



## Research article

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



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## ARTICLE INFO

## Article history:

Received 15 February 2016

Received in revised form

6 May 2016

Accepted 9 May 2016

## Keywords:

Clogging mechanism

Water purification

Fly ash

Bayer residue

## ABSTRACT

Slow sand filters 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 ( $\text{NH}_4\text{-N}$ ), nitrate ( $\text{NO}_3\text{-N}$ ) 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%  $\text{NH}_4\text{-N}$  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.

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## 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; Mauclair et al., 2004); however, clogging may also occur by chemical and physical mechanisms (Mauclair 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 (Mauclair 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 ( $\text{NO}_3\text{-N}$ ), ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ) 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  $200 \mu\text{g L}^{-1}$  (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  $\text{NO}_3\text{-N}$  in drinking water is  $10 \text{ mg L}^{-1}$  (SI No 278 of 2007), as consumption of high levels of  $\text{NO}_3\text{-N}$  may cause methemoglobinemia, and can have significant environmental impacts on agricultural and aquatic life (Bhatnagar and Sillanpää, 2011). Ammonium has a MAC of  $0.3 \text{ mg L}^{-1}$  in drinking water, and is generally present in source water due to anthropogenic activities. A residual presence of  $\text{NH}_4\text{-N}$  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,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and turbidity) of water.

