963	4.82E-07	0.000104618
	200-220	2.428571429	0.001963	3.57E-07	7.47966E-05
		2.428571429	0.001963	3.88E-07	8.14374E-05
	220-240	2.518518519	0.001963	4.02E-07	8.12252E-05
		2.518518519	0.001963	4.15E-07	8.39215E-05
	240-260	2.344827586	0.001963	6.88E-07	0.000149506
		2.344827586	0.001963	6.82E-07	0.000148058
	260-280	3.090909091	0.001963	7.2E-07	0.000118636
		3.090909091	0.001963	7.03E-07	0.00011589
	280-300	2.615384615	0.001963	1.24E-06	0.000241466
		2.615384615	0.001963	1.22E-06	0.000236598
S3	0-20	3.578947368	0.001963	4.43E-07	6.30878E-05
		3.578947368	0.001963	4.9E-07	6.97286E-05
	20-40	2.344827586	0.001963	3.47E-07	7.52959E-05
		2.344827586	0.001963	3.7E-07	8.03639E-05
	40-60	2.956521739	0.001963	5.57E-07	9.58924E-05
		2.956521739	0.001963	5.8E-07	9.99119E-05
	60-80	2.615384615	0.001963	7.63E-07	0.000148644
		2.615384615	0.001963	7.92E-07	0.000154162
	80-100	2.518518519	0.001963	4.15E-07	8.39215E-05
		2.518518519	0.001963	4.08E-07	8.25733E-05
	100-120	3.090909091	0.001963	5.32E-07	8.76039E-05
		3.090909091	0.001963	6.18E-07	0.000101884
	140-160	2.344827586	0.001963	1.27E-07	2.7512E-05
		2.344827586	0.001963	1.27E-07	2.7512E-05
	160-180	2.344827586	0.001963	1.8E-07	3.90959E-05
		2.344827586	0.001963	1.82E-07	3.94579E-05
	180-200	2.615384615	0.001963	3.47E-07	6.75067E-05
		2.615384615	0.001963	3.88E-07	7.56204E-05
	220-240	2.833333333	0.001963	6.82E-07	0.000122531
		2.833333333	0.001963	6.75E-07	0.000121332
	240-260	2.344827586	0.001963	1.2E-06	0.00026064
		2.344827586	0.001963	1.25E-06	0.0002715
I5	0-20	2.518518519	0.001963	2.63E-07	5.32514E-05
		2.518518519	0.001963	2.68E-07	5.42625E-05
		2.518518519	0.001963	2.58E-07	5.22403E-05
	20-40	3.25	0.001963	5.5E-08	8.61885E-06
		3.25	0.001963	4.83E-08	7.57414E-06
		3.25	0.001963	5E-08	7.83532E-06
	40-60	3.578947368	0.001963	1.23E-07	1.75507E-05
		3.578947368	0.001963	1.17E-07	1.6602E-05
		3.578947368	0.001963	1.13E-07	1.61277E-05
	60-80	2.954545455	0.001963	2.25E-07	3.87848E-05
		2.954545455	0.001963	2.37E-07	4.07959E-05

		2.954545455	0.001963	2.22E-07	3.82102E-05
	80-100	2.833333333	0.001963	4.92E-07	8.83778E-05
		2.833333333	0.001963	5E-07	8.98757E-05
		2.833333333	0.001963	5.07E-07	9.10741E-05
	100-120	2.708333333	0.001963	4.92E-07	9.24568E-05
		2.708333333	0.001963	5.03E-07	9.46507E-05
		2.708333333	0.001963	5.03E-07	9.46507E-05
I4	20-40	3.090909091	0.001963	1.02E-07	1.67518E-05
		3.090909091	0.001963	8.5E-08	1.40056E-05
	40-60	3.095238095	0.001963	4.5E-08	7.40438E-06
		3.095238095	0.001963	4.5E-08	7.40438E-06
	60-80	2.615384615	0.001963	1.23E-07	2.40168E-05
		2.615384615	0.001963	9.83E-08	1.91485E-05
	80-100	2.321428571	0.001963	8.67E-08	1.90137E-05
		2.321428571	0.001963	9.67E-08	2.12076E-05
	100-120	2.615384615	0.001963	3.02E-07	5.87438E-05
		2.615384615	0.001963	4.47E-07	8.69797E-05
	120-140	2.954545455	0.001963	4.82E-07	8.30283E-05
		2.954545455	0.001963	5.23E-07	9.02107E-05
I6	0-20	3.25	0.001963	1.33E-08	2.08942E-06
		2.5	0.001963	1.67E-08	3.39531E-06
	20-40	2.954545455	0.001963	5.67E-07	9.76803E-05
		2.708333333	0.001963	3.33E-07	6.26826E-05
	40-60	2.708333333	0.001963	1.39E-09	2.61177E-07
		2.954545455	0.001963	8.33E-09	1.43648E-06
	60-80	3.421052632	0.001963	1.67E-07	2.48118E-05
		2.954545455	0.001963	1.83E-07	3.16025E-05
	90-140	2.708333333	0.001963	5E-07	9.40238E-05
		2.5	0.001963	4E-07	8.14873E-05
	140-190	2.954545455	0.001963	5.67E-07	9.76803E-05
		2.708333333	0.001963	5E-07	9.40238E-05
S4	0-20	2.833333333	0.001963	2.67E-08	4.79337E-06
		2.833333333	0.001963	2.5E-08	4.49379E-06
	20-40	2.954545455	0.001963	3.43E-07	5.91828E-05
		2.954545455	0.001963	3.65E-07	6.29176E-05
	40-60	2.615384615	0.001963	2.68E-07	5.22528E-05
		2.615384615	0.001963	2.3E-07	4.47881E-05
	60-80	3.421052632	0.001963	4.78E-07	7.121E-05
		3.421052632	0.001963	4.17E-07	6.20296E-05
	80-100	2.615384615	0.001963	1.12E-07	2.17449E-05
		2.615384615	0.001963	8.33E-08	1.62276E-05
	100-120	2.24137931	0.001963	3.57E-07	8.10433E-05
		2.24137931	0.001963	3.13E-07	7.11969E-05

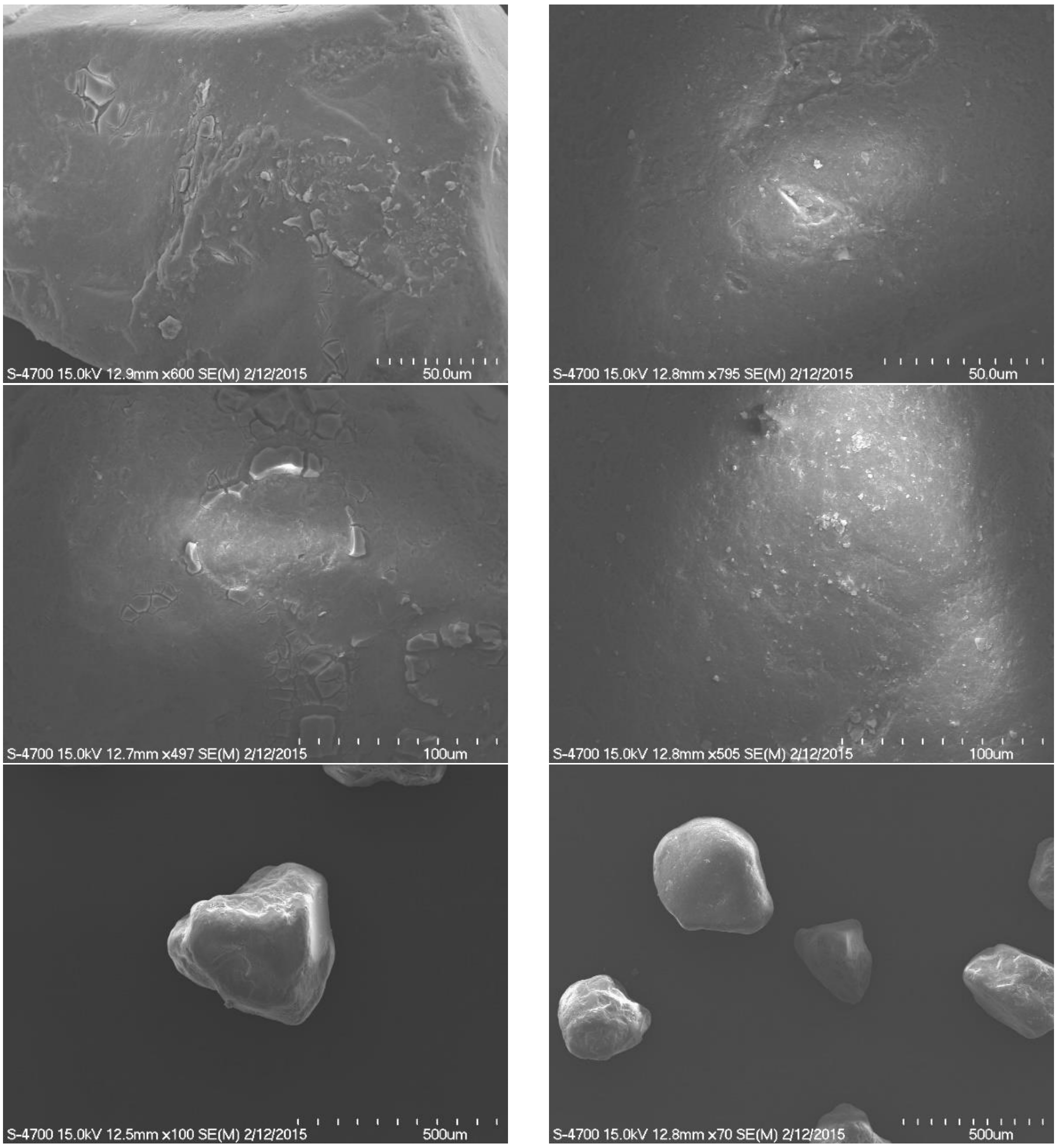
	120-140	2.833333333	0.001963	4.78E-07	8.59811E-05
		2.833333333	0.001963	4.17E-07	7.48964E-05
S6	0-20	2.344827586	0.001963	4.35E-07	9.44819E-05
		2.344827586	0.001963	5.07E-07	0.000110048
	20-40	2.954545455	0.001963	1.67E-09	2.87295E-07
		2.954545455	0.001963	1.67E-09	2.87295E-07
	40-60	3.238095238	0.001963	2.33E-07	3.66993E-05
		3.238095238	0.001963	1.78E-07	2.80487E-05
	60-80	2.826086957	0.001963	1.67E-09	3.00354E-07
		2.826086957	0.001963	1.67E-09	3.00354E-07
	80-100	3.090909091	0.001963	2.45E-07	4.03692E-05
		3.090909091	0.001963	2.2E-07	3.62499E-05
	100-120	3.421052632	0.001963	9.17E-08	1.36465E-05
		3.421052632	0.001963	8.33E-08	1.24059E-05
	120-140	3.578947368	0.001963	3.4E-07	4.83831E-05
		3.578947368	0.001963	2.9E-07	4.12679E-05
	140-160	2.708333333	0.001963	4.65E-07	8.74422E-05
		2.708333333	0.001963	4.58E-07	8.61885E-05
		2.5	0.001963	4.22E-07	8.59012E-05
S5	0-20	2.833333333	0.001963	3.07E-07	5.51238E-05
		2.833333333	0.001963	2.62E-07	4.7035E-05
	20-40	2.954545455	0.001963	9.33E-08	1.60885E-05
		2.954545455	0.001963	8.83E-08	1.52266E-05
	40-60	2.956521739	0.001963	2.55E-07	4.39268E-05
		2.956521739	0.001963	2.97E-07	5.11043E-05
	60-80	2.5	0.001963	5.83E-08	1.18836E-05
		2.5	0.001963	5.17E-08	1.05254E-05
	80-100	2.344827586	0.001963	4.93E-07	0.000107152
		2.344827586	0.001963	4E-07	8.68799E-05
	100-120	2.954545455	0.001963	1.77E-07	3.04533E-05
		2.954545455	0.001963	1.7E-07	2.93041E-05
	140-160	2.833333333	0.001963	2.23E-07	4.01445E-05
		2.833333333	0.001963	2.33E-07	4.1942E-05
	160-180	2.5	0.001963	4.45E-07	9.06547E-05
		2.5	0.001963	4.22E-07	8.59012E-05

