



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.

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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 $10 \text{ mg NO}_3^- \text{-N L}^{-1}$ (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 $0.3 \text{ mg NH}_4^+ \text{-N L}^{-1}$ (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 $100 \mu\text{g L}^{-1}$ 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 ($\text{PO}_4^{3-}\text{-P}$) 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^- (Cengelloglu 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, $\text{PO}_4^{3-}\text{-P}$, 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, $\text{PO}_4^{3-}\text{-P}$, 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 $\text{PO}_4^{3-}\text{-P}$ 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 $t = 24 \text{ h}$, the supernatant water in each container was filtered through $0.45 \mu\text{m}$ filters and analysed for the nutrient or metal of interest. The initial and final concentrations of NO_3^- -N, NH_4^+ -N, $\text{PO}_4^{3-}\text{-P}$ 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):

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

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 ($\text{m}^3 \text{g}^{-1}$) 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 ₂ O ₃	1.26	0.8–1.9	2.9 ± 1.5	43.8	8.27	–	–	–
Al ₂ O ₃	0.21	10.0–12	7.6 ± 0.9	15.04	20.53	10	–	–
K ₂ O	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 ₂ O	–	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 ₂ O 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 Aughtinish.

^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):

$$q = K_F C_e^{1/n} \quad (2)$$

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):

$$q_e = B_1 \ln(K_t C_e) \quad (3)$$

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):

$$\Delta G^\circ = -RT \ln K \quad (4)$$

where ΔG° is the adsorption energy (kJ mol^{-1}), R is the ideal gas constant ($0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$), 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, $\text{PO}_4^{3-}\text{-P}$, $\text{NH}_4^+\text{-N}$ 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 $\text{NH}_4^+\text{-N}$ 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 $0.255 \text{ Al mg L}^{-1}$ 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 _f	
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 PO₄³⁻-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 NH₄⁺-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 NO₃⁻-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.

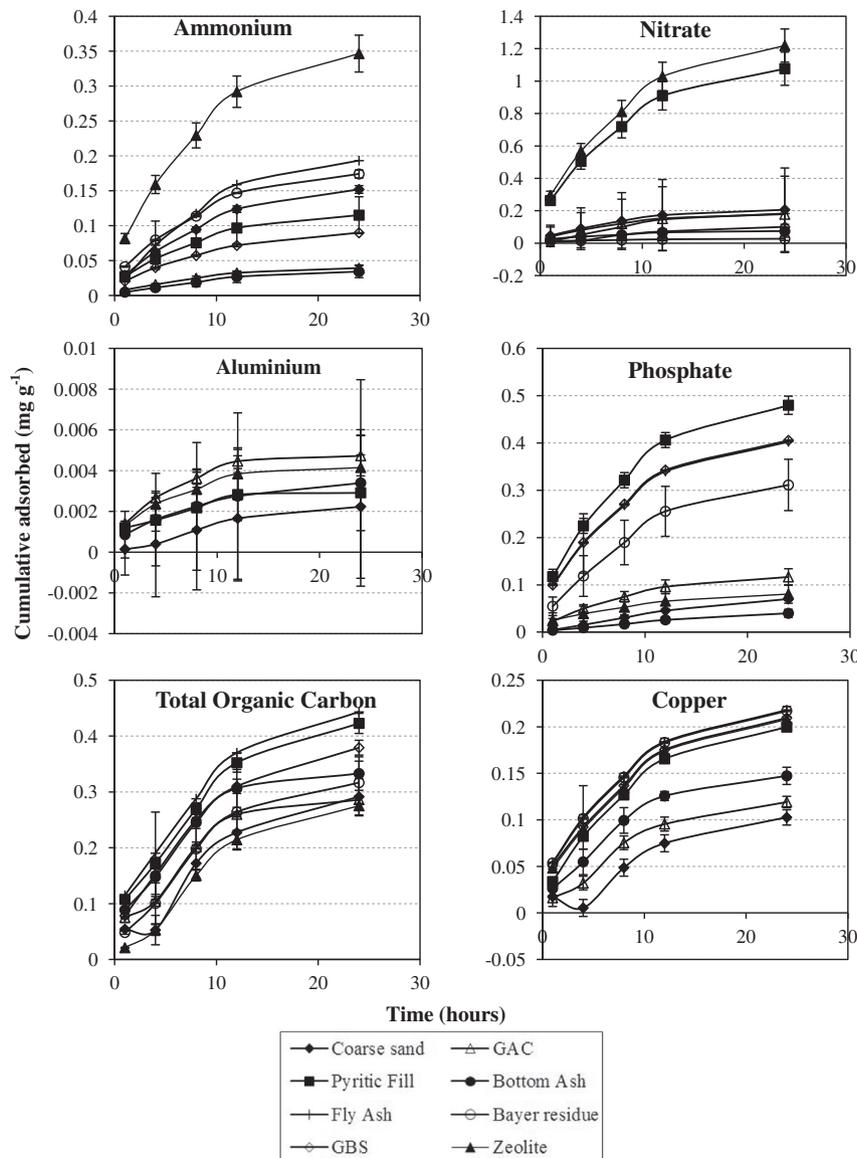


Fig. 1. Kinetic results over a 24 hour period at 19 °C.

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).

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		
	Sand	0.0031	0.0006		
Aluminium	Zeolite	0.0025	0.0012		
	Bottom ash	0.0010	0.0001		
	GAC	0.0018	0.0036		
	Pyritic fill	0.0013	0.0014		
	Zeolite	0.05	0.01		
Phosphate	GAC	0.04	0.04		
	GBS	0.21	3.61		
	Bayer residue	0.17	0.20		
	Sand	0.020	0.020		
Copper	Zeolite	0.020	0.771		
	Bottom ash	0.010	0.079		
	GAC	0.019	0.022		

pH adjustment allowed Bayer residue to slightly adsorb Al ($1 \mu\text{g g}^{-1}$), 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).

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 (ΔG°) 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
Pyritic fill	Phosphate	–32.32	–21.71	–26.18
	Copper	–33.11	–18.79	
	Aluminium		–36.62	–41.67
	Phosphate	–36.00	–15.31	
Bayer residue	Copper	–33.44	–18.66	–39.45
	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 $\text{PO}_4^{3-}\text{-P}$, 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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