## 2. Materials and methods

### 2.1. Filter construction

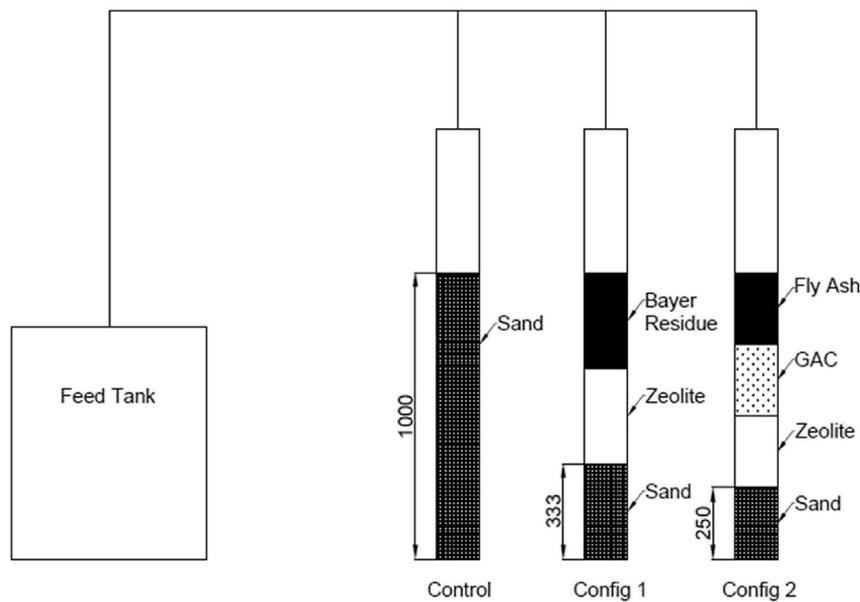
Three filter configurations, each replicated at  $n = 3$ , were examined with constantly loaded and intermittently loaded operational regimes, giving a total of 18 filters (Fig. 1). The first configuration ('Config 1') was a three-layer stratified filter (each layer had a depth of 0.33 m) containing (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  $\text{NH}_4\text{-N}$  removal was focused at the surface of the filter, and Al, TOC, and  $\text{NO}_3\text{-N}$  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  $0.1 \text{ m h}^{-1}$  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 <sup>-1</sup> )	Comment	Reference
Bayer Residue	Phosphorus	1.1	Initial Concentrations between 0.1 and 1 mg L <sup>-1</sup>	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
Fly Ash	Al	0.064		Komnitsas et al., 2004
	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
Zeolites	Zinc	2.54		Gupta and Ali 2000
	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<sub>4</sub><sup>+</sup>-N (synthesised using laboratory-grade NH<sub>4</sub>Cl to a concentration of 5 mg L<sup>-1</sup>), NO<sub>3</sub><sup>-</sup>-N (synthesised using laboratory-grade KNO<sub>3</sub> to a concentration of 20 mg L<sup>-1</sup>), Al (synthesised using laboratory-grade aluminium powder to a concentration of 2 mg L<sup>-1</sup>), and DOC (synthesised using laboratory-grade humic acid to a concentration of 10 mg L<sup>-1</sup>). 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<sup>-1</sup>, 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<sup>-1</sup> (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<sub>f</sub>s of between 10<sup>-2</sup> and 10<sup>-5</sup> m s<sup>-1</sup> (British Standard Institution, 1990b) and the falling head test (appropriate for media with a K<sub>f</sub>s ≤ 10<sup>-5</sup> m s<sup>-1</sup>, ASTM, 2007) were required to analyse the K<sub>f</sub>s of the filters. Samples of the virgin media were tested initially for K<sub>f</sub>s. At the end of the 90 day trial, samples of media were collected at incremental depths to analyse K<sub>f</sub>s variation with depth. The sample collection in each filter was terminated when the K<sub>f</sub>s 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 <sup>a</sup>	Zeolite <sup>b</sup>	Bayer residue <sup>c</sup>	Fly ash <sup>d</sup>	GAC <sup>e</sup>
Chemical					
SiO <sub>2</sub> (%)	97.72	65–72	8.9	60.37	–
Fe <sub>2</sub> O <sub>3</sub> (%)	1.26	0.8–1.9	43.8	8.27	–
Al <sub>2</sub> O <sub>3</sub> (%)	0.21	10.0–12	15.04	20.53	–
K <sub>2</sub> O (%)	0.05	2.3–3.5	–	1.89	–
L.O.I <sup>f</sup> (%)	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 <sub>2</sub> O (%)	–	0.3–0.65	5.32	0.65	–
TiO <sub>2</sub> (%)	–	0–0.1	9.2	1	–
MnO (%)	–	0–0.08	–	–	–
SO <sub>4</sub> (%)	–	–	0.41	2.15	–
P <sub>2</sub> O <sub>5</sub> (%)	–	–	0.36	0.22	–
Iodine No (mg gm <sup>-1</sup> )	–	–	–	–	1100
Moisture (%)	–	–	–	–	5
Ash (%)	–	–	–	–	4
Un-determined	–	–	–	0.71	–
Ca (%) <sup>*</sup>	–	–	–	–	9.85
K (%) <sup>*</sup>	–	–	–	–	77.73
Al (mg kg <sup>-1</sup> ) <sup>*</sup>	87	263	8388	1223	49
Cu (mg kg <sup>-1</sup> ) <sup>*</sup>	4.65	1.18	4.17	4.35	0.55
Fe (mg kg <sup>-1</sup> ) <sup>*</sup>	39	23	59	189	14
Mg (mg kg <sup>-1</sup> ) <sup>*</sup>	22.57	12.8	0.18	13.59	3.78
Mn (mg kg <sup>-1</sup> ) <sup>*</sup>	3	15	1	22	2
Na (mg kg <sup>-1</sup> ) <sup>*</sup>	15	655	18,280	175	219
P (mg kg <sup>-1</sup> ) <sup>*</sup>	4	3	10	1044	87
Zn (mg kg <sup>-1</sup> ) <sup>*</sup>	1.37	1.64	0.4	4.43	0.4
Total exchange capacity (meq 100 g <sup>-1</sup> ) <sup>*</sup>	0.96	22.13	108.8	0.06	0.58
Organic matter (%) <sup>*</sup>	0.1	0.1	5.7	0.22	72.3
Effective size, d <sub>10</sub> (mm)	1.31	1.02	0.06	0.06	0.58

\*Analysis by Brookside Laboratories.