Table C9: Hydraulic conductivity results from deconstruction of laboratory-scale filter columns

Column ID	Sample Depth	Average T1,2 (s)	A1*Average T (m^2 s)	K_{t1}	K_{t2}	Kav
I7	0-50	8.8	0.01727876	1.05E-04	8.56E-05	9.51E-05
		7.235	0.014205889	1.27E-04	1.04E-04	1.16E-04

	50-100	3.075	0.006037748	2.99E-04	2.45E-04	2.72E-04
		6.525	0.012811808	1.41E-04	1.15E-04	1.28E-04
	100-150	6.62	0.01299834	1.39E-04	1.14E-04	1.26E-04
		3.405	0.006685702	2.70E-04	2.21E-04	2.46E-04
	150-200	2.795	0.00548797	3.29E-04	2.70E-04	3.00E-04
		2.38	0.004673119	3.87E-04	3.17E-04	3.52E-04
I9	0-50	8.745	0.017170767	1.05E-04	8.62E-05	9.57E-05
		10.48	0.020577432	8.79E-05	7.19E-05	7.99E-05
	50-100	6.87	0.013489213	1.34E-04	1.10E-04	1.22E-04
		7.355	0.014441509	1.25E-04	1.02E-04	1.14E-04
	100-150	4.565	0.008963357	2.02E-04	1.65E-04	1.83E-04
		4.68	0.009189159	1.97E-04	1.61E-04	1.79E-04
	150-200	3.7	0.007264933	2.49E-04	2.04E-04	2.26E-04
		3.33	0.00653844	2.77E-04	2.26E-04	2.51E-04
S7	0-50	7.415	0.014559318	1.24E-04	1.02E-04	1.13E-04
		6.155	0.012085314	1.50E-04	1.22E-04	1.36E-04
	50-100	6.465	0.012693998	1.42E-04	1.17E-04	1.29E-04
		5.995	0.011771155	1.54E-04	1.26E-04	1.40E-04
	100-150	5.125	0.010062914	1.80E-04	1.47E-04	1.63E-04
		5.135	0.010082549	1.79E-04	1.47E-04	1.63E-04
	150-200	2.555	0.005016731	3.60E-04	2.95E-04	3.28E-04
		2.46	0.004830199	3.74E-04	3.06E-04	3.40E-04
S8	0-50	2.95	0.005792311	3.12E-04	2.55E-04	2.84E-04
		2.6	0.005105088	3.54E-04	2.90E-04	3.22E-04
	50-100	3.98	0.007814712	2.31E-04	1.89E-04	2.10E-04
		3.755	0.007372925	2.45E-04	2.01E-04	2.23E-04
	100-150	2.75	0.005399612	3.35E-04	2.74E-04	3.04E-04
		2.6	0.005105088	3.54E-04	2.90E-04	3.22E-04
	150-200	2.65	0.005203263	3.47E-04	2.84E-04	3.16E-04
		2.58	0.005065818	3.57E-04	2.92E-04	3.24E-04
S9	0-50	7.51	0.014745851	1.23E-04	1.00E-04	1.11E-04
		7.62	0.014961835	1.21E-04	9.89E-05	1.10E-04
	50-100	5.67	0.011133019	1.62E-04	1.33E-04	1.48E-04
		5.575	0.010946487	1.65E-04	1.35E-04	1.50E-04
	100-150	3.57	0.007009679	2.58E-04	2.11E-04	2.35E-04
		3.235	0.006351908	2.85E-04	2.33E-04	2.59E-04
	150-200	2.595	0.005095271	3.55E-04	2.90E-04	3.23E-04
		2.525	0.004957826	3.65E-04	2.98E-04	3.32E-04

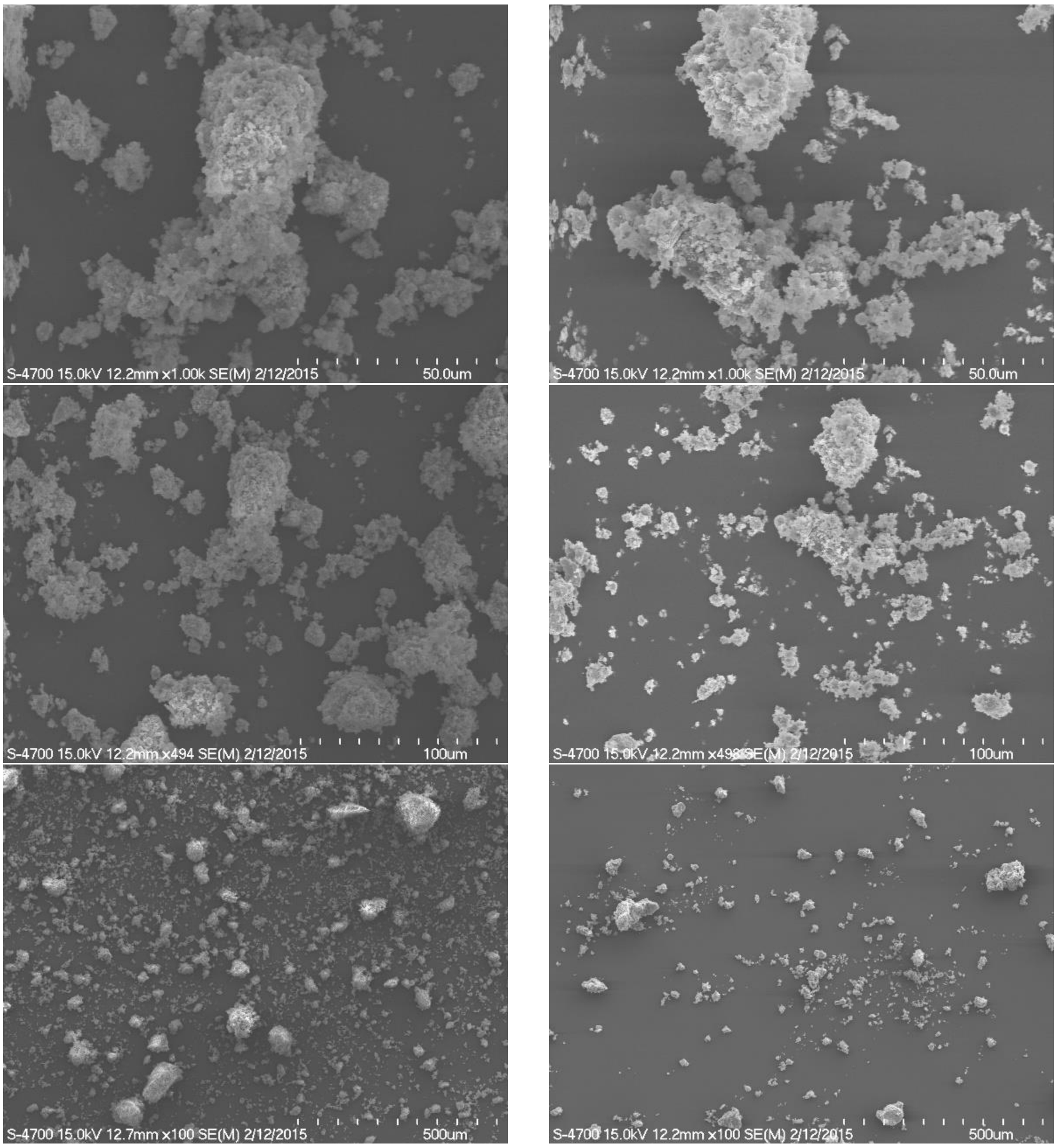
Table C10: SEM Results from deconstruction of laboratory-scale control filter columns



Sand from top of control column

Raw sand

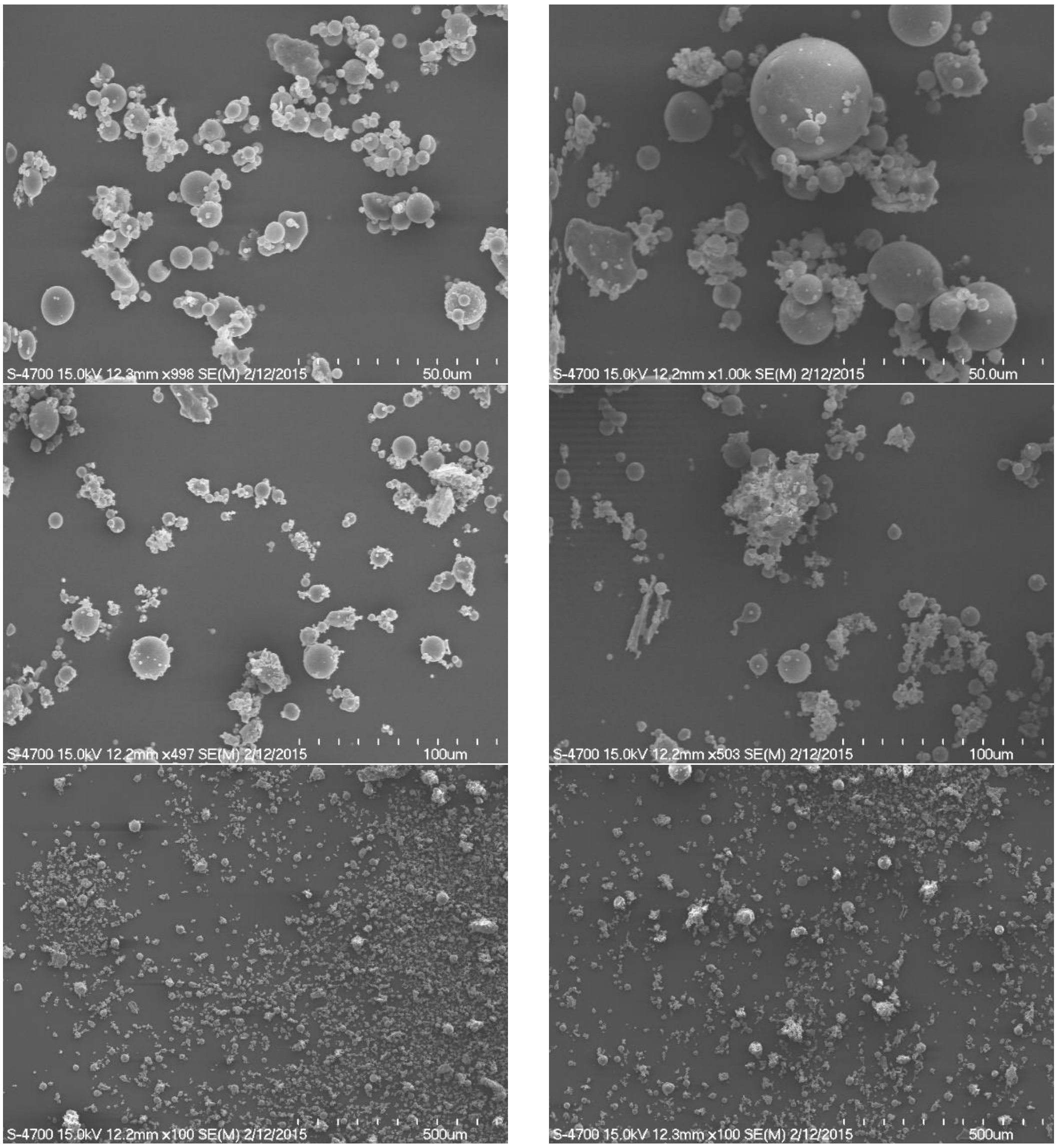
Table C11: SEM Results from deconstruction of laboratory-scale “Config 1” filter columns



