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1 **Characterization of aluminium-based water treatment residual for potential**  
2 **phosphorus removal in engineered wetlands**

3  
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30 **Abstract**

31 Aluminium-based water treatment residual (Al-WTR) is the most widely generated residual  
32 from water treatment facilities worldwide. It is regarded as a by-product of no reuse  
33 potential and landfilled. This study assessed Al-WTR as a potential phosphate-removing  
34 substrate in engineered wetlands for wastewater treatment. Results indicate the specific  
35 surface area ranged from 28.0 m<sup>2</sup> g<sup>-1</sup> to 41.4 m<sup>2</sup> g<sup>-1</sup> and this increased with increasing  
36 particle size. X-ray Diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and  
37 energy-dispersive X-ray spectroscopy all indicate that the Al-WTR is mainly composed of  
38 amorphous aluminium which influences its phosphorus (P) adsorption capacity. The pH  
39 and electrical conductivity ranged from 5.9 - 6.0 and 0.104 dS m<sup>-1</sup> - 0.140 dS m<sup>-1</sup>  
40 respectively, and both showed that it should suitably support plant growth. Batch tests  
41 showed a maximum P adsorption capacity of 31.9 mg-P g<sup>-1</sup> and significant P removal was  
42 achieved in column tests. Overall, results showed that Al-WTR can be a low-cost, easily  
43 and locally available substrate for enhanced P removal in engineered wetlands and it carries  
44 the benefits of reuse of a by-product that promotes sustainability.

45

46

47 **Capsule:**

48 **Aluminium-based water treatment residual can be used for enhancing phosphorus**  
49 **removal in engineered wetlands! Don't landfill it.**

50 **Key words:** Adsorption capacity; engineered wetlands; water treatment residual;  
51 phosphorus removal; wastewater treatment

## 52 **1. Introduction**

53  
54 There has been a substantial evolution in the use of engineered wetland systems as  
55 means of decentralized wastewater treatment. Engineered wetland systems have now  
56 become an effective means of advanced wastewater treatment with several integration of  
57 hydraulic and/or aeration machinery to increase their performance capabilities. However,  
58 one issue that is still generating much research attention is efficient phosphorus (P)  
59 removal.

60 The role of P as a major limiting nutrient in eutrophication of surface waters, and the  
61 need for its efficient removal from wastewaters before discharge into water courses is well  
62 understood. P removal in wetland systems can occur through a combination of several  
63 processes, but adsorption and precipitation within the substrate are widely acknowledged  
64 and known to play the greatest role. Therefore, to ensure efficient P removal, it is important  
65 to use substrates with high P removal capacity and suitable physicochemical properties. A  
66 review of several low-cost adsorbent materials tested for their potential for enhancing P  
67 removal has been published (Westholm, 2006). The use of such materials as substrates in  
68 wetland and filter systems to enhance P removal is now an emerging and promising trend.

69 A low-cost material that can enhance P removal is aluminium-based water treatment  
70 residual (Al-WTR), a by-product of water treatment facilities that use aluminium salts as  
71 coagulant. It is the most widely generated water treatment residual (WTR) worldwide, and  
72 is mostly landfilled at huge costs since it is regarded as a by-product of little known reuse

73 value. However, the chemical composition of Al-WTR gives it a highly reactive surface  
74 and a strong affinity for P (Elliot et al., 2002; Ippolito et al., 2003; Makris et al., 2005;  
75 Babatunde and Zhao, 2007). In addition, Al-WTR is an easily available by-product in  
76 towns, cities and metropolis regions worldwide that utilize surface waters as a drinking  
77 water source. And since Al-WTR is derived from residual of treatment of raw water which  
78 contains mainly turbidity, colour, suspended clays and humic substances, it is unlikely to  
79 contain a substantial quantity of toxic substances. Knowledge of its physicochemical  
80 characteristics and P adsorption capacity would be very useful for practical guidance in  
81 utilizing its P adsorption capacity and gaining future acceptance for Al-WTR based  
82 engineered wetland system.