<sup>a</sup> Irwin's Quality Aggregates.<sup>b</sup> Zeolite Ireland Ltd.<sup>c</sup> Rusal Aughinish.<sup>d</sup> ESB Energy International Moneypoint<sup>e</sup> Indo German Carbons Ltd.<sup>f</sup> 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  $200 \mu\text{g Al L}^{-1}$  (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  $\text{NH}_4^+$ -N removal, with significantly higher removal of  $\text{NH}_4^+$ -N occurring in Config 1 and 2, versus the Control, when operated under intermittent loading ( $p = 0.01$ ). The trend of  $\text{NO}_3^-$ -N production, coupled with high  $\text{NH}_4^+$ -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 (Mauclair 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 <sup>a</sup> ( $\text{L m}^{-2} \text{d}^{-1}$ )		1424 ± 48	600 ± 268	577 ± 12	676 ± 30	592 ± 228	655 ± 208
Influent ( $\text{mg L}^{-1}$ )	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
	$\text{NH}_4^+$ -N	5.9 ± 2	5.9 ± 2	5.9 ± 2	5.8 ± 1.3	5.8 ± 1.3	5.8 ± 1.3
	$\text{NO}_3^-$ -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
	$\text{NH}_4^+$ -N	56.5 ± 1.9	75.9 ± 10.9	88.5 ± 1.9	60.2 ± 3	84.7 ± 2.1	84.8 ± 2.8
	$\text{NO}_3^-$ -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 ( $\text{g m}^{-3} \text{d}^{-1}$ )	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
	$\text{NH}_4^+$ -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
	$\text{NO}_3^-$ -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

<sup>a</sup> Average hydraulic loading rate was calculated from the initial and final hydraulic loading rates, to best describe the columns as clogging occurred.