Bayer residue from top of config 1 column

Raw Bayer residue

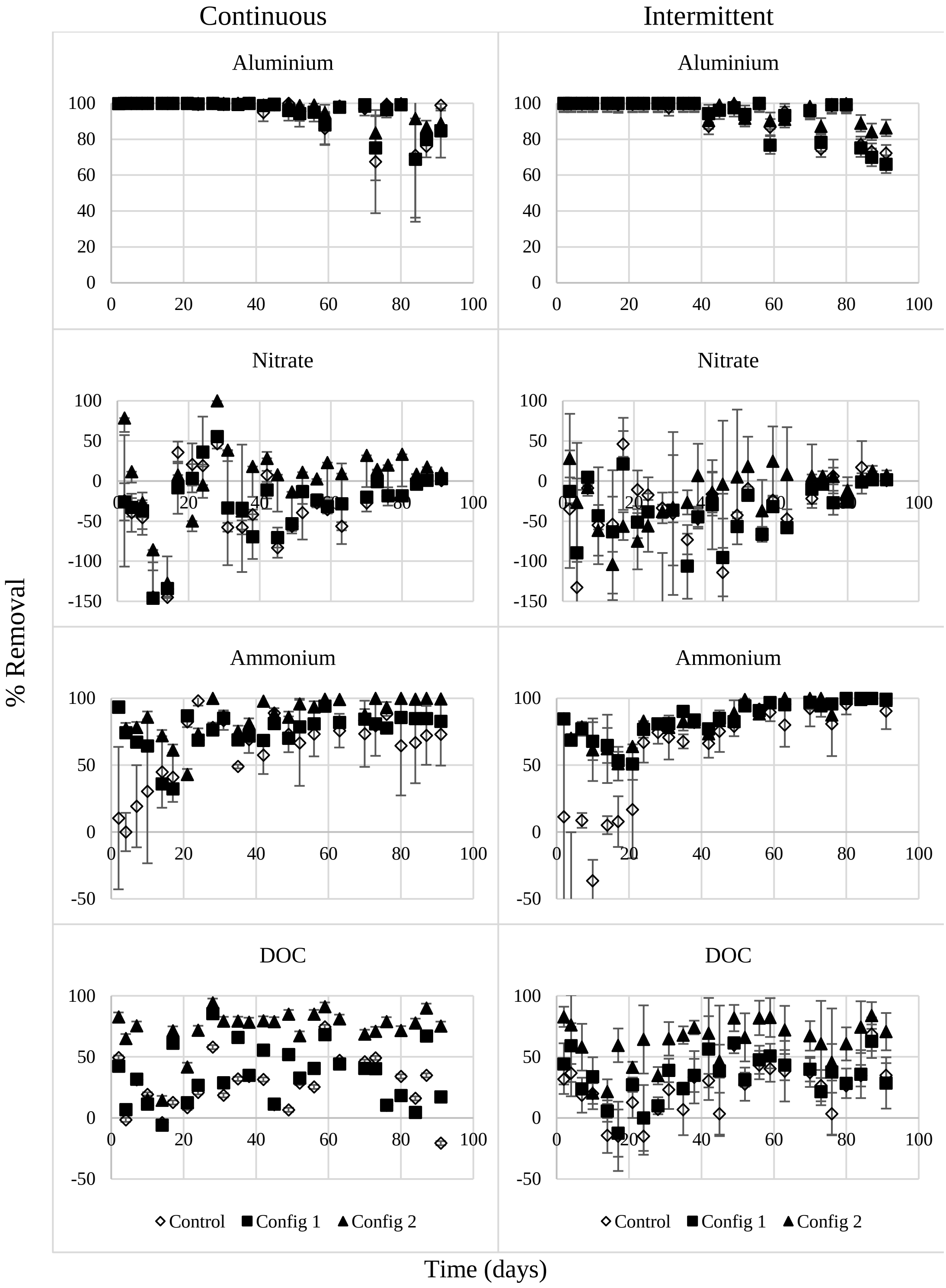
Table C12: SEM Results from deconstruction of laboratory-scale “Config 2” filter columns



Fly ash from top of config 2 column

Raw Fly ash

Figure C1: Time-series plots for contaminant removal in filters



Appendix D

Notation used in Appendix D

Days: Days of operation of filters
Ref: Column Reference
Port: Port Reference
Inf: Influent data
SB: Slow loaded Design A columns (in triplicate labelled 1, 2, and 3)
SG: Slow loaded Design B columns (in triplicate labelled 1, 2, and 3)
IB: Intermittently loaded Design A columns (in triplicate labelled 1, 2, and 3)
IG: Intermittently loaded Design B columns (in triplicate labelled 1, 2, and 3)
A: Port samples taken from the middle of the filter (i.e. at the base of the top layer)
B: Port samples taken from the middle of the filter (i.e. at the base of the second layer)

Table D1: Results from pilot-scale filter columns

Days	**Ref**	**Port**	**Flow Rate ml min^{-1}**	**PO4-P mg L^{-1}**	**NH4-N mg L^{-1}**	**NO3-N mg L^{-1}**	**NO2-N mg L^{-1}**	**DOC mg L^{-1}**	**DIC mg L^{-1}**	**UVA$_{254}$**	**Alkalinity mg L^{-1}**	**SUVA**
2	Inf	-	-	0.00	0.22	0.04	0.00	10.10	8.40	0.22	15.67	2.13
2	SB3	-	3.5	0.07	0.32	0.00	0.01	35.20	10.40	0.25	14.30	0.71
2	SB2	-	3.5	0.02	0.08	0.00	0.00	14.60	12.40	0.05	32.59	0.35
2	SB1	-	24	0.01	0.04	0.01	0.00	9.20	10.20	0.04	22.57	0.44
2	SG3	-	18	0.02	0.02	0.01	0.00	6.40	10.70	0.02	25.48	0.33
2	SG2	-	8	0.00	0.01	0.00	0.00	4.20	10.30	0.02	17.46	0.39
2	SG1	-	4	0.02	0.02	0.00	0.00	1.90	24.00	0.02	49.52	0.81
2	IB3	-	1.2	0.00	0.02	0.03	0.00	5.70	12.50	0.05	33.93	0.82
2	IB2	-	2.3	0.00	0.06	0.10	0.00	4.90	6.60	0.04	14.48	0.76
2	IB1	-	1.2	0.00	0.03	0.03	0.00	4.50	4.70	-	24.70	
2	IG3	-	6.4	0.00	0.03	0.04	0.00	3.30	14.40	0.01	26.60	0.42
2	IG2	-	9.6	0.00	0.01	0.02	0.00	3.00	11.80	0.03	21.30	0.85
2	IG1	-	10.9	0.00	0.01	0.04	0.00	3.50	11.20	0.01	19.53	0.36
7	Inf	-	-	0.04	0.08	0.01	0.00	7.70	8.60	0.44	46.73	5.73
7	SB3	-	8	0.01	0.01	0.02	0.00	3.10	6.90	0.03	38.79	0.85
7	SB2	-	4	0.00	0.00	0.01	0.00	2.90	8.90	0.30	48.40	10.24
7	SB1	-	9	0.01	0.02	0.01	0.00	3.30	10.20	0.11	51.76	3.48
7	SG3	-	28	0.07	0.00	0.00	0.00	1.30	9.60	0.22	57.35	16.64
7	SG2	-	5	0.03	0.00	0.00	0.00	1.20	10.90	0.25	68.31	21.02
7	SG1	-	29	0.21	0.00	0.01	0.00	3.30	13.30	0.19	49.20	5.63
7	IB3	-	1.2	0.02	0.00	0.02	0.00	1.40	6.20	0.02	36.26	1.69
7	IB2	-	2.8	0.00	0.02	0.02	0.00	2.00	5.02	0.02	36.81	1.19
7	IB1	-	0.8	0.01	0.02	0.02	0.00	2.35	7.50	0.02	51.68	0.77
7	IG3	-	3.7	0.01	0.00	0.00	0.00	1.20	12.50	0.00	56.19	0.30
7	IG2	-	14.2	0.03	0.00	0.01	0.00	0.90	10.90	0.13	57.23	14.08
7	IG1	-	16.9	0.03	0.00	0.00	0.00	1.00	12.30	0.17	46.50	17.10
15	Inf	-	-	0.00	0.00	0.00	0.00	7.83	8.19	0.20	18.50	2.61
15	SB3	-	16	0.06	0.01	0.03	0.00	5.20	8.62	0.09	26.70	1.81
15	SB2	-	31	0.03	0.00	0.02	0.00	5.12	8.89	0.10	27.70	1.94
15	SB1	-	29	0.04	0.02	0.02	0.00	5.77	9.48	0.13	28.60	2.32
15	SG3	-	10	0.06	0.01	0.01	0.00	1.67	11.13	0.01	29.70	0.79
15	SG2	-	29	0.08	0.00	0.01	0.00	1.49	9.31	0.01	28.60	0.42
15	SG1	-	10	0.08	0.00	0.45	0.00	1.36	11.43	0.00	31.20	0.28
15	IB3	-	1.33	0.03	0.00	0.05	0.00	1.31	6.60	0.02	18.50	1.24
15	IB2	-	3.33	0.03	0.02	0.03	0.00	2.12	4.87	0.03	13.20	1.20

15	IB1	-	1.17	0.05	0.00	0.04	0.00	2.31	6.92	0.01	19.50	0.64
15	IG3	-	2.67	0.03	0.05	0.01	0.00	1.25	14.30	0.00	34.00	0.30
15	IG2	-	34.17	0.04	0.00	0.01	0.00	1.23	10.13	0.00	27.10	0.06
15	IG1	-	42.5	0.06	0.00	0.00	0.00	1.49	9.30	0.01	25.50	0.40
15	SB3	A						13.20	9.40			0.00
15	SB2	A						9.80	7.90			0.00
15	SB2	B						14.80	27.80			0.00
15	SB1	A						14.40	10.20			0.00
15	SB1	B						17.90	47.60			0.00
15	SG3	A						16.00	11.20			0.00
15	SG3	B						1.89	3.32			0.00
15	SG2	A						10.50	8.40			0.00
15	SG2	B						7.40	9.20			0.00
15	SG1	B						4.59	9.80			0.00
15	IB3	A						8.46	9.33			0.00
15	IB3	B						21.40	66.20			0.00
15	IB2	A						19.20	9.60			0.00
15	IB2	B						23.00	33.20			0.00
15	IB1	A						14.40	9.70			0.00
15	IB1	B						12.20	50.40			0.00
15	IG3	A						13.20	10.50			0.00
15	IG3	B						5.48	16.03			0.00
15	IG2	A						17.66	8.37			0.00
15	IG2	B						7.56	8.87			0.00
15	IG1	A						3.99	1.40			0.00
15	IG1	B						3.63	6.16			0.00
21	Inf	-		0.15	0.03	0.00	0.00	8.30	10.00	0.20	1.80	2.37
21	SB3	-	22	0.05	0.04	0.00	0.00	4.70	10.00	0.08	15.10	1.75
21	SB2	-	38	0.09	0.07	0.00	0.00	8.00	13.50	0.13	7.20	1.68
21	SB1	-	20	0.04	0.03	0.00	0.00	6.40	10.80	0.12	2.90	1.87
21	SG3	-	44	0.05	0.03	0.00	0.00	2.80	10.30	0.01	1.10	0.19
21	SG2	-	48	0.04	0.00	0.00	0.00	0.90	9.60	0.00	1.30	0.24
21	SG1	-	44	0.01	0.00	0.00	0.00	0.70	10.10	0.01	0.00	1.20
21	IB3	-	2.5	0.06	0.09	0.00	0.00	3.30	5.50	0.02	0.00	0.62
21	IB2	-	4	0.03	0.07	0.00	0.00	3.40	5.40	0.04	0.00	1.12
21	IB1	-	0.4	0.03	0.03	0.00	0.00	3.90	6.80	0.02	0.00	0.43
21	IG3	-	4	0.04	0.01	0.00	0.00	1.10	15.70	0.00	11.00	0.03
21	IG2	-	38	0.06	0.03	0.00	0.00	1.90	10.00	0.00	0.70	0.20
21	IG1	-	40	0.06	0.00	0.00	0.00	2.00	8.60	0.02	0.00	0.99
21	SB3	A						8.10	13.80	0.20		2.53
21	SB2	A						8.08	9.58	0.21		2.55
21	SB2	B						12.18	28.38	0.35		2.87
21	SB1	A						8.10	8.70	0.47		5.85
21	SB1	B						8.09	37.30	0.21		2.58
21	SG3	A						9.60	9.20	0.04		0.38
21	SG3	B						4.23	9.20	0.20		4.64
21	SG2	A						8.40	9.01	0.03		0.30
21	SG2	B						3.70	10.40	0.20		5.43
21	SG1	B						2.50	10.05	0.02		0.76
21	IB3	A						8.18	10.04	0.49		6.00
21	IB3	B						7.47	28.06	0.24		3.15
21	IB2	A						12.60	9.60	0.28		2.26
21	IB2	B						10.80	22.75	0.22		2.01
21	IB1	A						8.40	10.40	0.42		4.99

