



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

Title	Use of industrial by-products and natural media to adsorb nutrients, metals and organic carbon from drinking water
Author(s)	M.A.. Grace, M.G. Healy, E.Clifford
Publication Date	2015

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

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

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

7 *Civil Engineering, College of Engineering and Informatics, National University of Ireland,*
8 *Galway*

9 **Corresponding author: Tel: +353 91 495364; fax: +353 91 494507. E-mail address:*

10 mark.healy@nuigalway.ie

11 **Abstract**

12 Filtration technology is well established in the water sector but is limited by inability to
13 remove targeted contaminants, found in surface and groundwater, which can be damaging to
14 human health. This study optimises the design of filters by examining the efficacy of seven
15 media (fly ash, bottom ash, Bayer residue, granular blast furnace slag (GBS), pyritic fill,
16 granular activated carbon (GAC) and zeolite), to adsorb nitrate, ammonium, total organic
17 carbon (TOC), aluminium, copper (Cu) and phosphorus. Each medium and contaminant was
18 modelled to a Langmuir, Freundlich or Tempkin adsorption isotherm, and the impact of pH
19 and temperature (ranging from 10°C to 29°C) on their performance was quantified. As
20 retention time within water filters is important in contaminant removal, kinetic studies were
21 carried out to observe the adsorption behaviour over a 24 h period. Fly ash and Bayer residue
22 had good TOC, nutrient and Cu adsorption capacity. Granular blast furnace slag and pyritic
23 fill, previously un-investigated in water treatment, showed adsorption potential for all

24 contaminants. In general, pH or temperature adjustment was not necessary to achieve
25 effective adsorption. Kinetic studies showed that at least 60% of adsorption had occurred
26 after 8 h for all media. These media show potential for use in a multifunctional water
27 treatment unit for the targeted treatment of specific contaminants.

28 **Keywords:** Adsorption isotherms, nutrients, metals, organic pollutants, environmental quality

29 **1. Introduction**

30 The demand for clean water is increasing due to population growth, urbanisation, climate
31 change and the development of technologies such as biofuels and hydropower (Bazilian et al.
32 2011; Olsson 2013). Many conventional water treatment processes rely heavily on chemicals
33 and energy, along with capital and expertise (Shannon et al. 2008). In the developing world,
34 there is a requirement for basic water treatment facilities that are effective but do not require
35 chemical and energy-intensive technologies. The development of decontamination
36 technologies or the modification of existing, established technologies with sustainable, low-
37 cost materials, is essential to promote good human health, protect the environment and reduce
38 water scarcity (Shannon et al. 2008).

39 The World Health Organisation (WHO) (WHO 2011) has identified nitrate (NO_3^-) as one of
40 the key chemicals that can cause widespread health effects following short-term exposure,
41 and, in Ireland the maximum allowable concentration (MAC) in drinking waters is 10 mg
42 NO_3^- -N L^{-1} (SI No 278 of 2007). Ammonium (NH_4^+) is also a parameter of concern,
43 particularly where further nitrification could occur within the water supply system, leading to
44 a suppressed pH and dissolved oxygen (DO) concentration (Wilczak et al. 1996), and
45 increased NO_3^- concentrations in the water supply (Lipponen et al. 2002). In Ireland, for
46 example, the MAC is 0.3 mg NH_4^+ -N L^{-1} (SI No 278 of 2007). Irish legislation is derived
47 from European Communities (Drinking Water) (No. 2) Regulations 2007, meaning that these