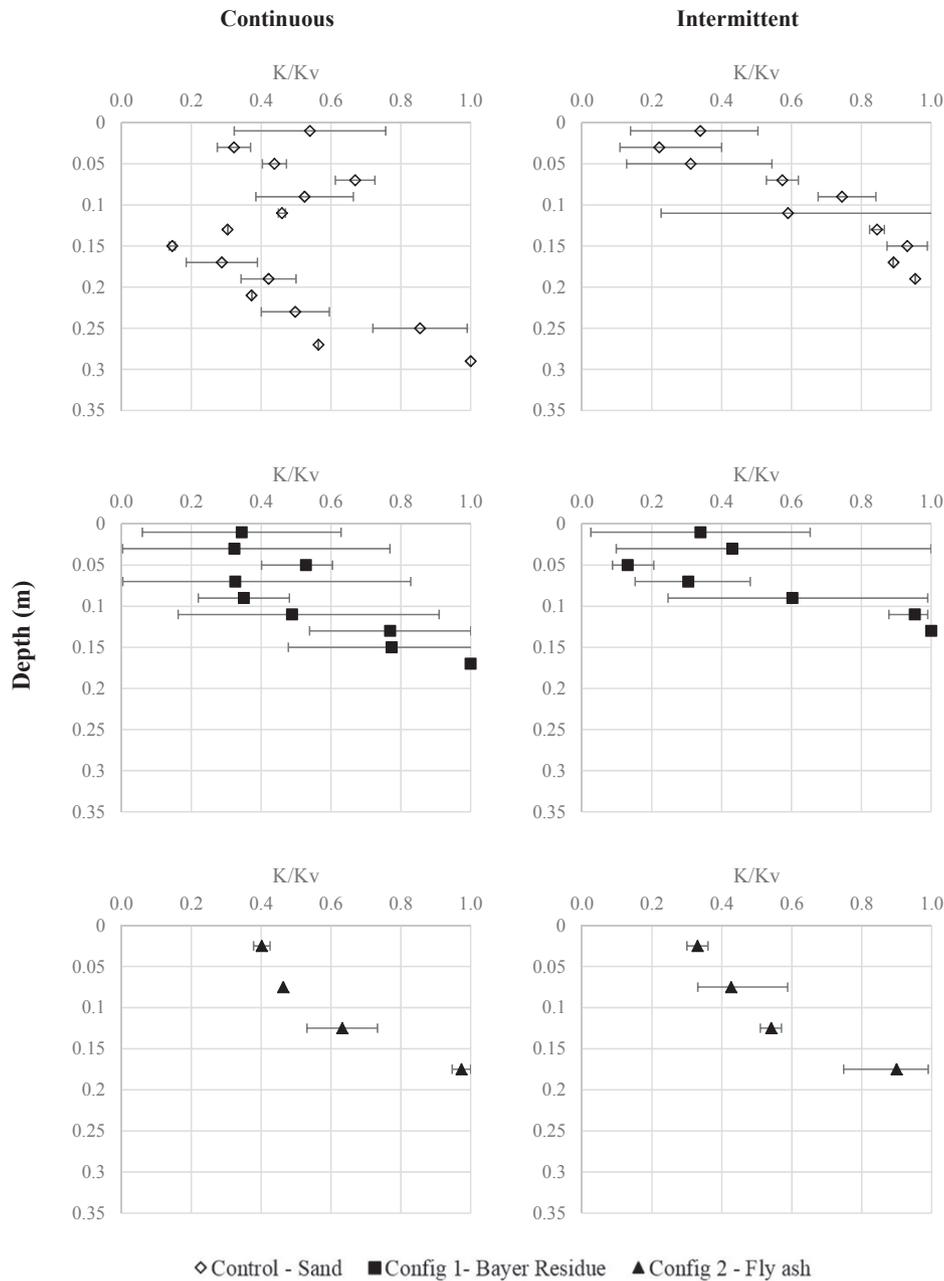


Fig. 2. Relative hydraulic conductivity variation in the uppermost layer with maximum and minimum values.

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

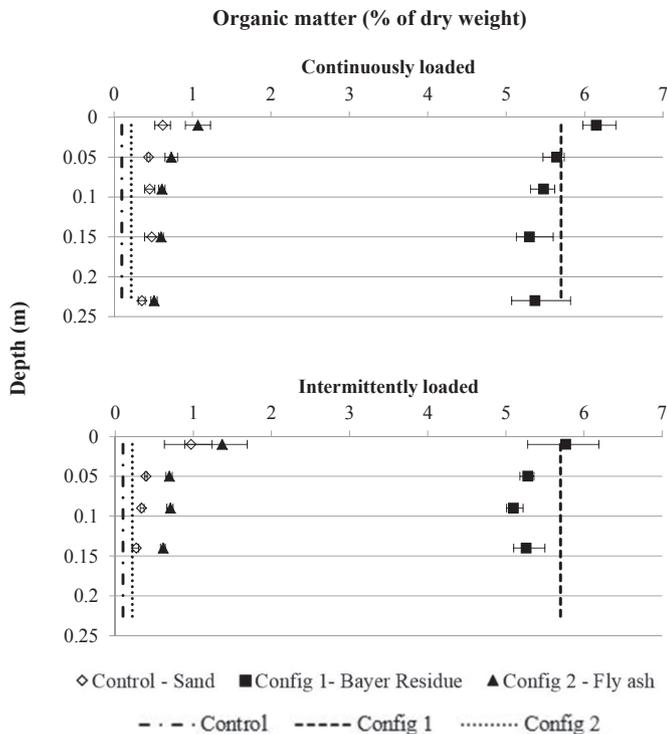


Fig. 3. Organic matter percentages of dry weight of media (with max and min) per depth in each configuration, with initial concentrations shown as vertical lines.

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.

#### Acknowledgements

The authors would like to acknowledge ESB Ireland, Rusal Aughinish and Zeolite Ireland for supplying the media for use in this study, and the financial support of the Irish Environmental Protection Agency (EPA Grant Number 2012-W-PhD-5).

#### 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>.

#### References

- Abdul, A.S., Gibson, T.L., Rai, D.N., 1990. Use of humic acid solution to remove organic contaminants from hydrogeologic systems. *Environ. Sci. Technol.* 333 (24), 333–337.
- Ali, I., 2012. *New Generation Adsorbents for Water Treatment*.
- ASTM, 2007. *Standard Test Method for Measurement of Hydraulic Conductivity of Porous Material Using a Rigid-Wall, Compaction-mold Permeameter*. ASTM