83

## 84 **2. Materials and methods**

85

### 86 **2.1 Al-WTR**

87 Al-WTR was obtained from the largest water treatment plant in Ireland, located in Co.  
88 Kildare, Ireland. The plant uses aluminium sulphate for reservoir water flocculation, and it  
89 generates 45-75 tons of Al-WTR daily. The Al-WTR is disposed off in landfills at an  
90 average cost of €130 per ton. The Al-WTR was collected fresh and transported to the  
91 laboratory where they were securely kept for analysis and subsequent tests.

92

### 93 **2.2 Physical and chemical properties**

94

#### 95 *2.2.1 Physical properties*

96

97 The Al-WTR was air-dried and ground to pass a 2-mm mesh sieve. Thereafter, specific  
98 physical properties were determined as follows. Porosity was determined from the amount

99 of water needed to saturate a known volume of the Al-WTR while bulk density was  
 100 determined from the volume of water displaced by a known mass of the Al-WTR sample  
 101 (n=5). Surface area was measured using nitrogen Brunauer Emmett Teller (BET) isotherms  
 102 on a Micromeritics Gemini 2375 volumetric analyzer. Total pore volume was calculated  
 103 from the amount of vapour absorbed at a relative pressure ( $P/P^o$ , where  $P$  is the equilibrium  
 104 pressure and  $P^o$  is the saturation pressure of the adsorbate) close to unity. Micropore  
 105 volume of the Al-WTR was calculated using the Dubinin-Radushkevich (DR) model of  
 106 micropore filling, which is based on the Polanyi's concept of characteristic curve to  
 107 describe adsorption into micropores (Gregg and Sing, 1982). The characteristic curve can  
 108 be expressed as in Eq. (1).

$$109 \quad \frac{V}{V^o} = \exp\left(-\frac{A}{\varepsilon\beta}\right)^2 \quad \text{Eq. (1)}$$

110 where  $V$  is the volume adsorbed at the relative pressure,  $V^o$  is the micropore volume,  $A$  is  
 111 the affinity or differential free energy of adsorption  $\left[ A = RT \ln\left(\frac{P^o}{P}\right) \right]$ ,  $\varepsilon$  is the  
 112 characteristic free energy of adsorption for a given system (equals  $A$  when  $V/V^o = 1/e =$   
 113  $0.368$ , where  $e$  is the base of natural logarithm) and  $\beta$  is the similarity factor. Substituting  
 114 for the value of  $A$  in Eq. (1) and taking logarithm gives the known DR equation as Eq. (2)

$$115 \quad \log V = \log V^o - D \log^2 \left[ \frac{P^o}{P} \right] \quad \text{Eq. (2)}$$

116 where  $D$  is a constant characteristic of the adsorbent structure related to the characteristic  
 117 energy according to Eq. (3)

119

$$D = \frac{R^2 T^2 \ln 10}{\varepsilon^2 \beta^2} \quad \text{Eq. (3)}$$

As a first approximation, the micropore volume can be determined directly from the BET-  
N<sub>2</sub> adsorption isotherm, and it corresponds to the volume of gas adsorbed at  $P/P^0$  of 0.15  
(Gregg, 1982). However, from Eq. (2), a graph of  $\log V$  against  $\log^2 (P^0/P)$  will give  
micropore volume of the Al-WTR,  $V^0$ , as the intercept when extrapolated from the linear  
portion of the DR plot, assuming that the pores are filled with the liquid adsorbent  
(Echeveria, 1999). The particle size distribution (PSD) of the Al-WTR was examined using  
standard sieve analysis technique and the values of  $d_{10}$  (the diameter corresponding to  
percents finer than 10%) and  $d_{60}$  (the diameter corresponding to percents finer than 60%)  
and the uniformity coefficient (UC) were determined. Surface morphology and  
microstructure were examined using scanning electron microscopy (SEM, JEOL JSM  
5510) to visualize inner porosity, surface properties, and potential environment for biofilm  
bacteria. Roger (2000) noted that biofilms bacteria need a potential environment typically  
1-3  $\mu\text{m}$ . The SEM was further combined with EDX (energy dispersive X-ray, INCAx-Sight  
model 6587, Oxford instruments, UK) to determine the composition and relative  
distribution of elements particularly on the Al-WTR surface. X-ray diffraction of randomly  
oriented powders of the samples was carried out on a Phillips PW 1050 diffractometer  
using monochromated CuK $\alpha$  radiation, operating at 40 kV and 30 mA, from 3° to 75° 2 $\theta$ ,  
with a scanning step of 0.02° at 1° per minute while the FTIR spectra was measured using  
the KBr wafer technique in a FTIR spectrometer (Excalibur series).