48 values are applicable not only in Ireland but across Europe, and in most cases compare to US
49 regulations (USEPA 2009). Total organic carbon (TOC) is a measure of the organic carbon
50 content of the water. Irish legislation does not state a MAC, but requires action if an
51 abnormal change is noted (SI No 278 of 2007). The presence of TOC indicates a potential for
52 disinfection by-product (DBP) formation once chlorination has occurred (Gopal et al. 2007).
53 High concentrations of TOC, particularly of the humic acid form, in water will react with
54 chlorine (Cl) to form disinfection by-products, frequently referred to as ‘emerging
55 contaminants’ (EC) (WHO 2011; Gibert et al. 2013). Disinfection by-products can take
56 different formations depending on the molecules available; the most common being total
57 trihalomethanes (TTHM) (Gang et al. 2003), which above a concentration of $100 \mu\text{g L}^{-1}$ may
58 be harmful to human health (Minear & Amy 1996; SI No 278 of 2007). Removal of organic
59 matter is seen as the most effective way to prevent trihalomethane (THM) formation.
60 Therefore, it is necessary to limit the potential of formation of DBPs by removing TOC at
61 source (Minear & Amy 1996).

62 Aluminium (Al) can also be an important indication operational efficiency in a water
63 treatment plant (WTP), as, for example, its presence can be caused by poor pH control (EPA
64 2010). For example, if pH is not sufficiently controlled, coagulation may not be effective,
65 resulting in Al traces in drinking water where aluminium sulphate is used as a coagulant. It is
66 also a naturally occurring metal, and due to the perceived association between it and
67 dementia, is an important contaminant to control (Calderon 2000). The MAC is 0.2 mg Al L^{-1}
68 (SI No 278 of 2007). The presence of copper (Cu) in drinking water results primarily from
69 interior copper plumbing. However, highly aggressive or acidic raw waters may result in
70 increased Cu concentrations. Removal of Cu is also important for good human health, as it is
71 known to result in gastric irritation (WHO 2011). The MAC of Cu varies from 1.3 mg L^{-1} in
72 the USA (USEPA 2009) to 2 mg L^{-1} in Ireland (SI No 278 of 2007). Phosphorus (P) is a

73 nutrient required in food production and can enter drinking water sources through surface
74 runoff and (in certain soil types) subsurface drainage from agricultural lands (Cordell et al.
75 2009). Low phosphate-phosphorus ($\text{PO}_4^{3-}\text{-P}$) concentration in water supplies is important to
76 restrict microbial growth in distribution systems (Miettinen et al. 1997). To achieve
77 successful decontamination of raw water supplies, it is essential to reduce the concentration
78 of each contaminant to below the specified MAC.

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

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

93 Adsorption is a surface phenomenon, and can be defined as the process whereby substances
94 in solution (adsorbate) are accumulated on a suitable interface (adsorbant) (Metcalf & Eddy
95 2003). Temperature, kinetics, pH, and the nature of the adsorbate and adsorbant can affect
96 adsorption (Ali & Gupta 2006). Adsorption isotherms, such as those developed by Langmuir,

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

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

108

109 **2. Materials and Methods**

110 *2.1 Media characterisation*

111 The composition of the media, as well as their effective sizes (d_{10}), as determined using BS
112 1377-2:1990 (BSI 1990) is shown in Table 1. Coarse sand was sourced from a quarry
113 specialising in water filter media. Zeolite contains naturally occurring clinoptilolite, which is
114 a known ion exchanger (Hendricks 2011). Granular activated carbon is formed by the
115 pyrolysis of a carbonaceous substance, followed by a controlled oxidation stage to activate
116 the carbon (Cooney 1999). Bayer residue is a waste product of the Al manufacturing process
117 and is stored in large lagoons, resulting in storage and potential environmental problems
118 (Brunori et al. 2005). Bottom ash and fly ash are by-products of incineration. Pyritic fill is a
119 waste product of the construction industry. Granular blast furnace slag is a by-product of the

120 steel manufacturing industry, and is mainly used as a cement substitute in a reduced carbon
121 footprint concrete mix.