21	IB1	B						8.89	29.10	0.18		2.06
21	IG3	A						8.90	10.20	0.02		0.24
21	IG3	B						2.00	12.33	0.21		10.26
21	IG2	A						9.33	8.89	0.07		0.72
21	IG2	B						5.75	9.47	0.21		3.62
21	IG1	A						9.40	5.60	0.06		0.59
21	IG1	B						4.70	8.40	0.23		4.85
29	Inf	-		0.03	0.13	0.01	0.00	11.90	8.40	0.21	20.80	1.78
29	SB3	-	22	0.04	0.04	0.01	0.00	7.79	12.03	0.12	31.20	1.57
29	SB2	-	30	0.02	0.00	0.00	0.01	6.50	8.72	0.11	25.20	1.76
29	SB1	-	10	0.02	0.00	0.02	0.00	7.01	10.08	0.11	29.20	1.52
29	SG3	-	38	0.02	0.00	0.00	0.00	5.55	9.80	0.03	25.50	0.55
29	SG2	-	32	0.02	0.00	0.00	0.00	3.44	9.80	0.01	24.90	0.40
29	SG1	-	36	0.02	0.00	0.00	0.00	4.46	10.20	0.03	25.70	0.66
29	IB3	-	16	0.01	0.00	0.00	0.00	5.06	5.90	0.05	14.00	0.93
29	IB2	-	12	0.01	0.00	0.16	0.01	5.17	7.09	0.07	21.10	1.38
29	IB1	-	4	0.02	0.00	0.00	0.01	4.81	8.11	0.02	19.60	0.48
29	IG3	-	30	0.01	0.00	0.00	0.00	2.58	9.57	0.00	24.10	0.10
29	IG2	-	22	0.02	0.00	0.01	0.00	3.05	10.60	0.02	27.10	0.51
29	IG1	-	54	0.02	0.00	0.00	0.00	4.01	10.05	0.06	25.40	1.42
29	SB3	A						8.07	11.29	0.21		3.01
29	SB2	A						7.60	8.54	0.20		3.64
29	SB2	B						6.91	18.54	0.20		2.99
29	SB1	A						5.32	5.16	0.20		3.43
29	SB1	B						6.75	42.15	0.39		2.66
29	SG3	A						8.40	9.20	0.19		2.45
29	SG3	B						4.04	7.24	0.10		0.78
29	SG2	A						7.59	8.83	0.20		2.64
29	SG2	B						4.87	9.67	0.08		1.77
29	SG1	B						4.25	9.62	0.07		1.72
29	IB3	A						7.90	9.32	0.24		3.07
29	IB3	B						7.78	25.11	0.28		3.56
29	IB2	A						6.56	6.41	0.21		3.15
29	IB2	B						7.31	20.04	0.18		2.49
29	IB1	B						7.79	9.34	0.18		2.30
29	IG3	A						8.70	9.36	0.21		2.36
29	IG3	B						2.07	10.04	0.03		1.51
29	IG2	A						8.06	9.05	0.20		2.48
29	IG2	B						4.97	8.79	0.09		1.74
29	IG1	A						8.05	8.14	0.23		2.83
29	IG1	B						3.31	4.73	0.11		3.30
34	Inf	-		0.00	0.05	0.01	0.00	8.70	8.45	0.19	19.70	2.21
34	SB3	-	5	0.01	0.06	0.01	0.00	6.90	11.40	0.10	27.80	1.44
34	SB2	-	36	0.00	0.00	0.04	0.00	8.30	8.70	0.13	29.60	1.56
34	SB1	-	10	0.00	0.01	0.06	0.00	6.90	10.60	0.11	30.60	1.55
34	SG3	-	28	0.01	0.00	0.01	0.00	4.90	10.20	0.04	25.60	0.91
34	SG2	-	30	0.01	0.01	0.01	0.00	5.20	10.10	0.03	25.50	0.54
34	SG1	-	29	0.01	0.01	0.01	0.00	3.40	12.90	0.02	31.20	0.53
34	IB3	-	14	0.01	0.08	0.04	0.00	6.10	7.60	0.07	22.70	1.07
34	IB2	-	37	0.01	0.00	0.02	0.00	7.10	8.20	0.11	23.40	1.61
34	IB1	-	7	0.00	0.17	0.06	0.00	5.20	8.30	0.04	17.60	0.69
34	IG3	-	36	0.00	0.00	0.01	0.00	3.30	10.50	0.00	25.10	0.10
34	IG2	-	60	0.00	0.02	0.01	0.00	6.60	10.30	0.08	25.30	1.14
34	IG1	-	92	0.00	0.31	0.01	0.00	7.10	9.60	0.11	24.40	1.55

34	SB3	A						7.90	13.50	0.19		2.38
34	SB2	A						8.10	8.50	0.20		2.44
34	SB2	B						9.00	12.20	0.16		1.73
34	SB1	A						9.00	9.60	0.19		2.16
34	SB1	B						6.60	18.70	0.34		5.19
34	SG3	A						9.90	10.50	0.19		1.94
34	SG3	B						6.20	10.20	0.11		1.81
34	SG2	A						6.40	7.20	0.19		3.03
34	SG2	B						6.40	11.00	0.11		1.66
34	SG1	B						2.40	6.60	0.06		2.37
34	IB3	A						8.01	9.10	0.22		2.72
34	IB3	B						6.10	26.40	0.36		5.91
34	IB2	A						5.01	3.14	0.20		3.93
34	IB2	B						6.16	16.90	0.17		2.68
34	IB1	A						6.90	9.60	0.18		2.62
34	IG3	A						7.80	9.20	0.20		2.52
34	IG3	B						2.60	10.10	0.04		1.46
34	IG2	A						7.90	8.10	0.20		2.50
34	IG2	B						6.60	9.60	0.14		2.14
34	IG1	A						9.18	13.50	0.21		2.28
34	IG1	B						4.60	10.20	0.15		3.33
42	Inf	-		0.02	0.04	0.05	0.00	9.30	7.50	0.21	20.15	2.24
42	SB3	-	24	0.02	0.06	0.03	0.00	6.20	12.02	0.13	31.22	2.12
42	SB2	-	40	0.02	0.00	0.05	0.00	6.10	7.10	0.14	21.03	2.26
42	SB1	-	26	0.02	0.00	0.04	0.00	4.20	7.10	0.10	20.46	2.46
42	SG3	-	25	0.02	0.01	0.12	0.00	2.90	11.30	0.03	29.70	0.99
42	SG2	-	28	0.02	0.00	0.03	0.00	1.60	10.55	0.02	26.70	1.26
42	SG1	-	30	0.02	0.00	0.04	0.00	1.05	10.20	0.02	26.40	2.03
42	IB3	-	2	0.04	0.04	0.38	0.00	4.90	6.70	0.11	30.80	2.14
42	IB2	-	0.5	0.02	0.07	0.06	0.00	5.90	15.70	0.12	34.60	1.95
42	IB1	-	2	0.02	0.50	0.23	0.00	6.90	10.50	0.12	39.70	1.70
42	IG3	-	10	0.03	0.06	0.06	0.00	3.20	11.20	0.02	27.20	0.49
42	IG2	-	19	0.02	0.00	0.04	0.00	2.50	11.40	0.02	29.70	0.98
42	IG1	-	15	0.02	0.00	0.04	0.00	1.60	7.50	0.03	31.10	2.00
42	SB3	A						5.60	10.40	0.19		3.43
42	SB2	A						7.20	7.70	0.22		3.05
42	SB2	B						4.20	7.60	0.16		3.91
42	SB1	A						7.20	9.90	0.20		2.85
42	SB1	B						7.10	11.70	0.26		3.69
42	SG3	A						6.00	11.50	0.26		4.36
42	SG3	B						1.50	12.30	0.20		13.49
42	SG2	A						6.10	8.20	0.07		1.10
42	SG2	B						2.10	12.20	0.19		9.20
42	SG1	B						0.56	6.50	0.07		11.63
42	IB3	A						5.30	8.40	0.03		0.54
42	IB3	B						9.20	6.90	0.20		2.16
42	IB2	A										#DIV/0!
42	IB2	B						7.20	20.00	0.35		4.91
42	IB1	A						3.80	5.20	0.19		4.92
42	IG3	A										#DIV/0!
42	IG3	B										#DIV/0!
42	IG2	A										#DIV/0!
42	IG2	B						2.70	8.35	0.09		3.40
42	IG1	A										#DIV/0!