### 143 2.2.2 Chemical properties

144

145 Chemical properties were determined as follows: pH was taken as the pH of a 0.01 M  
146 CaCl<sub>2</sub> solution of the Al-WTR (McLean, 1982) (particle size < 2 mm, Al-WTR: solution  
147 ratio of 1:10). Loss of ignition (LOI) was determined in accordance with standards (British  
148 Standards Institution, 1990). Electrical conductivity (EC) was measured at 25°C using a  
149 Radiometer CDM83 electrical conductivity meter (Smith and Doran, 1996). The elemental  
150 metal composition was carried out by carefully weighing ca. 0.025 g of the air-dried Al-  
151 WTR samples (particle size < 2 mm) into clean TMF vessels followed by addition of 4 ml  
152 HNO<sub>3</sub> + 200 µl HF + 4 ml H<sub>2</sub>O. Samples were then digested using a low volume microwave  
153 digestion technique (Sandroni et al., 2003), and the digestates analysed for dissolved metals  
154 using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Specific anions (Cl<sup>-</sup>,  
155 SO<sub>4</sub><sup>2-</sup>, SiO<sub>4</sub><sup>2-</sup>) and humic acid (expressed as total organic carbon (TOC)) of the Al-WTR  
156 were determined separately as described in Yang et al. (2006).

157

## 158 2.3 P adsorption

### 159 2.3.1 Adsorption isotherm experiments

160 P adsorption behavior and maxima, and effects of adsorbent dosage, equilibration time  
161 and initial P concentration on P adsorption were investigated. For determining equilibrium  
162 adsorption time, different masses of Al-WTR (0.5, 1.0, 1.5 and 2.0 g) were shaken with 100  
163 ml each of P solutions (5, 30 and 120 mg-P L<sup>-1</sup>) contained in 250ml bottles for 1 to 120  
164 hours using a rotary shaker. For the optimal dosage determination, a wide range of  
165 adsorbent masses (0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0 and 3.0 g) were shaken with 100 ml  
166 each of four P solutions (5, 30, 120 and 360 mg L<sup>-1</sup>) contained in 250 ml bottles for 48



167 hours (predetermined equilibration time) using a rotary shaker. Finally, batch experiments  
168 were conducted to determine the P adsorption capacity and adsorption parameters. 1.0 g of  
169 the Al-WTR was equilibrated with 100 ml of varying P concentrations ranging from 0 to  
170 360 mg-P L<sup>-1</sup> for 48 hours at different pH levels (pH 4, 7 and 9). Data obtained were  
171 analyzed using the Langmuir and Freundlich models to determine the relevant adsorption  
172 parameters. In all cases, P solutions were made up from stock standard KH<sub>2</sub>PO<sub>4</sub> solution  
173 while P analysis was carried out using a HACH DR/2400 spectrophotometer according to  
174 standard operating procedures.

175

### 176 *2.3.2 Column experiments*

177 Five columns using different proportions of Al-WTR as substrate were set up as shown in  
178 Fig.1 (only one representative unit shown). The substrate layout and design of all the  
179 columns is presented in Table 1. The columns were used to simulate sub-surface vertical  
180 flow engineered wetland systems. Similar configuration utilizing columns to depict  
181 laboratory scale wetland systems are used in such laboratory scale studies (Sun et al., 2005  
182 and Lee and Scholz, 2006). The columns were fed with wastewater collected periodically  
183 from the secondary holding tank of an animal research farm, and it had a P-PO<sub>4</sub><sup>3-</sup>  
184 concentration of about 48-90 mg-P L<sup>-1</sup>. On being brought to the laboratory, the wastewater  
185 was allowed to settle overnight and the supernatant was then collected and used. However,  
186 the supernatant was sometimes diluted with tap water or spiked with artificial P solution to  
187 give a range of P concentrations used to examine the response and individual P removal  
188 behaviour of the columns. Accordingly, influent P concentration into the system ranged  
189 from 18.1 to 346.1 mg-P L<sup>-1</sup>. This range was chosen to accommodate possible levels of P in