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

125 *2.2 Adsorption isotherms*

126 One gram of each media, with particle sizes as tabulated in Table 1, was placed in separate 50
127 mL capacity containers (at n=3), and was overlain by 25 mL of deionised water made up to
128 concentrations of 0, 5, 10, 20, 30, 50, 60 and 100 mg L⁻¹ of either NO₃⁻-N, NH₄⁺-N, PO₄³⁻-P,
129 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
130 of Al. Nitrate, NH₄⁺-N and PO₄³⁻-P were made up using KNO₃, NH₄Cl and K₂PO₄ reagent-
131 grade powders, respectively (APHA 1995). Total organic carbon was made up using
132 laboratory-grade humic acid, adapted from the method described in Abdul et al. (1990).
133 Solutions of Cu and Al were sourced from a supplier (Hach Lange, Germany). Each sample
134 mixture was placed on a reciprocal shaker for 24 h at 250 rpm. At t=24 h, the supernatant
135 water in each container was filtered through 0.45 µm filters and analysed for the nutrient or
136 metal of interest. The initial and final concentrations of NO₃⁻-N, NH₄⁺-N, PO₄³⁻-P and Al
137 were analysed using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland).
138 Total organic carbon was analysed using a TOC analyser (BioTector Analytical Systems Ltd)
139 and Cu was analysed using a spectrophotometer (Hach Lange, Germany). To ascertain
140 whether any of the media released metals, the 0 mg L⁻¹ samples were split and sent for metal
141 analysis by ICP-MS. The suite of metals included Al, barium, calcium (Ca), cadmium,
142 magnesium, potassium, chromium, iron (Fe), mercury, manganese, nickel, lead, boron,
143 copper and sodium.

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

$$148 \quad q_i = q_{max} \left(\frac{k_A C_e}{1 + k_A C_e} \right) \quad \text{Eqn 1}$$

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

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

$$155 \quad q = K_F C_e^{1/n} \quad \text{Eqn 2}$$

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

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

$$161 \quad q_e = B_1 \ln(K_t C_e) \quad \text{Eqn 3}$$

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

166 *2.3 Kinetics of adsorption*

167 The rate at which adsorption occurred was measured using kinetic studies. In these studies,
168 the samples were prepared as in Section 2.2, placed on the reciprocating shaker for 24 h, and
169 2.5 mL samples were taken at t=1, 4, 8, 12 and 24 h. Analysis of the data accounted for the
170 volume withdrawn at each sampling interval, and the mass adsorbed over time was
171 calculated.

172 *2.4 Effect of pH on adsorption*

173 The effect of pH on adsorption was examined by adjusting the pH of each sample before
174 shaking on the reciprocal shaker. The pH was adjusted to approximately 4 by the addition of
175 1 mol L⁻¹ HCl to the supernatant-spiked water. The unadjusted pH was between 6 and 11.
176 The samples were then shaken for 24 h at room temperature and the appropriate adsorption
177 isotherm was fitted to the data. The pH-adjusted samples were analysed with the Langmuir or
178 Freundlich isotherms, depending on best fit.

179 *2.5 Effect of temperature on adsorption*

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

186
$$\Delta G^\circ = -RT \ln K$$
 Eqn 7

187 where ΔG° is the adsorption energy (kJ mol⁻¹), R is the ideal gas constant (0.008314 kJ mol⁻¹
188 K⁻¹), T is the temperature (degrees Kelvin), and K is the Langmuir equilibrium constant. It is
189 known that the equilibrium constant of adsorption depends on the isotherm model selected,

190 and constants determined by different methods are not comparable (Liu 2009). For this
191 reason, only data fitting to the Langmuir isotherm were compared.