- International.
- Bailey, S.E., et al., 1999. A review of potentially low-cost sorbents for heavy metals. *Water Res.* 33 (11), 2469–2479.
- Baveye, P., et al., 1998. Environmental impact and mechanisms of the biological clogging of saturated soils and aquifer materials. *Crit. Rev. Environ. Sci. Technol.* 28, 123–191. February 2015.
- Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption—A review. *Chem. Eng. J.* 171 (3), 811–840. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894711005845>. Accessed July 10, 2014.
- Bhatnagar, A., Sillanpää, M., 2011. A review of emerging adsorbents for nitrate removal from water. *Chem. Eng. J.* 168 (2), 493–504. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894711001689>. Accessed January 1, 2015.
- Bhatnagar, A., Sillanpää, M., 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review. *Chem. Eng. J.* 157 (2–3), 277–296. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894710000288>. Accessed July 13, 2014.
- Bondy, S.C., 2010. The neurotoxicity of environmental aluminum is still an issue. *Neurotoxicology* 31 (5), 575–581. Available at: <http://www.sciencedirect.com/science/article/pii/S0161813X10000975>.
- British Standard Institution, 1990a. *Methods of Test for Soils for Civil Engineering Purposes — Part 2: Classification Tests*, Britain.
- British Standard Institution, 1990b. *Methods of Test for Soils for Civil Engineering Purposes—Part 5: Compressibility, Permeability and Durability Tests*, Britain.
- Calderon, R.L., 2000. The epidemiology of chemical contaminants of drinking water. Food and chemical toxicology. *Int. J. Publ. Br. Ind. Biol. Res. Assoc.* 38 (Suppl. 1), S13–S20. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/10717366>.
- Cengeloglu, Y., et al., 2006. Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol.* 51 (3), 374–378. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894710000694>. Accessed March 5, 2013.
- Chuang, Y.-H., Wang, G.-S., Tung, H., 2011. Chlorine residuals and haloacetic acid reduction in rapid sand filtration. *Chemosphere* 85 (7), 1146–1153.
- Le Coustumier, S., et al., 2012. The influence of design parameters on clogging of stormwater biofilters: a large-scale column study. *Water Res.* 46, 6743–6752.
- Craig, R., 2004. *Soil Mechanics*, seventh ed. Spon Press, London.
- Dahnke, W., 1990. Testing soils for available nitrogen. In: Westerman, R.L. (Ed.), *Soil Testing and Plant Analysis*. Soil Sci. Soc. Am., Madison, WI, pp. 120–140.
- EAA, 2013. *Bauxite residue management: Best Practice*, London, UK.
- Elfarissi, F., et al., 1998. Polyelectrolytic nature of humic substances-aluminum ion complexes Interfacial characteristics and effects on colloid stability. *Colloids Surf. A Physicochem. Eng. Asp.* 131 (1–3), 281–294. Available at: <http://www.scopus.com/inward/record.url?eid=2-s2.0-0031933333&partnerID=tZOTx3y1>.
- EPA, 2015. *Drinking Water Report 2013*. Johnstown Castle, Wexford, Ireland.
- EPA, 2008. *Water Quality in Ireland 2004–2006*. Johnstown Castle, Wexford, Ireland.
- EPA, 2011. *Water Treatment Manual: Disinfection*. Johnstown Castle, Wexford, Ireland. Available at: [https://www.epa.ie/pubs/advice/drinkingwater/Disinfection2\\_web.pdf](https://www.epa.ie/pubs/advice/drinkingwater/Disinfection2_web.pdf).
- EPA, 1995. *Water Treatment Manuals: Filtration*. Johnstown Castle, Wexford, Ireland. Available at: [https://www.epa.ie/pubs/advice/drinkingwater/EPA\\_water\\_treatment\\_manual\\_filtration1.pdf](https://www.epa.ie/pubs/advice/drinkingwater/EPA_water_treatment_manual_filtration1.pdf).
- Exley, C., Vickers, T., 2014. Elevated brain aluminium and early onset Alzheimer's disease in an individual occupationally exposed to aluminium: a case report. *J. Med. Case Rep.* 8 (1), 41. Available at: <http://www.jmedicalcasereports.com/content/8/1/41>.
- Feng, S., et al., 2012. Ammonium removal pathways and microbial community in GAC-sand dual media filter in drinking water treatment. *J. Environ. Sci.* 24 (9), 1587–1593. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1001074211609650>. Accessed October 29, 2014.
- Flaten, T.P., 2001. Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water. *Brain Res. Bull.* 55 (2), 187–196.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manag.* 92 (3), 407–418. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/21138785>. Accessed July 9, 2014.
- Gang, D., Clevenger, T.E., Banerji, S.K., 2003. Relationship of chlorine decay and THMs formation to NOM size. *J. Hazard. Mater.* 96 (1), 1–12.
- Gavlak, R., et al., 2003. *Soil, Plant, and Water Reference Methods for the Western Regions*. WCC-103.
- 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. *Sci. Total Environ.* 518–519 (278), 491–497. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0048969715002272>.
- Gupta, V.K., Ali, I., 2000. Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. *Sep. Purif. Technol.* 18 (2), 131–140.
- Hand, V.L., et al., 2008. Experimental studies of the influence of grain size, oxygen availability and organic carbon availability on bioclogging in porous media. *Environ. Sci. Technol.* 42 (5), 1485–1491.
- Hatt, B.E., Fletcher, T.I.M.D., 2008. Hydraulic and pollutant removal performance of fine media stormwater filtration systems. *Environ. Sci. Technol.* 42 (7), 2535–2541.
- Hua, G.F., et al., 2010. Clogging pattern in vertical-flow constructed wetlands: insight from a laboratory study. *J. Hazard. Mater.* 180 (1–3), 668–674. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/20472337>. Accessed October 29, 2014.