190 both domestic and industrial wastewaters as well as a worst case scenario. Inflow and  
191 outflow were regulated by peristaltic pumps and samples were collected over a period of 25  
192 weeks. Only the analysis for reactive P (RP, conducted on unfiltered samples) and soluble  
193 reactive P (SRP, conducted on filtered samples using a 0.45  $\mu\text{m}$  membrane filter) are  
194 presented and discussed. RP is a measure of reactive orthophosphate present in the  
195 wastewater and which is either soluble or attached to suspended solids while SRP is a  
196 measure of soluble orthophosphate, the filterable (soluble, inorganic) fraction of  
197 phosphorus and the form directly taken up by plant cells. SRP can thus be viewed as the  
198 soluble component of the RP. It is necessary to distinguish between these two analytical  
199 forms of P so as to point out the role of the Al-WTR in the systems. In the systems, RP can  
200 be removed by both filtration and/or adsorption on the Al-WTR (i.e. filtration of RP  
201 attached to the solid particles and adsorption of the soluble component of the RP which is  
202 the SRP), whereas SRP would be solely removed by adsorption on the Al-WTR. Therefore,  
203 the contribution of the Al-WTR to the overall P removal in the systems can be determined.  
204 P removal efficiency data were plotted as a function of the pore volumes to reduce the  
205 effect of flow variation if the data is plotted as a function of time. The plot was also used to  
206 examine individual P removal in the systems.

207

[INSERT FIG 1 HERE]

209

[INSERT TABLE 1 HERE]

211

212

213 2.3.3 Modelling P removal in subsurface flow system

214 Generally, wetland systems are assumed to be attached growth biological plug flow  
215 reactors operating with first-order kinetics. Therefore, models of the treatment performance  
216 are often based on biological removal kinetics which assumes an exponential decrease in  
217 pollutant concentration from the inlet to the outlet. Phosphorus removal kinetics are equally  
218 suggested to be describable by such a relationship (Rousseau et al., 2004, Kadlec and  
219 Knight, 1996) and the rate of removal is then calculated assuming first-order plug-flow  
220 system. However, it has been reported that a modified first-order model (Eq. (4)) can be  
221 used to describe the relationship between P removal and hydraulic retention time (HRT)  
222 (Kadlec and Knight, 1996; Tang et al., 2008).

223

$$224 \quad C_e = (C_i - C^*) \exp\left(\frac{-kHRT}{h}\right) + C^* \quad \text{Eq. (4)}$$

225 From Eq. (4), the background concentration ( $C^*$ , in  $\text{mg L}^{-1}$ ) is often depleted (Kadlec and  
226 Knight, 1996) leading to a simplified equation (Eq. (5)).

227

$$228 \quad C_e = C_i \exp\left(\frac{-kHRT}{h}\right) \quad \text{Eq. (5)}$$

229

230 where  $C_i$  and  $C_e$  are influent and effluent P concentrations respectively, in  $\text{mg L}^{-1}$ ,  $k$  is the  
231 removal rate constant ( $\text{m day}^{-1}$ ), HRT is the hydraulic retention time (day), and  $h$  is the  
232 effective depth of the wetland. Eq. (5) was fitted to the column data and the mean values of  
233  $k$  were determined at two different HRT's. Similar approach was used by Tang et al. (2008)

234 to examine the relationship between P removal and HRT using data from laboratory scale  
235 vertical subsurface wetland systems.