192 **3. Results and Discussion**

193 *3.1 Adsorption Isotherms*

194 Many of the industrial by-products examined had good potential as adsorption media for
195 nutrients and metals (Table 2). Fly ash performed well, particularly with regard to TOC,
196 $\text{PO}_4^{3-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and Cu. The presence of surface oxides on fly ash may adsorb organic
197 compounds, such as TOC (Cooney 1999). Fly ash also had a high total exchange capacity,
198 which promotes $\text{NH}_4^+\text{-N}$ and metal adsorption (Rengaraj et al. 2004; Widiastuti et al. 2011).
199 Phosphorus adsorption is indicative with the presence of binding elements such as Ca, Fe and
200 Al on fly ash (Table 1). These results are consistent with previous work (Ali & Gupta 2006;
201 Li et al. 2006). However, fly ash desorbed Al, resulting in a concentration of $0.255 \text{ Al mg L}^{-1}$
202 after shaking with deionised water for 24 h. Adsorption capacities of Cu of up to 18.8 mg g^{-1}
203 have also been observed (Visa 2012).

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

209 Granular blast furnace slag is not currently studied in terms of nutrient or metal adsorption, as
210 its sole use is in cement production. However, based on the analysis in Table 1, the high
211 cation exchange capacity and the metals present would indicate that this medium does have
212 adsorption potential. However, its tendency to solidify when saturated with water may be a

213 limiting factor in its use for water treatment. It was also observed that GBS desorbed Al after
214 shaking for 24 h, and had a final concentration of 3.6 mg L⁻¹.

215 Bottom ash did not appear to be as effective as the other industrial by-products in nutrient or
216 metal adsorption. However, pyritic fill performed well across all six contaminants (Table 2),
217 but did not rank highest in the removal of any contaminant. The composition of pyritic fill
218 may be predominantly mudstone or sandstone, depending on the location in which it is
219 quarried, so its adsorption capacity is potentially variable. However, mineral pyrite has been
220 recognised as an adsorbant, particularly regarding P, and adsorption capacities of up to 1.6 mg
221 PO₄³⁻-P g⁻¹ have been measured (Chen et al. 2014). It is known that P binding occurs in the
222 presence of Ca, Al and Fe oxides (Egemose et al. 2012), which explains the results of the
223 pyritic fill adsorption studies.

224 The performance of zeolite in NH₄⁺-N removal, at 1.04 mg g⁻¹, was lower than that observed
225 with Australian zeolite (Widiastuti et al. 2011). This could be attributed to the difference in
226 location of the mined zeolite. Ortho-phosphate adsorption was poor and shaking with NO₃⁻-N
227 resulted in desorption, meaning anion adsorption was poor. However, metal adsorption by
228 zeolite was very effective, in terms of both Cu and Al, and was due to the ion exchanging
229 capacity of zeolite (Hendricks 2011).

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

237 *3.2 Kinetics of Adsorption*

238 Figure 1 shows the kinetic results for the contaminants and media tested. All the media
239 adsorbed 60% of the NH_4^+ -N within 8 h of contact. Nitrate, Al and P adsorption followed the
240 same trend. Copper adsorption was slightly different, in that for zeolite, pyritic fill, GBS,
241 Bayer residue and fly ash, almost all adsorption had taken place after 4 h. Total organic
242 carbon adsorption by fly ash occurred almost immediately, with 96% of adsorption occurring
243 within one hour. There was a decrease in the rate of adsorption for all media after 8 h. This
244 was most likely due to adsorption sites becoming unavailable. This was to be expected, as
245 initially, the concentration of the adsorbate is high, and all sites are vacant (Widiastuti et al.
246 2011).

247 *3.3 Effect of pH on adsorption*

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

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

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

265 pH adjustment allowed Bayer residue to slightly adsorb Al ($1 \mu\text{g g}^{-1}$), which desorbed at an
266 unadjusted pH. pH adjustment had a tendency to improve Al adsorption except in the case of
267 GAC, where the adsorption capacity was halved with pH adjustment. pH adjustment was not
268 necessary to improve PO_4^{3-} -P removal, except with bottom ash, where it improved
269 adsorption. Previous studies have noted a positive relationship between pH and retention
270 capacity for P with rates of adsorption increasing with pH (Egemose et al. 2012). Copper
271 adsorption proved to be more effective at a unadjusted pH, reflecting other studies, where it
272 has been found that adsorption can increase as much as 85% when the pH is increased from
273 2.5 to 8 (Chen et al. 1996).