42	IG1	B										#DIV/0!
48	Inf	-		0.02	0.10	0.05	0.00	8.33	8.46	0.25	21.60	3.00
48	SB3	-	20	0.03	0.02	0.08	0.00	8.50	13.23	0.17	26.60	1.97
48	SB2	-	36	0.03	0.02	0.08	0.00	7.14	9.42	0.16	24.00	2.20
48	SB1	-	24	0.02	0.03	0.07	0.00	6.28	8.51	0.12	29.80	1.86
48	SG3	-	24	0.03	0.02	0.05	0.00	3.82	11.15	0.05	27.10	1.19
48	SG2	-	32	0.03	0.03	0.05	0.00	3.25	10.26	0.05	30.20	1.55
48	SG1	-	26	0.03	0.02	0.05	0.00	2.12	11.68	0.03	50.60	1.59
48	IB3	-	1.5	0.12	0.12	0.36	0.00	7.96	8.80	0.17	43.60	2.13
48	IB2	-	3.5	0.05	0.07	0.20	0.00	7.71	15.19	0.16	29.70	2.02
48	IB1	-	1	0.11	0.17	0.23	0.00	4.48	6.98	0.08	41.30	1.81
48	IG3	-	2.5	0.03	0.07	0.06	0.00	5.39	16.09	0.01	34.50	0.24
48	IG2	-	22	0.02	0.10	0.05	0.00	3.21	13.48	0.03	40.10	0.82
48	IG1	-	16	0.03	0.29	0.14	0.00	2.52	15.31	0.03	21.60	1.34
56	Inf	-		0.02	0.01	0.04	0.00	8.86	7.90	0.22	21.60	2.49
56	SB3	-	20	0.01	0.10	0.03	0.00	6.58	13.10	0.17	36.70	2.60
56	SB2	-	26	0.02	0.00	0.09	0.00	6.37	9.60	0.16	26.70	2.58
56	SB1	-	24	0.02	0.02	0.06	0.00	6.99	8.80	0.13	24.90	1.90
56	SG3	-	20	0.03	0.01	0.03	0.00	3.73	11.60	0.05	30.60	1.26
56	SG2	-	24	0.03	0.00	0.04	0.00	3.60	11.20	0.06	29.20	1.74
56	SG1	-	20	0.02	0.00	0.03	0.00	2.20	11.30	0.05	30.10	2.16
56	IB3	-	0.5	0.10	0.07	0.10	0.00	8.40	22.90	0.21	74.60	2.55
56	IB2	-	4	0.06	0.22	0.01	0.00	7.30	13.90	0.15	49.30	2.05
56	IB1	-	0.5	0.10	0.22	0.02	0.00	8.08	19.60	0.16	48.60	1.93
56	IG3	-	3	0.06	0.05	0.05	0.00	3.90	17.40	0.03	47.80	0.65
56	IG2	-	14	0.03	0.01	0.04	0.00	2.50	13.40	0.03	35.20	1.32
56	IG1	-	4	0.02	0.01	0.04	0.00	2.00	15.30	0.03	41.10	1.52
63	Inf	-		0.04	0.01	0.06	0.00	7.67	8.18	0.22	25.20	2.82
63	SB3	-	24	0.09	0.10	0.06	0.00	3.18	16.80	0.10	50.40	3.07
63	SB2	-	28	0.07	0.01	0.09	0.00	2.02	12.90	0.07	30.20	3.64
63	SB1	-	32	0.04	0.00	0.08	0.00	4.28	10.90	0.15	26.90	3.41
63	SG3	-	28	0.04	0.01	0.06	0.00	4.03	12.04	0.05	31.20	1.18
63	SG2	-	32	0.04	0.01	0.06	0.00	6.08	9.30	0.09	29.30	1.45
63	SG1	-	36	0.04	0.00	0.05	0.00	6.84	10.10	0.02	34.20	0.36
63	IG3	-	14	0.04	0.00	0.06	0.00	6.20	17.20	0.01	45.07	0.12
63	IG2	-	24	0.03	0.00	0.06	0.00	4.02	4.30	0.04	35.45	0.97
63	IG1	-	14	0.03	0.00	0.06	0.00	3.67	5.02	0.03	39.45	0.86
63	SB3	A						6.87	10.67	0.20		2.85
63	SB2	A						9.72	8.30	0.22		2.30
63	SB2	B						4.10	14.90	0.18		4.47
63	SB1	A						5.10	13.40	0.22		4.27
63	SB1	B						2.44	4.90	0.15		6.20
63	SG3	A						3.60	12.80	0.22		6.13
63	SG3	B						6.03	5.10	0.11		1.86
63	SG2	A						6.96	8.60	0.22		3.13
63	SG2	B						4.60	5.90	0.16		3.37
63	SG1	B						2.99	3.40	0.03		1.12
63	IG2	B						5.23	10.50	0.11		2.16
70	Inf	-		0.05	0.01	0.06	0.00	9.33	8.30	0.21	22.20	2.28
70	SB3	-	32	0.18	0.15	0.10	0.00	10.50	17.40	0.16	56.50	1.50
70	SB2	-	28	0.07	0.04	0.12	0.00	8.90	10.80	0.17	31.00	1.94
70	SB1	-	30	0.07	0.02	0.11	0.00	7.80	10.10	0.15	28.00	1.92
70	SG3	-	22	0.06	0.04	0.07	0.00	5.50	11.80	0.07	31.00	1.20
70	SG2	-	28	0.06	0.02	0.09	0.00	5.20	11.70	0.09	30.80	1.67

70	SG1	-	30	0.06	0.02	0.07	0.00	4.40	12.80	0.05	33.90	1.10
70	IG3	-	22	0.04	0.02	0.07	0.00	1.50	17.80	0.00	47.50	0.02
70	IG2	-	32	0.04	0.01	0.08	0.00	3.70	13.70	0.04	36.00	1.15
70	IG1	-	26	0.15	0.01	0.08	0.00	2.10	15.80	0.03	41.20	1.58
78	Inf	-		0.08	0.02	0.10	0.00	8.80	8.20	0.21	20.99	2.36
78	SB3	-	32	0.14	0.10	0.10	0.00	8.10	13.90	0.16	38.78	1.99
78	SB2	-	30	0.12	0.02	0.14	0.00	6.80	10.20	0.16	28.40	2.31
78	SB1	-	28	0.10	0.01	0.15	0.00	5.40	9.60	0.14	26.50	2.53
78	SG3	-	28	0.34	0.07	0.11	0.00	5.70	11.60	0.08	46.40	1.32
78	SG2	-	32	0.14	0.07	0.13	0.00	5.20	12.10	0.08	32.30	1.62
78	SG1	-	34	0.14	0.03	0.10	0.00	2.30	15.70	0.03	40.80	1.12
78	IG3	-	32	0.08	0.01	0.11	0.00	4.10	13.20	0.07	34.70	1.64
78	IG2	-	32	0.13	0.03	0.43	0.00	2.63	0.60	0.04	42.70	1.46
78	IG1	-	24	0.10	0.02	0.16	0.00	2.40	10.20	0.04	37.80	1.77
85	Inf	-		0.08	0.01	0.14	0.00	8.80	8.07	0.22	24.60	2.45
85	SB3	-	22	0.44	0.09	0.15	0.00	10.80	18.00	0.23	62.10	2.09
85	SB2	-	28	0.15	0.19	0.25	0.00	7.50	10.70	0.17	31.10	2.33
85	SB1	-	28	0.15	0.05	0.18	0.00	6.80	9.70	0.15	28.10	2.25
85	SG3	-	28	0.14	0.05	0.14	0.00	5.33	11.60	0.09	31.70	1.61
85	SG2	-	30	0.10	0.02	0.15	0.00	3.50	12.50	0.06	33.50	1.77
85	SG1	-	30	0.10	0.04	0.13	0.00	2.40	12.60	0.04	34.30	1.61
85	IG3	-	32	0.10	0.05	0.15	0.00	3.80	18.70	0.02	51.00	0.50
85	IG2	-	32	0.09	0.03	0.16	0.00	5.60	13.20	0.09	34.70	1.55
85	IG1	-	36	0.10	0.01	0.14	0.00	3.60	12.70	0.04	33.20	1.11
85	SB3	A						6.80	13.10	0.17		2.56
85	SB2	A						7.90	8.60	0.24		3.00
85	SB2	B						7.20	12.30	0.18		2.49
85	SB1	A						8.10	10.50	0.12		1.47
85	SB1	B						6.00	11.40	0.15		2.48
85	SG3	A						5.70	7.50	0.22		3.82
85	SG3	B						6.10	12.30	0.16		2.62
85	SG2	A						7.20	10.80	0.21		2.96
85	SG2	B						5.70	11.70	0.15		2.57
85	SG1	B						2.90	11.40	0.06		2.07
98	Inf	-		0.00	0.02	0.02	0.00	11.50	10.84	0.29	26.80	2.52
98	SB3	-	24	0.00	0.09	0.09	0.00	8.46	7.29	0.18	45.10	2.07
98	SB2	-	30	0.00	0.00	0.09	0.00	7.65	6.46	0.18	31.60	2.33
98	SB1	-	30	0.00	0.00	0.01	0.00	6.49	8.84	0.17	28.60	2.63
98	SG3	-	24	0.00	0.00	0.03	0.00	4.90	8.40	0.09	34.50	1.83
98	SG2	-	28	0.00	0.00	0.01	0.00	5.10	7.90	0.12	33.10	2.40
98	SG1	-	28	0.00	0.00	0.02	0.00	4.49	9.15	0.09	32.20	2.02
98	IG3	-	32	0.00	0.00	0.03	0.00	5.37	5.45	0.11	34.50	2.07
98	IG2	-	32	0.00	0.02	0.01	0.00	3.15	8.54	0.03	41.50	1.03
98	IG1	-	24	0.00	0.00	0.08	0.00	4.80	5.78	0.10	32.90	2.01
112	Inf	-		0.08	0.05	0.19	0.08	12.40	9.30	0.28	26.00	2.28
112	SB3	-	28	0.04	0.11	0.13	0.06	8.30	16.00	0.17	45.00	2.07
112	SB2	-	36	0.08	0.24	0.65	0.06	8.50	16.40	0.17	43.00	2.04
112	SB1	-	32	0.07	0.04	0.37	0.06	8.20	12.90	0.16	34.00	1.91
112	SG3	-	32	0.02	0.42	0.19	0.09	9.40	16.90	0.11	44.00	1.19
112	SG2	-	32	0.01	0.18	0.13	0.08	5.60	17.90	0.11	45.00	1.95
112	SG1	-	28	0.02	0.10	0.12	0.08	3.60	14.90	0.05	40.00	1.41
112	IG3	-	40	0.01	0.06	0.16	0.08	5.10	18.40	0.04	47.00	0.73
112	IG2	-	32	0.01	0.04	0.23	0.16	3.40	21.20	0.07	54.00	2.04
112	IG1	-	32	0.02	0.04	0.14	0.06	6.30	12.90	0.16	33.00	2.50

112	SC3	-	38	0.02	0.08	0.16	0.08	10.00	9.40	0.28	24.00	2.81
112	SC1	-	40	0.01	0.06	0.15	0.08	9.60	8.90	0.29	21.00	2.97
112	IC3	-	28	0.03	0.03	0.17	0.05	10.00	9.70	0.27	24.00	2.70
112	IC2	-	12	0.04	0.04	0.16	0.06	8.40	10.10	0.26	24.00	3.05
112	IC1	-	40	0.04	0.05	0.16	0.06	10.80	10.50	0.29	25.00	2.67
112	SB3	A						8.20	13.00	0.21		2.54
112	SB2	A						8.80	11.40	0.26		2.99
112	SB2	B						8.10	12.00	0.18		2.26
112	SB1	A						8.70	13.10	0.25		2.90
112	SB1	B						5.20	12.00	0.13		2.51
112	SG3	A						2.40	21.00	0.05		2.07
112	SG3	B						1.02	2.00	0.26		25.69
112	SG2	A						10.60	11.60	0.18		1.68
112	SG2	B						3.60	7.50	0.25		7.06
112	SG1	B						0.90	16.60	0.02		2.72
119	Inf	-		0.22	0.03	0.03	0.00	10.70	8.20	0.27	21.00	2.55
119	SB3	-	16	0.03	0.18	0.02	0.02	8.50	16.40	0.20	50.00	2.31
119	SB2	-	28	0.04	0.03	0.23	0.24	7.90	14.70	0.19	41.00	2.41
119	SB1	-	40	0.03	0.02	0.07	0.02	7.00	10.70	0.22	30.00	3.10
119	SG3	-	24	0.03	0.02	0.00	0.00	6.60	12.70	0.14	34.00	2.13
119	SG2	-	20	0.03	0.01	0.02	0.01	5.30	13.50	0.14	36.00	2.67
119	SG1	-	20	0.03	0.01	0.00	0.00	3.90	12.90	0.10	34.00	2.63
119	IG3	-	32	0.03	0.03	0.03	0.01	4.40	10.30	0.14	78.00	3.23
119	IG2	-	32	0.02	0.03	0.03	0.01	5.40	11.30	0.14	76.00	2.63
119	IG1	-	32	0.02	0.01	0.03	0.00	6.01	14.50	0.15	38.00	2.57
119	SC3	-	40	0.03	0.05	0.04	0.00	8.90	9.40	0.27	26.00	3.00
119	SC1	-	28	0.03	0.03	0.03	0.01	8.20	9.40	0.26	26.00	3.23
119	IC3	-	32	0.04	0.02	0.03	0.01	9.80	9.10	0.26	25.00	2.61
119	IC2	-	6	0.05	0.02	0.03	0.01	8.40	9.50	0.27	26.00	3.17
119	IC1	-	6	0.04	0.05	0.05	0.00	11.50	9.10	0.27	26.00	2.34
128	Inf	-		0.04	0.07	0.00	0.00	12.25	9.40	0.26	23.00	2.12
128	SB3	-	36	0.04	0.38	0.00	0.00	8.30	14.80	0.14	38.00	1.68
128	SB2	-	12	0.04	0.06	0.00	0.00	9.30	13.10	0.16	35.00	1.71
128	SB1	-	20	0.04	0.06	0.00	0.00	8.80	13.50	0.17	34.00	1.91
128	SG3	-	24	0.10	0.08	0.00	0.00	8.20	4.80	0.11	39.00	1.35
128	SG2	-	32	0.09	0.04	0.00	0.00	6.20	5.10	0.11	39.00	1.84
128	SG1	-	28	0.10	0.08	0.00	0.00	7.00	5.20	0.12	39.00	1.73
128	IG3	-	32	0.10	0.13	0.00	0.00	7.00	19.30	0.02	50.00	0.26
128	IG2	-	18	0.06	0.03	0.00	0.00	5.09	27.50	0.06	74.00	1.17
128	IG1	-	36	0.05	0.01	0.00	0.00	6.80	15.90	0.15	39.00	2.14
128	SC3	-	30	0.15	0.14	0.00	0.00	13.06	14.40	0.27	29.00	2.04
128	SC1	-	32	0.18	0.02	0.00	0.00	17.70	12.80	0.26	46.00	1.50
128	IC3	-	22	0.09	0.11	0.00	0.00	10.80	11.40	0.25	28.00	2.31
128	IC2	-	32	0.06	0.03	0.00	0.00	10.70	9.80	0.26	24.00	2.42
128	IC1	-	36	0.05	0.10	0.00	0.00	8.80	10.30	0.26	24.00	2.93
154	Inf	-		0.08	0.09	0.00	0.00	10.60	8.50	0.29	36.00	2.76
154	SB3	-	32	0.08	0.23	0.00	0.00	11.90	17.10	0.23	57.00	1.96
154	SB2	-	4	0.15	0.06	0.00	0.00	8.90	15.90	0.19	49.00	2.08
154	SB1	-	32	0.14	0.05	0.00	0.00	9.00	11.90	0.20	43.00	2.25
154	SG3	-	28	0.11	0.04	0.00	0.00	7.30	15.50	0.14	48.00	1.85
154	SG2	-	16	0.09	0.04	0.00	0.00	4.50	21.10	0.08	57.00	1.72
154	SG1	-	32	0.09	0.05	0.00	0.00	2.80	21.50	0.05	57.00	1.75
154	IG3	-	24	0.09	0.03	0.00	0.00	3.60	12.50	0.03	42.00	0.92
154	IG2	-	32	0.09	0.03	0.00	0.00	6.90	16.90	0.18	55.00	2.64