236

### 237 **3. Results and discussion**

238

#### 239 **3.1 Physical properties**

240

241 The Al-WTR had a bulk density of  $1.18 \pm 0.11 \text{ g cm}^{-3}$  and a porosity of 45%, both of  
242 which are comparable to values of 0.7 to  $1.83 \text{ g cm}^{-3}$  (bulk density) and 30 to 54.4%  
243 (porosity) reported in literature for potential candidate materials for wetland systems  
244 (Roger, 2000; Drizo et al., 1999; Del Bubba et al., 2003). From the PSD, the values of  $d_{10}$   
245 and  $d_{60}$  and UC were computed to be 0.5, 1.8 and 3.6 respectively and these are consistent  
246 with several guidelines for securing adequate hydraulic conductivity and minimizing risk of  
247 clogging (Vymazal, 1998; IWA, 2000). Qualitative assessment of the elemental distribution  
248 on the surface of the Al-WTR by the SEM-EDX showed the predominance of aluminium  
249 and this was expected to highly influence its P adsorption ability (See Fig. 2 (top)). Ippolito  
250 et al. (2003) found similar results using SEM-EDX. The microstructure of the Al-WTR as  
251 examined by SEM (Fig. 2 (bottom)) suggests a 'rough' surface that would be ideal for  
252 biofilm growth and in particular, the presence of  $2 \text{ }\mu\text{m}$  pores. Roger (2000) noted that  
253 biofilms bacteria need a potential environment typically 1-3  $\mu\text{m}$ . The samples were further  
254 analyzed using  $\text{N}_2$  adsorption. The  $\text{N}_2$  adsorption isotherm plot obtained beared a strong  
255 resemblance to the IUPAC type IV isotherm, with a  $\text{H}_2$  type of hysteresis loop. The specific  
256 surface area (SSA) ranged from 28.0 to  $41.4 \text{ m}^2\text{g}^{-1}$ . Makris et al. (2004) found that WTRs  
257 can have SSA up to  $105 \text{ m}^2 \text{ g}^{-1}$ . Furthermore, the SSA of the Al-WTR was found to increase  
258 with increasing particle size suggesting large inner porosity in the grains.

[INSERT FIG 2 HERE]

259

260

261 In comparison to the range of SSA of other candidate wetland materials reported in  
262 literature such as 2.6-3.9 m<sup>2</sup> g<sup>-1</sup> (Roger, 2000) and 6.8-31.4 m<sup>2</sup> g<sup>-1</sup> (Drizo et al., 1999), the  
263 Al-WTR used herein can be seen to have a comparatively higher SSA. This further relates  
264 to having adequate surface area for biofilm growth and attachment. The micropore,  
265 mesopore and pore volumes of the Al-WTR were determined to be 0.0125 cm<sup>3</sup> g<sup>-1</sup>, 0.0210  
266 cm<sup>3</sup> g<sup>-1</sup> and 0.0410 cm<sup>3</sup> g<sup>-1</sup> respectively. The mesopore volume was about 1.7 times the  
267 micropore volume and the mesopores also account for about 51.2% of the entire pore  
268 volume of the Al-WTR. The XRD diffraction pattern did not reveal any sharp diffraction  
269 characteristic peak over a broad range of *d*-spacings (10-80°, 2Θ). This indicates poorly  
270 ordered particles within the Al-WTR and it also illustrates that, even though the SEM-EDX  
271 results highlight the predominance of aluminium in the Al-WTR, it is likely to be  
272 amorphous aluminium. This observation is also in agreement with other authors (Dayton  
273 and Basta, 2001; Makris and O'Connor, 2007). Similarly, the FTIR spectrum ranging from  
274 500 to 4000 cm<sup>-1</sup> did not provide clear information regarding peaks.

275

### 276 **3.2 Chemical properties**

277 The electrical conductivity of the Al-WTR ranged from 0.104 to 0.140 dS m<sup>-1</sup>, and thus  
278 the Al-WTR can be considered nonsaline (Smith and Doran, 1996). The EC of the Al-WTR  
279 is also well below the 4 dSm<sup>-1</sup> associated with reduced plant growth due to salinity (Dayton  
280 and Basta, 2001). It is important to note that microbial mediated processes, which are the  
281 basis of wetland operations are very sensitive to soil EC, hence the importance of EC. The

282 Al-WTR had a residual pH in the range of 5.9 – 6.0, which was within typical pH range of  
283 5.1 to 8.0 for water treatment residuals reported by Dayton and Basta (2001). The main  
284 concern about pH effect is on Al toxicity due to the quantity of aluminium present in the  
285 Al-WTR. However, given the circumneutral pH of the Al-WTR, it is expected that this will  
286 pose no problem. It is well known that Al speciation is highly pH dependent, with the  
287 soluble species present in higher concentrations at pH levels less than 6. In a recent study,  
288 Mortula et al. (2007) reported that P adsorption can make physical and chemical changes to  
289 Al-WTR and the changes can have an effect on the leachability of Al-WTRs. It was further  
290 reported that P treatment using oven-dried Al-WTR showed considerable reduction in  
291 aluminium leaching while none of the WTRs released high amounts of aluminium during  
292 the tests to assess aluminium leaching in surface water. The pH is also equally important in  
293 determining the relative predominance and activity of different microbial groups,  
294 particularly with regards to microbial mediated processes such as nitrification and  
295 denitrification. For instance, the optimum pH range for denitrifiers is reported to be  
296 between pH 6 and 8 (Vymazal, 2007).