274 *3.4 Effect of temperature on adsorption*

275 Table 4 displays the data from the thermodynamic study. The data analysis was limited due to
276 the use of the Langmuir adsorption isotherm to calculate the equilibrium constant used in Eqn
277 7. Therefore, data not modelled to Langmuir across more than one temperature range were
278 excluded from the table for clarity. The negative values of the adsorption energy (ΔG°)
279 indicate that the adsorption process was of a spontaneous nature, and heat energy was
280 released, for each set of reactions modelled (Widiastuti et al. 2011). Coarse sand adsorption is
281 more energetically favourable at lower temperatures for both NH_4^+ -N and Cu, as indicated by
282 decreasing values at lower temperatures. Zeolite adsorption was more energetically
283 favourable with increasing temperature for PO_4^{3-} -P, similar to earlier studies investigating
284 zeolite adsorption of nutrients (Widiastuti et al. 2011). It has been noted that Cu adsorption is
285 not radically affected by temperature (Gündoğan et al. 2004). However, the results of the

286 current study indicate that it is more favourable at a lower temperature – a positive result for
287 a filtration unit that would most likely be located outdoors. Granular activated carbon
288 adsorption tended to be more energetically favourable at lower temperatures, as expected, as
289 adsorption onto carbon is likely to be lower as the temperature increases (Cooney 1999). For
290 pyritic fill, the lower temperatures were also more effective.

291 *3.5 Impact of adsorption isotherm studies on filter design*

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

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

309

310 **4. Conclusions**

311 The main conclusions from the study were:

- 312 • Fly ash and Bayer residue, which have been previously identified as having
313 adsorption potential, were shown in this study to successfully adsorb TOC, nutrients
314 and Cu, and thus, improving environmental quality by re-using industrial waste
315 products for pollution control.
- 316 • Granular blast furnace slag and pyritic fill have good adsorption potential (unreported
317 to date). Granular activated carbon and zeolite, known ion exchangers and adsorptive
318 media, proved successful with each contaminant analysed in this study.
- 319 • Improved adsorption occurs at lower pH for TOC. However, for other water
320 parameters, depending on the media, pH adjustment is not necessary for optimal
321 adsorption. In this study, there was no instance in which pH adjustment was necessary
322 for adsorption; therefore adjusting pH is unlikely to be a cost-effective intervention to
323 improve adsorption kinetics. In the case of Cu and $\text{PO}_4^{3-}\text{-P}$, it was found that optimal
324 adsorption occurred at the unadjusted pH.
- 325 • Kinetic adsorption studies showed that at least 60% of adsorption (where adsorption
326 occurred) had taken place after eight hours. This would be useful in designing a filter
327 using these media, as the retention time can be adjusted to achieve the required
328 adsorption.