- Huang, W., et al., 2008. Phosphate removal from wastewater using red mud. *J. Hazard. Mater.* 158 (1), 35–42.
- Kildsgaard, J., Engesgaard, P., 2002. Tracer tests and image analysis of biological clogging in a two dimensional sandbox experiment. *Groundw. Monit. Remediat.* 22 (2), 60–67.
- Kim, J., Kang, B., 2008. DBPs removal in GAC filter-adsorber. *Water Res.* 42 (1–2), 145–152.
- Knowles, P., et al., 2011. Clogging in subsurface-flow treatment wetlands: occurrence and contributing factors. *Ecol. Eng.* 37 (2), 99–112. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0925587410002600>. Accessed October 10, 2014.
- Knowles, P.R., Griffin, P., Davies, P.A., 2010. Complementary methods to investigate the development of clogging within a horizontal sub-surface flow tertiary treatment wetland. *Water Res.* 44 (1), 320–330. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/19800651>. Accessed October 29, 2014.
- Komnitsas, K., Bartzas, G., Paspaliaris, I., 2004. Efficiency of limestone and red mud barriers: laboratory column studies. *Miner. Eng.* 17 (2), 183–194. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0892687503004072>. Accessed January 13, 2015.
- Kurniawan, T.A., et al., 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci. Total Environ.* 366 (2–3), 409–426. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/16300818>. Accessed December 8, 2014.
- Leverenz, H.L., Tchobanoglous, G., Darby, J.L., 2009. Clogging in intermittently dosed sand filters used for wastewater treatment. *Water Res.* 43 (3), 695–705. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/19054539>. Accessed March 19, 2013.
- Li, W., Kiser, C., Richard, Q., 2005. Development of a filter cake permeability test methodology. In: *American Filtration & Separations Society 2005 International Topical Conferences & Exposition*. Ann Arbor, Michigan, pp. 1–8. Abstract.
- Li, Y., et al., 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *J. Hazard. Mater.* 137 (1), 374–383.
- Mauclair, L., et al., 2004. Sand filtration in a water treatment plant: biological parameters responsible for clogging. *J. Water Supply Res. Technol.—AQUA* 53, 93–108.
- McKinley, J.W., Siegrist, R.L., 2011. Soil clogging genesis in soil treatment units used for onsite wastewater reclamation: a review. *Crit. Rev. Environ. Sci. Technol.* 41 (24), 2186–2209. Available at: <http://www.tandfonline.com/doi/abs/10.1080/10643389.2010.497445>. Accessed October 29, 2014.
- Mehlich, A., 1984. Mehlich-3 soil test extractant: a modification of Mehlich-2 extractant. *Commun. Soil Sci. Plant Anal.* 15, 1409–1416.
- Mehta, P.K., 2002. Greening of the concrete industry for sustainable development. *Concr. Int.* 23 (7), 23–28.
- Misaelides, P., 2011. Application of natural zeolites in environmental remediation: a short review. *Microporous Mesoporous Mater.* 144 (1–3), 15–18. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S138718111001314>. Accessed January 19, 2015.
- Nayak, P., 2002. Aluminum: impacts and disease. *Environ. Res.* 89 (2), 101–115.
- Nguyen, T.C., et al., 2015. Simultaneous adsorption of Cd, Cr, Cu, Pb, and Zn by an iron-coated Australian zeolite in batch and fixed-bed column studies. *Chem. Eng. J.* 270, 393–404. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894715002454>.
- Nieć, J., Spychała, M., 2014. Hydraulic conductivity estimation test impact on long-term acceptance rate and soil absorption system design. *Water* 6, 2808–2820. Available at: [www.mdpi.com/journal/water](http://www.mdpi.com/journal/water).
- Nivala, J., et al., 2012. Clogging in subsurface-flow treatment wetlands: measurement, modeling and management. *Water Res.* 46 (6), 1625–1640. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/22284912>. Accessed October 22, 2014.
- Noubactep, C., et al., 2010. Extending service life of household water filters by mixing metallic iron with sand. *Clean.—Soil, Air, Water* 38 (10), 951–959.
- Pedescoll, A., et al., 2009. Practical method based on saturated hydraulic conductivity used to assess clogging in subsurface flow constructed wetlands. *Ecol. Eng.* 35 (8), 1216–1224. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0925587409001025>. Accessed October 29, 2014.
- Pesavento, M., et al., 1998. Investigation of the Speciation of Aluminium in Drinking Waters by Sorption on a Strong Anionic-exchange Resin. *AG1X8*, 367.
- Rahman, I.M.M., et al., 2013. Decontamination of spent iron-oxide coated sand from filters used in arsenic removal. *Chemosphere* 92 (2), 196–200. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0045653513004542>.
- Rodgers, M., Mulqueen, J., Healy, M.G., 2004. Surface clogging in an intermittent stratified sand filter. *Soil Sci. Soc. Am.* 68, 1–6.
- Ross, D., 1995. Recommended soils test for determining exchange capacity. In: *Recommended Soil Testing Procedures for the Northeastern United States*, pp. 62–69.
- Schulte, E., Hopkins, B., 1996. Estimation of soil organic matter by weight Loss-On-Ignition. In: Magdoff, F.R., Tabatabai, M.A., Hanlon, E.A.J. (Eds.), *Soil Organic Matter: Analysis and Interpretation*. Soil Sci. Soc. Am., Madison, WI, pp. 21–32.
- SI No 278 of, 2007. *European Communities (Drinking Water) (No. 2) Regulations 2007*, Ireland. Available at: <http://www.environ.ie/en/Legislation/Environment/Water/FileDownload,14547,en.pdf>.
- Tanner, C.C., Sukias, J.P.S., Upsdell, M.P., 1998. Organic matter accumulation during maturation of gravel-bed constructed wetlands treating farm dairy wastewaters. *Water Res.* 32 (10), 3046–3054.
- Thullner, M., 2010. Comparison of bioclogging effects in saturated porous media