297 Mean TOC of the Al-WTR averaged 97.5 mg g<sup>-1</sup> (Yang et al., 2006), while LOI  
298 averaged 49.4%. These values may be attributed to humic substances contained in the raw  
299 water being treated. The presence of humic substances in raw water being treated has also  
300 been reported by other authors (Dormany et al., 2002). The elemental composition of the  
301 Al-WTR, in comparison with some other wetland materials is given in Table 2. It is clear  
302 that the primary coagulant (aluminium sulphate) used during the water treatment process is  
303 reflected in the composition of the Al-WTR. The aluminium component in the Al-WTR is  
304 about 1-5 orders of magnitude greater than all other elements analyzed in the Al-WTR.

[INSERT TABLE 2 HERE]

305

306

307 The aluminium content is also quite high when compared with some other potential  
308 wetland filters as reported by Kvarnstrom et al. (2004), but the calcium and iron levels in  
309 the Al-WTR are comparatively low. Aluminium (expressed as Al<sub>2</sub>O<sub>3</sub>) accounted for 8.1%  
310 by composition of the sampled Al-WTR. Aluminium is known to play a key role in P  
311 adsorption/precipitation by solid matrices via ligand exchange by phosphate ion reactions  
312 with aluminium oxides forming inner-sphere complexes (Ippolito et al., 2003; Yang et al.,  
313 2006). Hence, substrates that are particularly rich in aluminium can effectively remove P by  
314 adsorption and/or precipitation of chemically stable phosphate phases. Table 2 further  
315 shows that the concentration of the major constituents in the Al-WTR are within the typical  
316 ranges as reported in literature for WTRs (DeWolfe, 2006; Babatunde and Zhao, 2007;  
317 Makris and O'Connor, 2007) although a wide variability amongst samples is observed. The  
318 arsenic concentration in the Al-WTR is however much greater than the mean value of  
319 0.0113 mg g<sup>-1</sup> reported for five Al-WTRs as reported by Makris and O'Connor (2007)  
320 while levels of lead and zinc in the Al-WTR are below their typical levels in  
321 uncontaminated soils (Babatunde, 2007).

322

323

### 324 **3.3 P adsorption tests**

325

#### 326 *3.3.1 Batch tests- P adsorption behavior and determination of adsorption isotherm* 327 *constants*

328

329 The P uptake kinetic profile at an initial P concentration of 5 mg-P L<sup>-1</sup> is shown in Fig.  
330 3 with results indicating the process to be initially rapid. The same trend was observed for

331 all the initial P concentrations used, therefore, only the plot of initial P concentration of 5  
332 mg-P L<sup>-1</sup> is shown to illustrate the general trend. However, in all cases, the initial rapid rate  
333 of adsorption decreased with time, giving way to a very slow rate of approach to  
334 equilibrium, and equilibrium concentrations were generally reached within 6 to 24h  
335 depending on dosage and initial P concentration. Accordingly, an equilibrium time of 48  
336 hours was adopted. The biphasic pattern of P adsorption suggests that the initial fast rate is  
337 due to characteristic P retention on highly accessible surfaces like particle exteriors and  
338 macropores, while the slower stage is characterized as P adsorption via intraparticle  
339 diffusion in meso- and micropores and/or diffusion within the organic matter (Axe and  
340 Trivedi, 2002; Makris et al., 2004).