329 **Acknowledgements**

330 The authors would like to acknowledge the financial support of the Environmental Protection
331 Agency (EPA).

332

333 **References**

- 334 Abdul, A.S., Gibson, T.L. & Rai, D.N., 1990. Use of Humic Acid Solution To Remove
335 Organic Contaminants from Hydrogeologic Systems. *Environmental science &*
336 *technology*, 333(24), pp.333–337.
- 337 Ali, I. & Gupta, V.K., 2006. Advances in water treatment by adsorption technology. *Nature*
338 *Protocols*, 1(6), pp.2661–7.
- 339 APHA, 1995. *Standard methods for the examination of water and wastewater*, Washington:
340 American Public Health Association (APHA).
- 341 Arias, C.A., Del Bubba, M. & Brix, H., 2001. Phosphorus removal by sands for use as media
342 in subsurface flow constructed reed beds. *Water Research*, 35(5), pp.1159–68.
- 343 Bazilian, M. et al., 2011. Considering the energy, water and food nexus: Towards an
344 integrated modelling approach. *Energy Policy*, 39(12), pp.7896–7906.
- 345 British Standards Institution, 1990. *British standard methods of test for soils for civil*
346 *engineering purposes. Determination of particle size distribution. BS 1377*, London:
347 BSI.
- 348 Brunori, C. et al., 2005. Reuse of a treated red mud bauxite waste: studies on environmental
349 compatibility. *Journal of hazardous materials*, 117(1), pp.55–63.
- 350 Calderon, R.L., 2000. The epidemiology of chemical contaminants of drinking water. *Food*
351 *and chemical toxicology : an international journal published for the British Industrial*
352 *Biological Research Association*, 38(1 Suppl), pp.S13–20.
- 353 Cengeloglu, Y. et al., 2006. Removal of nitrate from aqueous solution by using red mud.
354 *Separation and Purification Technology*, 51(3), pp.374–378.
- 355 Chen, J., Yiacoumi, S. & Blaydes, T.G., 1996. Equilibrium and kinetic studies of copper
356 adsorption by activated carbon. *Separations Technology*, 6(2), pp.133–146.
- 357 Chen, T.-H. et al., 2014. Phosphorus removal from aqueous solutions containing low
358 concentration of phosphate using pyrite calcinate sorbent. *International Journal of*
359 *Environmental Science and Technology*.
- 360 Cooney, D.O., 1999. *Adsorption design for wastewater treatment*, FL: CRC Lewis.
- 361 Cordell, D., Drangert, J.-O. & White, S., 2009. The story of phosphorus: Global food security
362 and food for thought. *Global Environmental Change*, 19(2), pp.292–305.
- 363 Egemose, S. et al., 2012. Crushed Concrete as a Phosphate Binding Material: A potential new
364 management tool. *Journal of Environmental Quality*, (41), pp.647–653.
- 365 EPA, 2010. *The Provision and Quality of Drinking Water in Ireland*,

- 366 EPA, 1995. *Water Treatment Manuals: Filtration*,
- 367 Foo, K.Y. & Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems.
368 *Chemical Engineering Journal*, 156(1), pp.2–10.
- 369 Gang, D., Clevenger, T.E. & Banerji, S.K., 2003. Relationship of chlorine decay and THMs
370 formation to NOM size. *Journal of hazardous materials*, 96(1), pp.1–12.
- 371 Gibert, O. et al., 2013. Fractionation and removal of dissolved organic carbon in a full-scale
372 granular activated carbon filter used for drinking water production. *Water research*,
373 47(8), pp.2821–9.
- 374 Gopal, K. et al., 2007. Chlorination byproducts, their toxicodynamics and removal from
375 drinking water. *Journal of hazardous materials*, 140(1-2), pp.1–6.
- 376 Gündoğan, R., Acemioğlu, B. & Alma, M.H., 2004. Copper (II) adsorption from aqueous
377 solution by herbaceous peat. *Journal of Colloid and Interface Science*, 269(2), pp.303–
378 309.
- 379 Hendricks, D., 2011. *Fundamentals of Water Treatment Unit Processes* 1st ed., CRC Press.
- 380 Khan, A.A. & Singh, R., 1987. Adsorption Thermodynamics of Carbofuran on Sn(IV)
381 Arsenosilicate on H, Na and Ca forms.pdf. *Colloids and Surfaces*, 24, pp.33–42.
- 382 Li, Y. et al., 2006. Phosphate removal from aqueous solutions using raw and activated red
383 mud and fly ash. *Journal of hazardous materials*, 137(1), pp.374–83.
- 384 Lipponen, M.T.T., Suutari, M.H. & Martikainen, P.J., 2002. Occurrence of nitrifying bacteria
385 and nitrification in Finnish drinking water distribution systems. *Water research*, 36(17),
386 pp.4319–29.
- 387 Liu, Y., 2009. Is the Free Energy Change of Adsorption Correctly Calculated? *Journal of*
388 *Chemical & Engineering Data*, 54(7), pp.1981–1985.
- 389 Lopez, E. et al., 1998. Adsorbent properties of red mud and its use for wastewater
390 treatment.pdf. *Water Research*, 32(4), pp.1314 – 1322.
- 391 McBride, M., 2000. Chemisorption and precipitation reactions. In *Handbook of Soil Science*.
392 Boca Raton, FL: CRC Press, pp. B264–B302.
- 393 Mehlich, A., 1984. Mehlich-3 soil test extractant: A modification of Mehlich-2 extractant.
394 *Commun. Soil Sci Plant Anal*, 15, p.14091416.
- 395 Metcalf & Eddy, 2003. *Wastewater Engineering Treatment and Reuse* 4th ed., McGraw Hill.
- 396 Miettinen, I.T., Vartiainen, T. & Martikainen, P.J., 1997. Phosphorus and Bacterial Growth in
397 Drinking Water. *Applied and Environmental Microbiology*, 63(8).
- 398 Minear, R.A. & Amy, G.L., 1996. *Disinfection by-products in water treatment: the chemistry*
399 *of their formation and control*, FL: CRC Press.