154	IG1	-	24	0.15	0.06	0.00	0.00	5.40	10.00	0.10	53.00	1.93
154	SC3	-	36	0.10	0.04	0.00	0.00	10.10	9.90	0.27	39.00	2.70
154	SC2	-	32	0.10	0.04	0.00	0.00	9.20	9.30	0.28	38.00	3.09
154	SC1	-	36	0.10	0.04	0.00	0.00	9.40	9.30	0.28	37.00	3.02
154	IC3	-	32	0.09	0.04	0.00	0.00	10.10	10.40	0.28	39.00	2.74
154	IC2	-	32	0.09	0.04	0.00	0.00	9.80	9.90	0.29	38.00	2.93
154	IC1	-	32	0.09	0.04	0.00	0.00	10.00	9.70	0.27	38.00	2.73
163	Inf	-		0.10	0.06	0.00	0.00	11.60	8.70	0.30	37.00	2.61
163	SB3	-	36	0.07	0.27	0.00	0.00	7.90	13.50	0.17	48.00	2.15
163	SB2	-	36	0.08	0.27	0.00	0.00	7.90	13.50	0.17	48.00	2.15
163	SB1	-	40	0.11	0.28	0.00	0.00	10.70	9.30	0.26	39.00	2.44
163	SG3	-	24	0.08	0.07	0.00	0.00	7.30	12.50	0.18	43.00	2.51
163	SG2	-	24	0.08	0.07	0.00	0.00	7.30	12.50	0.18	43.00	2.51
163	SG1	-	28	0.11	0.08	0.00	0.00	6.20	13.60	0.10	45.00	1.67
163	IG3	-	32	0.12	0.10	0.00	0.00	9.50	11.60	0.15	43.00	1.56
163	IG2	-	24	0.20	0.28	0.00	0.00	9.80	15.70	0.28	53.00	2.84
163	IG1	-	32	0.13	0.06	0.00	0.00	8.60	16.20	0.22	49.00	2.51
163	SC3	-	24	0.08	0.10	0.00	0.00	10.20	10.90	0.26	41.00	2.55
163	SC2	-	28	0.08	0.10	0.00	0.00	10.20	10.90	0.26	41.00	2.55
163	SC1	-	24	0.09	0.08	0.00	0.00	10.70	9.40	0.29	39.00	2.68
163	IC3	-	28	0.14	0.08	0.00	0.00	10.10	9.70	0.29	39.00	2.92
163	IC2	-	28	0.12	0.08	0.00	0.00	12.20	9.50	0.30	40.00	2.45
163	IC1	-	36	0.12	0.08	0.00	0.00	10.20	9.30	0.29	39.00	2.87
163	SB3	A						11.20	13.60	0.21		1.86
163	SB2	A						11.10	11.60	0.21		1.87
163	SB2	B						9.40	9.50	0.22		2.32
163	SB1	A						11.40	15.70	0.32		2.84
163	SB1	B						9.38	9.37	0.16		1.72
163	SG3	A						9.50	6.78	0.30		3.11
163	SG3	B						8.42	12.35	0.26		3.04
163	SG2	A						9.50	6.78	0.30		3.11
163	SG2	B						8.42	12.35	0.16		1.88
163	SG1	B						7.23	2.90	0.14		1.92
168	Inf	-		0.02	0.05	0.00	0.00	12.20	8.00	0.31	36.00	2.58
168	SB3	-	28	0.03	0.22	0.00	0.00	7.70	13.80	0.19	50.00	2.41
168	SB2	-	32	0.03	0.13	0.00	0.00	8.90	11.00	0.19	45.00	2.08
168	SB1	-	36	0.04	0.04	0.00	0.00	10.10	9.70	0.26	40.00	2.61
168	SG3	-	24	0.05	0.11	0.00	0.00	9.70	12.10	0.21	43.00	2.21
168	SG2	-	32	0.05	0.08	0.00	0.00	9.75	12.20	0.21	43.00	2.16
168	SG1	-	24	0.04	0.06	0.00	0.00	9.80	12.40	0.15	43.00	1.55
168	IG3	-	32	0.03	0.09	0.00	0.00	7.60	11.20	0.16	41.00	2.08
168	IG2	-	32	0.03	0.03	0.00	0.00	9.60	14.50	0.22	47.00	2.34
168	IG1	-	32	0.07	0.05	0.00	0.00	7.40	8.10	0.24	49.00	3.28
168	SC3	-	36	0.02	0.03	0.00	0.00	11.50	8.60	0.31	37.00	2.66
168	SC2	-	36	0.02	0.03	0.00	0.00	10.90	8.80	0.30	37.00	2.80
168	SC1	-	40	0.03	0.07	0.00	0.00	11.90	8.50	0.32	37.00	2.72
168	IC3	-	28	0.05	0.03	0.00	0.00	10.50	9.30	0.30	38.00	2.83
168	IC2	-	28	0.14	0.08	0.00	0.00	8.90	5.10	0.31	40.00	3.47
168	IC1	-	24	0.19	0.13	0.00	0.00	8.60	5.90	0.34	44.00	3.94
175	Inf	-		0.09	0.05	0.00	0.00	12.50	8.60	0.32	37.00	2.52
175	SB3	-	28	0.02	0.21	0.00	0.00	8.08	14.10	0.19	47.00	2.35
175	SB2	-	32	0.05	0.16	0.00	0.00	8.60	11.60	0.18	49.00	2.07
175	SB1	-	28	0.03	0.03	0.00	0.00	10.80	9.70	0.28	39.00	2.59
175	SG3	-	24	0.04	0.03	0.00	0.00	6.60	15.30	0.16	48.00	2.39

175	SG2	-	32	0.05	0.03	0.00	0.00	4.80	20.40	0.07	56.00	1.36
175	SG1	-	24	0.05	0.03	0.00	0.00	12.10	14.90	0.08	47.00	0.67
175	IG3	-	32	0.05	0.02	0.00	0.00	11.70	15.10	0.19	42.00	1.58
175	IG2	-	32	0.05	0.03	0.00	0.00	9.90	18.40	0.24	49.00	2.42
175	IG1	-	32	0.07	0.03	0.00	0.00	10.80	16.70	0.23	52.00	2.13
175	SC3	-	36	0.04	0.02	0.00	0.00	10.10	8.90	0.30	37.00	2.98
175	SC2	-	36	0.04	0.11	0.00	0.00	9.60	10.80	0.29	39.00	3.05
175	SC1	-	32	0.04	0.04	0.00	0.00	11.60	9.10	0.30	38.00	2.59
175	IC3	-	24	0.19	0.06	0.00	0.00	12.60	11.30	0.30	41.00	2.41
175	IC2	-	28	0.49	0.14	0.00	0.00	16.30	10.40	0.35	42.00	2.15
175	IC1	-	24	0.25	0.10	0.00	0.00	14.45	10.80	0.30	37.00	2.11
182	Inf	-		0.08	0.04	0.02	0.00	8.50	6.30	0.31	36.00	3.65
182	SB3	-	28	0.09	0.17	0.00	0.00	5.90	8.70	0.17	45.00	2.93
182	SB2	-	24	0.13	0.05	0.14	0.00	6.10	11.10	0.15	46.00	2.52
182	SB1	-	28	0.09	0.02	0.06	0.00	5.90	8.10	0.21	39.00	3.51
182	SG3	-	24	0.08	0.04	0.03	0.00	6.70	9.30	0.22	44.00	3.35
182	SG2	-	20	0.07	0.03	0.00	0.00	4.30	10.70	0.14	44.00	3.30
182	SG1	-	24	0.05	0.02	0.00	0.00	2.60	8.40	0.08	41.00	3.21
182	IG3	-	32	0.05	0.03	0.00	0.00	6.10	8.20	0.19	38.00	3.08
182	IG2	-	24	0.05	0.02	0.00	0.00	5.50	10.30	0.22	43.00	3.95
182	IG1	-	32	0.05	0.02	0.00	0.00	5.40	13.10	0.22	48.00	3.98
182	SC3	-	36	0.05	0.02	0.03	0.00	7.70	6.50	0.27	37.00	3.55
182	SC2	-	36	0.05	0.13	0.01	0.00	7.30	6.03	0.29	35.00	3.97
182	SC1	-	32	0.05	0.04	0.02	0.00	6.80	6.30	0.29	36.00	4.22
182	IC3	-	24	0.05	0.02	0.02	0.00	6.60	5.40	0.24	34.00	3.62
182	IC2	-	28	0.05	0.02	0.03	0.00	7.20	6.80	0.28	37.00	3.92
182	IC1	-	30	0.05	0.02	0.02	0.00	6.90	7.20	0.28	37.00	4.09
182	SB3	A						5.70	8.90	0.22		3.78
182	SB2	A						6.60	6.70	0.26		3.96
182	SB2	B						8.40	15.60	0.17		2.02
182	SB1	A						5.50	4.20	0.40		7.23
182	SB1	B						5.70	9.30	0.18		3.24
182	SG3	A						6.60	6.60	0.30		4.58
182	SG3	B						7.20	8.40	0.28		3.86
182	SG2	A						7.60	7.00	0.31		4.12
182	SG2	B						5.80	9.80	0.11		1.96
182	SG1	B						3.90	7.90	0.17		4.25
189	Inf	-		0.04	0.05	0.00	0.00	6.90	5.20	0.26	34.00	3.81
189	SB3	-	28	0.04	0.21	0.00	0.00	4.40	9.50	0.17	47.00	3.82
189	SB2	-	30	0.15	0.36	0.27	0.00	7.00	10.80	0.19	46.00	2.77
189	SB1	-	24	0.06	0.25	0.06	0.00	7.20	10.00	0.23	39.00	3.19
189	SG3	-	24	0.05	0.06	0.00	0.00	5.50	9.40	0.22	42.00	4.03
189	SG2	-	32	0.05	0.08	0.00	0.00	5.50	9.20	0.20	41.00	3.72
189	SG1	-	26	0.04	0.34	0.00	0.00	4.40	10.30	0.11	38.00	2.57
189	IG3	-	32	0.04	0.04	0.02	0.00	4.80	9.10	0.18	42.00	3.78
189	IG2	-	24	0.04	0.04	0.00	0.00	5.80	12.10	0.23	47.00	3.93
189	IG1	-	32	0.04	0.06	0.00	0.00	6.70	12.40	0.22	48.00	3.35
189	SC3	-	40	0.06	0.07	0.06	0.00	6.70	6.70	0.28	37.00	4.23
189	SC2	-	36	0.06	0.09	0.09	0.00	7.00	7.10	0.29	38.00	4.16
189	SC1	-	32	0.04	0.09	0.07	0.00	7.80	7.30	0.29	38.00	3.71
189	IC3	-	30	0.04	0.03	0.03	0.00	6.80	5.90	0.27	37.00	4.01
189	IC2	-	28	0.04	0.04	0.04	0.00	8.40	6.40	0.30	37.00	3.54
189	IC1	-	24	0.05	0.06	0.11	0.00	8.30	6.80	0.28	38.00	3.41
210	Inf	-		0.08	0.05	0.02	0.00	7.10	6.00	0.31	35.00	4.35