341

[INSERT FIG 3 HERE]

343

344 Fig. 4 shows plot of percentage P removal by the Al-WTR plotted alongside P-uptake  
345 using 48-hour equilibration time and P concentration of 5 mg-P L<sup>-1</sup>. The figure shows  
346 percentage P-removal increased steadily with increase in adsorbent dosage up to 10 g L<sup>-1</sup>  
347 suggesting that phosphate adsorption onto Al-WTR depends on availability of positively  
348 charged adsorption sites. Similar trend was observed for all the initial P concentrations used  
349 and only the plot of initial P concentration of 5 mg-P L<sup>-1</sup> is shown to illustrate the general  
350 trend. However, at dosages beyond 10 g L<sup>-1</sup>, increase in P-removal (%) became marginal  
351 and P-uptake decreased with increase in adsorbent dosage. This is consistent with the  
352 expectation that higher adsorbent dosages will result in lower adsorption efficiencies per  
353 gram, as the adsorbed phosphate is distributed among more available binding sites.



[INSERT FIG 4 HERE]

354

355

356 At adsorbent dosages greater than  $10 \text{ g L}^{-1}$ , P removal was fairly constant with a  
357 continuing decrease in specific P uptake. Thus phosphorus adsorption optimisation would  
358 be better achieved using a dosage of  $10 \text{ g L}^{-1}$ . The constant parameters obtained from the  
359 fitting of the linear form of the Langmuir model to the batch data were used to determine the  
360 maximum P adsorption capacity of the Al-WTR and other parameters and presented in  
361 Table 3. From Table 3, it can be seen that the adsorption capacity decreased with an  
362 increase in pH from 4 to 9, indicating that the adsorption process is more favoured under  
363 acidic conditions. A decrease in the Al-WTR adsorption maxima with increasing pH can be  
364 attributed to change of surface potential and competitive adsorption between phosphate and  
365 hydroxyl ions. The pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) also plays an important role in the  
366 adsorption phenomenon. The Al-WTR used in this study had a  $\text{pH}_{\text{pzc}}$  of 8.5 (Yang et al.,  
367 2006). At pH below the  $\text{pH}_{\text{pzc}}$ , the surface would be positively charged. Therefore, at low pH  
368 (with abundant positive sites), phosphate adsorption will be facilitated by electrostatic and  
369 chemical attraction onto the positively charged surface, but as the pH rises towards and  
370 above the  $\text{pH}_{\text{pzc}}$ , the surface becomes predominantly negatively charged due to competitive  
371 adsorption of  $\text{OH}^-$  and phosphate adsorption decreases. A maximum adsorption capacity of  
372  $31.9 \text{ mg-P g}^{-1}$  was obtained at pH 4, about three times the value obtained at pH 9. Several  
373 industrial by-products including slags, shale, fly ash and bottom ash have been tested for  
374 their P removal capacities. Their removal capacities evaluated from batch studies ranged  
375 from  $0.31 \text{ mg-P g}^{-1}$  to  $44.2 \text{ mg-P g}^{-1}$  (Westholm, 2006). In comparison, the Al-WTR used  
376 herein can be seen to have a comparable P adsorption capacity.

[INSERT TABLE 3 HERE]

377

378

379 The adsorption constants and correlation coefficients obtained from the fitting of  
380 Freundlich model to the batch data at different pH values are also listed in Table 3. From  
381 Table 3, it can be seen that values of  $k_f$  decreased as pH increased from 4 to 9. Also, by  
382 determining the values of  $n$  from the results of  $n^{-1}$  presented in the table, it can be seen that  
383 in all cases,  $n > 1$ , but the  $n$  value increased when pH increased from 4 to 7. There was no  
384 difference in  $n$  values between pH 7 and 9. The Freundlich  $k_f$  can be related to the affinity  
385 of Al-WTR for P. The fact that a greater  $k_f$  value was obtained at lower pH suggest greater  
386 mobility of the aluminium ions towards phosphate ions in solution under acidic conditions,  
387 thus influencing the degree of affinity. The value of  $n$ , which was greater than 1 in all cases,  
388 also indicates that the adsorption of P onto the Al-WTR can be described as favourable.