- 400 Olsson, G., 2013. Water, energy and food interactions—Challenges and opportunities.
401 *Frontiers of Environmental Science & Engineering*, 7(5), pp.787–793.
- 402 Peña, Y.P. De et al., 2000. Synthetic zeolites as sorbent material for on-line preconcentration
403 of copper traces and its determination using flame atomic absorption spectrometry.
404 *Analytica Chimica Acta*, 403(1-2), pp.249–258.
- 405 Ross, D., 1995. Recommended soils test for determining exchange capacity. In
406 *Recommended soil testing procedures for the northeastern United States*. pp. 62–69.
- 407 Shannon, M. a et al., 2008. Science and technology for water purification in the coming
408 decades. *Nature*, 452(7185), pp.301–10.
- 409 SI No 278 of, 2007. *European Communities (Drinking Water) (No. 2) Regulations 2007*,
410 Available at:
411 <http://www.environ.ie/en/Legislation/Environment/Water/FileDownload,14547,en.pdf>.
- 412 USEPA, 2009. *National Primary Drinking Water Regulations C. O. F. Regulations*, ed.,
413 Environmental Protection Agency.
- 414 Vijayaraghavan, K. et al., 2006. Biosorption of nickel(II) ions onto *Sargassum wightii*:
415 application of two-parameter and three-parameter isotherm models. *Journal of*
416 *hazardous materials*, 133(1-3), pp.304–8.
- 417 Visa, M., 2012. Applied Surface Science Tailoring fly ash activated with bentonite as
418 adsorbent for complex wastewater treatment. *Applied surface science*, 263, pp.753–762.
- 419 WHO, 2011. *WHO guidelines for drinking-water quality*.
- 420 Widiastuti, N. et al., 2011. Removal of ammonium from greywater using natural zeolite.
421 *Desalination*, 277(1-3), pp.15–23.
- 422 Wilczak, A. et al., 1996. Occurrence of nitrification in chloraminated distribution systems.
423 *American Water Works Association*, 88(7).
- 424
- 425
- 426
- 427
- 428
- 429

430 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 ^g	GAC ^h
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 ⁱ	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	18280	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

431 ^a Irwin's Quality Aggregates; ^b Zeolite Ireland Ltd; ^c Sandberg LLP; ^d Rusal Aughinish; ^e ESB Energy
432 International Moneypoint; ^f Ecocem Ireland Ltd; ^g ESB Energy International Moneypoint; ^h Indo German
433 Carbons Ltd
434 ⁱ Loss on Ignition

435

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	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	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

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

Media	Contaminant	$\Delta G @ 10^\circ\text{C}$	$\Delta G @ 19^\circ\text{C}$	$\Delta G @ 29^\circ\text{C}$
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