210	SB3	-	32	0.09	0.17	0.00	0.00	4.70	9.60	0.17	48.00	3.72
210	SB2	-	36	0.12	0.06	0.00	0.00	5.00	6.70	0.14	47.00	2.82
210	SB1	-	24	0.16	0.04	0.00	0.00	6.00	10.50	0.18	44.00	3.06
210	SG3	-	24	0.13	0.02	0.00	0.00	3.40	12.10	0.15	47.00	4.30
210	SG2	-	20	0.12	0.02	0.00	0.00	4.80	9.10	0.24	41.00	4.93
210	SG1	-	26	0.14	0.03	0.00	0.00	4.00	9.80	0.14	42.00	3.52
210	IG3	-	28	0.12	0.04	0.31	0.00	6.50	8.90	0.22	44.00	3.31
210	IG2	-	24	0.14	0.03	0.00	0.00	5.30	10.80	0.26	45.00	4.85
210	IG1	-	36	0.14	0.07	0.02	0.00	5.80	10.70	0.26	44.00	4.50
210	SC3	-	36	0.14	0.03	0.03	0.00	7.30	7.00	0.31	37.00	4.22
210	SC2	-	24	0.13	0.02	0.04	0.00	6.60	7.00	0.31	37.00	4.65
210	SC1	-	32	0.13	0.05	0.05	0.00	6.80	7.30	0.31	37.00	4.50
210	IC3	-	30	0.08	0.03	0.04	0.00	7.10	7.30	0.30	38.00	4.21
210	IC2	-	28	0.08	0.03	0.02	0.00	6.50	6.70	0.31	36.00	4.76
210	IC1	-	30	0.08	0.03	0.02	0.00	6.30	6.70	0.31	36.00	4.91
210	SB3	A						5.20	8.70	0.22		4.30
210	SB2	A						6.20	22.20	0.32		5.09
210	SB2	B						3.90	10.20	0.19		4.74
210	SB1	A						7.20	12.20	0.39		5.47
210	SB1	B						4.40	16.00	0.16		3.55
210	SG3	A						5.40	9.50	0.32		5.95
210	SG3	B						4.80	12.00	0.24		5.02
210	SG2	A						7.00	7.80	0.31		4.42
210	SG2	B						6.20	7.90	0.27		4.38
210	SG1	B						6.60	8.00	0.25		3.86
216	Inf	-		0.04	0.04	0.00	0.00	8.00	6.20	0.32	36.00	3.95
216	SB3	-	14	0.04	0.07	0.00	0.00	4.40	6.20	0.12	35.00	2.74
216	SB2	-	30	0.04	0.10	0.00	0.00	4.00	8.50	0.13	44.00	3.29
216	SB1	-	20	0.04	0.10	0.00	0.00	6.90	7.60	0.26	41.00	3.77
216	SG3	-	26	0.17	0.08	0.00	0.00	7.40	0.12	0.26	46.00	3.45
216	SG2	-	32	0.06	0.04	0.00	0.00	7.70	9.20	0.25	43.00	3.22
216	SG1	-	28	0.04	0.05	0.00	0.00	5.90	7.70	0.24	38.00	4.04
216	IG3	-	28	0.53	0.15	0.00	0.00	31.50	24.80	0.41	95.00	1.30
216	IG2	-	28	0.19	0.11	0.00	0.00	14.00	13.10	0.31	52.00	2.20
216	IG1	-	28	0.08	0.05	0.00	0.00	7.90	9.60	0.22	43.00	2.76
216	SC3	-	40	0.05	0.07	0.00	0.00	8.60	7.50	0.31	38.00	3.55
216	SC2	-	28	0.03	0.04	0.00	0.00	7.00	7.40	0.30	37.00	4.31
216	SC1	-	32	0.04	0.03	0.00	0.00	6.90	7.30	0.30	38.00	4.41
216	IC3	-	24	0.07	0.07	0.00	0.00	9.60	7.80	0.32	39.00	3.30
216	IC2	-	28	0.06	0.09	0.00	0.00	8.30	6.90	0.32	37.00	3.81
216	IC1	-	30	0.05	0.05	0.00	0.00	7.50	7.10	0.31	37.00	4.12
223	Inf	-		0.03	0.03	0.00	0.00	7.20	6.20	0.32	35.00	4.43
223	SB3	-	20	0.19	0.08	0.00	0.00	5.40	8.60	0.13	48.00	2.32
223	SB2	-	5	0.10	0.05	0.00	0.00	4.70	10.40	0.14	46.00	3.06
223	SB1	-	22	0.05	0.04	0.00	0.00	5.10	8.80	0.23	41.00	4.45
223	SG3	-	40	0.05	0.04	0.00	0.00	5.90	8.90	0.26	44.00	4.39
223	SG2	-	5	0.04	0.03	0.00	0.00	3.60	12.10	0.17	47.00	4.70
223	SG1	-	30	0.03	0.03	0.00	0.00	4.60	8.40	0.24	40.00	5.30
223	IG3	-	32	0.03	0.04	0.00	0.00	5.40	9.30	0.21	41.00	3.81
223	IG2	-	32	0.02	0.04	0.00	0.00	5.70	10.90	0.26	44.00	4.54
223	IG1	-	20	0.02	0.04	0.00	0.00	5.10	11.50	0.26	45.00	5.08
223	SC3	-	20	0.05	0.04	0.00	0.00	7.60	7.70	0.30	39.00	3.91
223	SC2	-	36	0.04	0.03	0.00	0.00	6.30	7.40	0.30	41.00	4.74
223	SC1	-	20	0.03	0.04	0.00	0.00	5.90	6.90	0.31	36.00	5.26

223	IC3	-	20	0.02	0.06	0.00	0.00	6.80	7.50	0.31	38.00	4.50
223	IC2	-	32	0.02	0.04	0.00	0.00	6.50	6.90	0.31	36.00	4.80
223	IC1	-	20	0.03	0.05	0.00	0.00	6.30	7.10	0.31	37.00	4.96
227	Inf	-		0.03	0.03	0.00	0.00	8.40	6.10	0.34	35.00	4.05
227	SB3	-	8	0.03	0.05	0.00	0.00	4.60	6.20	0.11	38.00	2.33
227	SB2	-	4	0.06	0.06	0.00	0.00	4.30	5.90	0.17	43.00	3.92
227	SB1	-	12	0.02	0.03	0.00	0.00	5.60	8.60	0.22	40.00	3.99
227	SG3	-	32	0.04	0.03	0.00	0.00	7.50	9.00	0.26	41.00	3.46
227	SG2	-	36	0.03	0.03	0.00	0.00	4.90	13.80	0.16	51.00	3.30
227	SG1	-	30	0.03	0.03	0.00	0.00	5.80	8.60	0.25	40.00	4.37
227	IG3	-	24	0.07	0.05	0.00	0.00	6.10	10.10	0.20	43.00	3.28
227	IG2	-	24	0.05	0.04	0.00	0.00	6.40	11.60	0.26	46.00	4.05
227	IG1	-	16	0.06	0.04	0.00	0.00	6.30	12.40	0.26	48.00	4.14
227	SC3	-	34	0.03	0.03	0.00	0.00	7.90	7.90	0.30	39.00	3.77
227	SC2	-	32	0.03	0.03	0.00	0.00	7.70	6.80	0.32	37.00	4.10
227	SC1	-	28	0.03	0.03	0.00	0.00	7.50	6.70	0.32	36.00	4.23
227	IC3	-	30	0.08	0.05	0.00	0.00	7.80	7.50	0.31	38.00	3.95
227	IC2	-	28	0.21	0.06	0.00	0.00	10.50	7.40	0.33	39.00	3.11
227	IC1	-	32	0.20	0.07	0.00	0.00	17.70	7.80	0.34	43.00	1.90
239	Inf	-		0.03	0.06	0.00	0.00	13.70	7.40	0.31	35.00	2.24
239	SB3	-	8	0.03	0.05	0.00	0.00	6.50	6.20	0.08	34.00	1.18
239	SB2	-	4	0.02	0.13	0.00	0.00	8.90	10.80	0.12	40.00	1.33
239	SB1	-	12	0.03	0.04	0.00	0.00	9.80	9.30	0.26	38.00	2.63
239	SG3	-	32	0.08	0.07	0.00	0.00	9.50	10.70	0.23	41.00	2.45
239	SG2	-	36	0.05	0.05	0.00	0.00	9.00	11.30	0.22	41.00	2.48
239	SG1	-	30	0.05	0.05	0.00	0.00	6.00	10.80	0.10	40.00	1.72
239	IG3	-	20	0.03	0.08	0.00	0.00	10.00	11.50	0.17	41.00	1.72
239	IG2	-	32	0.02	0.05	0.00	0.00	9.50	12.00	0.25	43.00	2.62
239	IG1	-	16	0.03	0.03	0.00	0.00	9.20	12.10	0.25	43.00	2.73
239	SC3	-	34	0.07	0.06	0.00	0.00	12.30	12.30	0.23	43.00	1.90
239	SC2	-	32	0.05	0.03	0.00	0.00	11.10	8.40	0.30	37.00	2.72
239	SC1	-	28	0.04	0.04	0.00	0.00	10.70	8.00	0.29	36.00	2.72
239	IC3	-	30	0.03	0.05	0.00	0.00	11.50	8.80	0.29	37.00	2.52
239	IC2	-	28	0.02	0.04	0.00	0.00	10.00	8.80	0.30	36.00	2.97
239	IC1	-	32	0.02	0.05	0.00	0.00	11.40	9.00	0.30	37.00	2.63
239	SB3	A						9.90	8.40	0.30		3.00
239	SB2	A						12.50	8.80	0.30		2.38
239	SB2	B						7.20	13.50	0.16		2.28
239	SB1	A						12.80	5.40	0.34		2.62
239	SB1	B						7.70	12.30	0.18		2.35
239	SG3	A						15.00	8.40	0.44		2.91
239	SG3	B						11.00	13.20	0.41		3.73
239	SG2	A						16.00	7.20	0.30		1.88
239	SG2	B						12.00	9.00	0.26		2.18
239	SG1	B						7.10	9.90	0.11		1.60

Table D2: Weather data from pilot-scale filter columns

Day of operation	Max Temp °C	Min Temp °C	Rainfall (mm)
1.00	17.1	8.1	0
2.00	20.7	9.6	0
3.00	14.9	10.9	0.6
4.00	13.7	8	0