- within one- and two-dimensional flow systems. *Ecol. Eng.* 36, 176–196.
- Thullner, M., et al., 2002. Interaction between water flow and spatial distribution of microbial growth in a two-dimensional flow field in saturated porous media. *J. Contam. Hydrol.* 58, 169–189.
- Tombácz, E., et al., 2000. Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide. *Colloid & Polym. Sci.* 278, 337–345. Available at: <http://link.springer.com/10.1007/s003960050522>.
- Turon, C., Comas, J., Poch, M., 2009. Constructed wetland clogging: a proposal for the integration and reuse of existing knowledge. *Ecol. Eng.* 35 (12), 1710–1718. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0925857409001876>. Accessed October 29, 2014.
- Vohla, C., et al., 2011. Filter materials for phosphorus removal from wastewater in treatment wetlands—A review. *Ecol. Eng.* 37 (1), 70–89. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0925857409002419>. Accessed November 27, 2014.
- Wang, S., Peng, Y., 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.* 156 (1), 11–24. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1385894709007219>. Accessed July 11, 2014.
- Wang, W., et al., 2007. Risk assessment on disinfection by-products of drinking water of different water sources and disinfection processes. *Environ. Int.* 33 (2), 219–225. Available at: <http://www.ncbi.nlm.nih.gov/pubmed/17056115>. Accessed January 6, 2015.
- Water\_Team, E., 2012. Secure Archive for Environmental Research Data. Drinking Water Monitoring Results and Water Supply Details for Ireland. Available at: <http://erc.epa.ie/safer/resource?id=c434eae6-697f-11e3-b233-005056ae0019>.
- Widiastuti, N., et al., 2011. Removal of ammonium from greywater using natural zeolite. *Desalination* 277 (1–3), 15–23.
- Wilczak, A., et al., 1996. Occurrence of nitrification in chloraminated distribution systems. *Am. Water Works Assoc.* 88 (7).
- Zhao, L., Zhu, W., Tong, W., 2009. Clogging processes caused by biofilm growth and organic particle accumulation in lab-scale vertical flow constructed wetlands. *J. Environ. Sci.* 21 (6), 750–757. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S1001074208623360>. Accessed October 27, 2014.