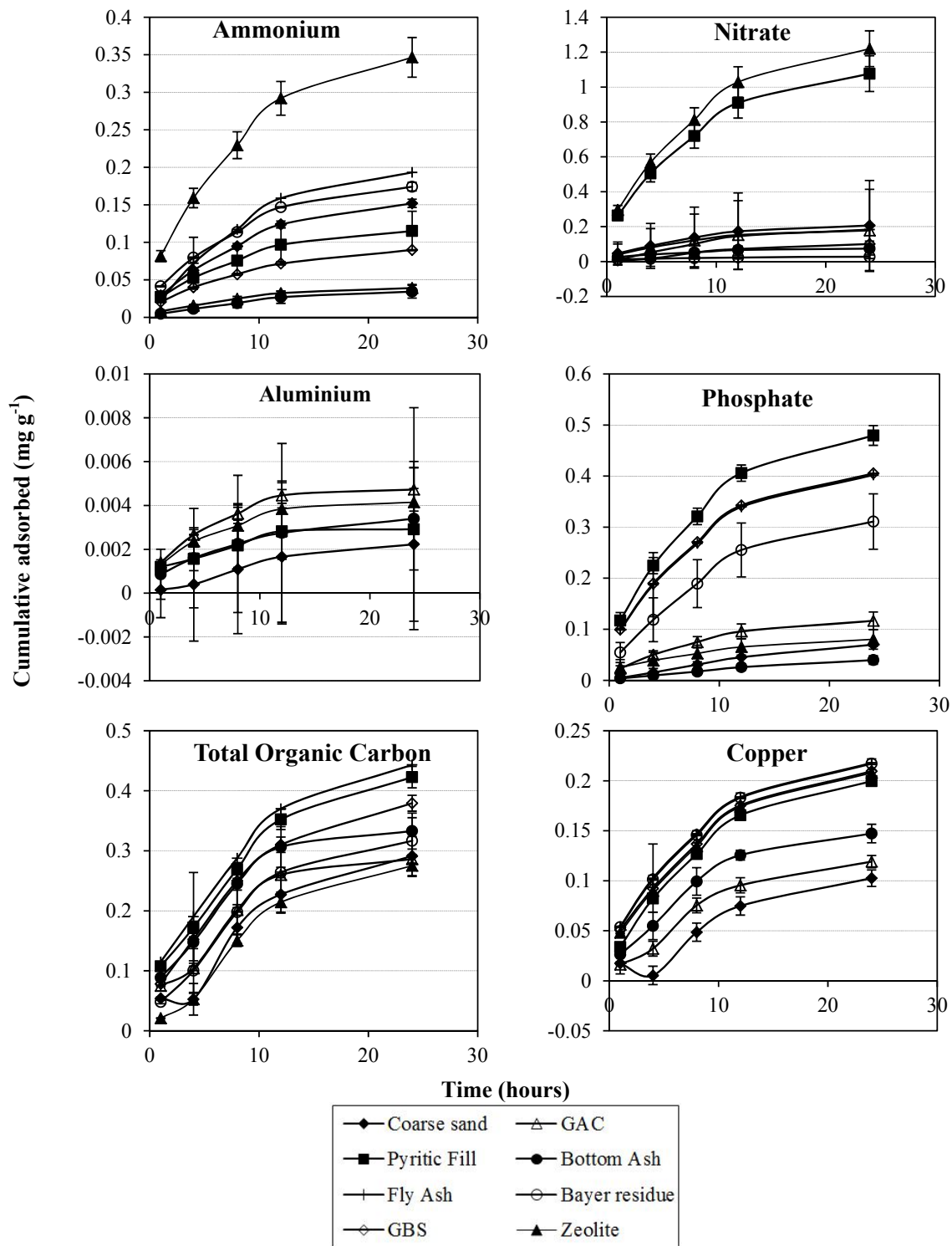


Figure 1: Kinetic results over a 24 hour period at 19°C