5.00	15.2	7.7	0
6.00	15.1	10	0
7.00	14.1	12.5	0.5
8.00	14.3	10.9	1.2
9.00	13.2	10.7	0
10.00	13.9	10.6	0.8
11.00	15.1	11.6	0.8
12.00	13.3	9.8	0.3
13.00	17.3	9.5	0
14.00	16.4	8.4	0
15.00	16.1	12.8	1.1
16.00	16.9	13.1	3.5
17.00	16.3	13.5	2.3
18.00	15.3	13.5	15
19.00	16.1	12.9	1.1
20.00	16.4	13.9	3.2
21.00	16.8	13.8	0.5
22.00	16.1	12.2	7.9
23.00	18.1	13	0.1
24.00	20.9	14.4	5.6
25.00	16.6	13.7	0.7
26.00	16.9	12.8	0.2
27.00	17.1	12.5	10.9
28.00	14.5	12.8	4.8
29.00	15.6	11.7	0
30.00	15.8	11.4	1.8
31.00	16.4	13.6	5
32.00	15.6	13.1	5
33.00	16.4	12.9	1.5
34.00	17.6	12.3	8.4
35.00	19.2	11	1.6
36.00	16.5	10	0
37.00	17.2	12	3
38.00	15.2	11.8	1.4
39.00	14.7	11.2	24.6
40.00	15.6	12.1	2
41.00	16.6	11.8	3.7
42.00	15.9	12.1	0.8
43.00	16	11.3	0.8
44.00	15.8	10.7	0.6
45.00	16.1	8.7	0
46.00	15.4	9.2	2.6
47.00	16.1	11.8	25.2
48.00	14.9	11.4	1.7
49.00	14.6	10.8	1.2
50.00	15.3	10.9	0.1

51.00	15.7	10.9	2.5
52.00	15.5	11.7	4.5
53.00	16.1	11.1	2.5
54.00	15.9	12.6	15.2
55.00	15.8	12.1	8.3
56.00	16	12.7	0.2
57.00	16.2	11.6	7.4
58.00	16	12	0.5
59.00	16.6	10.1	0
60.00	14.9	13.1	1.3
61.00	14.9	13.6	1.6
62.00	15.2	12.1	5
63.00	15.7	11	0.1
64.00	15.5	10.3	0
65.00	16.4	10.2	0.1
66.00	14.8	11.4	0.5
67.00	16	11.3	0.5
68.00	17.1	12.1	1.1
69.00	19	12.7	0.1
70.00	17.9	11.5	0
71.00	15.6	13.5	4.6
72.00	17.2	14	4
73.00	16.8	14.2	0
74.00	17.1	13.6	0
75.00	15.5	12.6	2.3
76.00	15.1	12	0.2
77.00	16.1	11.7	12.2
78.00	15.8	11.1	5.8
79.00	16.2	12.3	2.8
80.00	16.5	12.3	1.6
81.00	16.1	12.8	0.4
82.00	16.8	13.5	0
83.00	17.6	11.3	0.5
84.00	15.9	11.3	0.6
85.00	15.3	10.8	0.1
86.00	15.7	10.4	0
87.00	16.9	11.5	0
88.00	16.7	8.5	0
89.00	13.8	7.6	0
90.00	14.1	11.4	0
91.00	19.9	11.7	
92.00	18.3	12.4	0
93.00	17.8	13.3	7.6
94.00	14.9	12.3	58.4
95.00	14.6	10.7	3.7
96.00	14.9	9.2	48.8

97.00	14.2	9	20.1
98.00	15.7	11.2	0
99.00	14.1	7.8	0.2
100.00	16.1	12	1.7
101.00	16.5	12.2	0.1
102.00	15.8	11.9	0
103.00	14.8	11.4	9.9
104.00	15.1	10.1	4.2
105.00	15	9.7	2
106.00	14.8	10.7	2.2
107.00	13.5	10.1	1.6
108.00	14.1	12.4	0
109.00	15.3	12.7	0
110.00	16.8	11.6	0
111.00	17.4	11.1	0
112.00	17.5	10.1	0
113.00	16.3	8	0.1
114.00	16.7	8	0.1
115.00	14.3	7.7	0.2
116.00	12.7	5.3	0
117.00	14.8	6.5	0
118.00	14.7	11.4	2
119.00	14.5	11.1	0.3
120.00	14.4	10.8	0.2
121.00	15.1	10.9	0
122.00	15	12.6	1.8
123.00	15.1	10.3	0.3
124.00	15	9.6	0
125.00	14.1	6	0
126.00	13	5.7	0
127.00	13.9	7.6	0
128.00	13.3	7.8	0
129.00	13.5	5.8	0
130.00	11.5	7.8	0
131.00	11.8	8.3	0
132.00	13.8	7.9	0
133.00	13.6	11.7	2.7
134.00	13.8	12	1.2
135.00	13.2	10.6	0
136.00	13.9	10	19.6
137.00	11.4	8.9	2.9
138.00	12.4	10.6	0.4
139.00	14.9	10.8	4.2
140.00	13	9.3	2.3
141.00	14.1	8.2	4.1
142.00	13	9.9	3.1

143.00	14.8	11	15.4
144.00	13.9	11	0.1
145.00	14.3	9.7	0.1
146.00	15.4	11	0
147.00	13.8	9.2	0.1
148.00	11.9	8.6	0
149.00	13.5	10.9	9.5
150.00	13.6	11.3	9.9
151.00	13.3	9.4	7.2
152.00	13.3	10	3.8
153.00	14.7	11.3	12.4
154.00	14.2	12.1	2.6
155.00	13.1	9.2	3.6
156.00	13.7	6.2	5.8
157.00	10.4	5.4	2.5
158.00	13.9	7.7	21.8
159.00	13.8	9.5	5.6
160.00	10	7.7	0.2
161.00	13.1	7.1	7.2
162.00	13	9.8	5.1
163.00	10.9	7.8	0.6
164.00	9	4	1.6
165.00	8.6	4.8	5.6
166.00	9.5	4.9	0.8
167.00	11.9	7.2	4.2
168.00	10.8	9.5	0.6
169.00	11.9	10.5	0
170.00	11.9	11	0.6
171.00	11.7	5	5
172.00	10.5	6.2	4.2
173.00	11.9	6.8	4
174.00	12.2	5.6	16.4
175.00	13.1	8.8	4.8
176.00	12.8	5.3	5.8
177.00	10.4	5.9	5.4
178.00	12.4	9.1	10.6
179.00	12.5	11.5	31.6
180.00	12.7	5.6	3.8
181.00	13.3	6.5	3.8
182.00	11.7	6.6	3.5
183.00	12.2	8.2	9.6
184.00	9.3	5.1	3.4
185.00	9.2	5.4	0.5
186.00	6.2	1.6	17.1
187.00	10.7	2	3.1
188.00	11	9.1	6.4

189.00	12	9.8	3.5
190.00	13	10.3	0.9
191.00	12.8	11.3	6.6
192.00	13.2	11.2	11.4
193.00	13.3	9.5	2.3
194.00	10.7	7.4	3.8
195.00	12.4	8.1	10.2
196.00	12.9	6.2	9.1
197.00	11.7	5.2	11.3
198.00	9.7	4.1	4.4
199.00	7.8	3.4	2.6
200.00	7.4	3.4	0
201.00	12.1	7.1	1
202.00	12.4	6.9	11.2
203.00	12.6	6.4	10.8
204.00	10.1	4.3	13.6
205.00	7.8	1.3	8.7
206.00	9.4	4.8	8.8
207.00	8.4	4.6	2.9
208.00	9.5	5.4	13.2
209.00	8.6	5.6	2.6
210.00	8.8	5.4	0
211.00	9.1	3.5	11.3
212.00	7.6	4.2	2.2
213.00	8	3.4	11.3
214.00	7.7	2.8	7.4
215.00	7.7	4.2	3.4
216.00	7.4	4	2.1
217.00	7.4	4.5	0.8
218.00	6.7	4	6.6
219.00	5.8	3.1	2.5
220.00	7.8	2.2	1.8
221.00	9.1	1.9	0.1
222.00	9.1	5.2	3.9
223.00	8.7	6.7	5.5
224.00	7.6	4.3	0.3
225.00	9.1	5.9	3.2
226.00	11	9.1	16.2
227.00	10.9	8.6	4.8
228.00	11.1	8.5	3.5
229.00	12.1	10.9	1.2
230.00	11.9	6.1	5.6
231.00	11.9	6.9	19.3
232.00	7.8	4.6	6.2
233.00	10.9	6.1	5.1
234.00	10.9	4.7	2.8

235.00	6.7	2	4.1
236.00	11.1	6.1	4
237.00	11.2	6.2	1.3
238.00	7.6	2.6	2.5
239.00	10.3	4.7	1.4

Table D3: Results from filter column deconstruction

Sample Description	Depth (mm)	Organic matter %
SB1	0-50	0.3
SB1	250-300	0.27
SB1	350-400	4.82
SB1	600-650	5.42
SB1	700-750	0.44
SB1	900-950	
SB2	0-50	0.21
SB2	300-350	0.14
SB2	400-450	4.79
SB2	600-650	
SB2	700-750	0.53
SB2	900-950	
SB3	0-50	
SB3	300-350	
SB3	400-450	4.74
SB3	550-600	
SB3	650-700	0.39
SB3	900-950	0.13
SG1	0-50	0.21
SG1	200-250	0.12
SG1	300-350	5.82
SG1	550-600	5.28
SG1	650-700	0.18
SG1	900-950	0.1
SG2	0-50	0.22
SG2	300-350	0.16
SG2	400-450	9.64
SG2	650-700	9.16
SG2	750-800	< 0.10
SG2	950-1000	0.23
SG3	0-50	< 0.10
SG3	300-350	0.17
SG3	400-450	7.79
SG3	650-700	6.99
SG3	750-800	0.21
SG3	950-1000	0.15
SC1	0-50	< 0.10
SC1	300-350	< 0.10
SC1	350-400	< 0.10
SC1	650-700	< 0.10
SC1	700-750	< 0.10
SC1	850-900	< 0.10
SC2	0-50	0.16
SC2	300-350	< 0.10

SC2	350-400	< 0.10
SC2	650-700	< 0.10
SC2	700-750	< 0.10
SC2	900-950	< 0.10
SC3	0-50	< 0.10
SC3	300-350	< 0.10
SC3	350-400	< 0.10
SC3	650-700	< 0.10
SC3	700-75	0.11
SC3	950-1000	< 0.10
IB1	0-50	0.15
IB1	250-300	0.19
IB1	350-400	4.76
IB1	550-600	4.95
IB1	700-750	0.5
IB1	950-1000	< 0.10
IB2	0-50	0.25
IB2	300-350	0.21
IB2	350-400	4.6
IB2	550-600	5.06
IB2	650-700	0.45
IB2	900-950	0.25
IB3	0-50	0.15
IB3	300-350	0.17
IB3	400-450	5.05
IB3	600-650	5.28
IB3	700-750	0.23
IB3	950-1000	0.15
IG1	0-50	0.25
IG1	300-350	0.25
IG1	400-450	7.73
IG1	700-750	7.56
IG1	750-800	0.31
IG1	950-1000	0.56
IG2	0-50	
IG2	300-350	0.26
IG2	400-450	7.61
IG2	600-650	7.81
IG2	700-750	0.48
IG2	900-950	0.33
IG3	0-50	0.27
IG3	250-300	0.22
IG3	350-400	5.65
IG3	650-700	6.38
IG3	750-800	0.35
IG3	900-950	0.34
IC1	0-50	0.22
IC1	300-350	0.19
IC1	350-400	< 0.10
IC1	650-700	< 0.10
IC1	700-75	< 0.10
IC1	950-1000	< 0.10
IC2	0-50	< 0.10
IC2	300-350	< 0.10

IC2	350-400	< 0.10
IC2	650-700	0.11
IC2	700-75	< 0.10
IC2	850-900	< 0.10
IC3	0-50	< 0.10
IC3	300-350	< 0.10
IC3	350-400	< 0.10
IC3	650-700	< 0.10
IC3	700-75	< 0.10
IC3	950-1000	< 0.10
Raw Sand		< 0.10
Raw Sand		< 0.10
Raw Sand Mix		< 0.10
Raw Sand Mix		< 0.10
Raw Bayer Residue		5.08
Raw Bayer Residue		5.7
Raw Pyritic Fill		1.09
Raw Pyritic Fill		1.02
Raw GAC		< 0.10
Raw GAC		< 0.10

Figure D1: Empty Bed Contact Time plots for DOC removal