### 389 3.3.2 Column tests

390 Fig. 5 shows a plot of the removal efficiency for RP and SRP in the five systems as a  
391 function of pore volumes. Note that all the columns have different substrate configuration  
392 as listed in Table 1. A clear influence of the proportion of Al-WTR can be observed in the  
393 pattern of the removal efficiencies. All the columns removed P effectively particularly over  
394 the first 100 pore volumes during which average influent P was 18.5 mg-P L<sup>-1</sup> (RP) and  
395 10.0 mg-P L<sup>-1</sup> (SRP). During this period, average removal efficiencies for the columns were  
396 91.2, 91.3, 90.9, 88.9, 93.2% (RP) and 92.7, 94.8, 94.8, 93.1 and 95.4% (SRP) for columns  
397 1-5 respectively. Columns began to lose the P adsorptive capacity after variable lengths of  
398 time. This was particularly evident in column 4, which had the least proportion of the Al-  
399 WTR in composition (40%).

[INSERT FIG 5 HERE]

400

401

402 The influent P concentration was increased to an average of 36.0 mg-P L<sup>-1</sup> (RP) and  
403 19.4 mg-P L<sup>-1</sup> (SRP) at the 128<sup>th</sup> pore volume and 54.2 mg-P L<sup>-1</sup> (RP) and 34.9 mg-P L<sup>-1</sup>  
404 (SRP) at the 248<sup>th</sup> pore volume. During these periods, columns 1, 2, 3 and 5 maintained  
405 fairly stable removal efficiency for both RP and SRP although there was an initial decrease  
406 in the SRP removal efficiency after the first increase. Influent P was increased to 211.4 mg-  
407 P L<sup>-1</sup> (RP) and 175.7 mg-P L<sup>-1</sup> (SRP) at the 428<sup>th</sup> pore volume and 353.1 mg-P L<sup>-1</sup> (RP) and  
408 316.1 mg-P L<sup>-1</sup> (SRP) at the 650<sup>th</sup> pore volume. Similar high P concentrations have been  
409 used in past studies to examine P removal in columns (Drizo et al., 2006). Despite these  
410 increases, P saturation was not achieved in any of the columns during the timeframe of the  
411 experiment, but the removal efficiency in column 4 steadily declined to an average of  
412 53.8% (RP) and 49.2% (SRP) during the last phase of the experiments.

413 Column1 presented the best P removal performance overall and the column P removal  
414 efficiencies decreased in the order of 1 > 2 > 5 > 3 > 4 for both RP and SRP. This closely  
415 followed the percent of Al-WTR in each column. However, SRP removal was greater than  
416 RP in columns 1, 2, 3 and 5. SRP, being composed of soluble reactive phosphate will  
417 largely be removed in the system by adsorption on the Al-WTR as opposed to RP which is  
418 composed of particulate phosphates (which will largely be removed by filtration) and SRP.  
419 By juxtaposing this result with the columns configuration layout in Table 1, it can be  
420 inferred that P removal efficiency decreased in the columns with an increase in the  
421 proportion of gravel used and this highlights the influence of the Al-WTR in P removal in  
422 the columns.

### 423 3.3.3 HRT influence on phosphorus removal and determination of $k$ values

424 Empirical equations describing the relationship between  $C_e$  and  $C_i$  for both RP and SRP  
425 at different HRT's are presented in Table 4. Generally, the  $r^2$  values indicate a good fit of  
426 the equations. More importantly, the reasonably high positive correlation between  $C_e$  and  $C_i$   
427 for both RP and SRP in most of the cases illustrate the fact that effluent P concentration  
428 increased with corresponding increase in influent P concentration. Other authors have  
429 reported similar observation for P behaviour in subsurface flow wetland systems (Pant et  
430 al., 2001; Tang et al., 2008). Furthermore, Table 4 shows that the  $r^2$  values were mostly  
431 greater for RP than for SRP in each HRT. It therefore follows that under the same HRT,  
432 effluent RP concentrations were more dependent on influent concentrations. The modified  
433 first-order removal model (Eq. 5, section 2.3.3.) could estimate the actual  $k$  value since  
434 other parameters are known.  $C^*$  was set to zero based on common assumptions (Tang et al.,  
435 2008).

436 The model implies that the effluent P concentrations decrease with increasing HRT, and  
437 therefore, values of  $k$  increase with increasing HRT. However, in the current study,  $k$  values  
438 did not increase with increase in HRT. This suggests that an increase of the HRT may not  
439 have improved P removal. In a similar work by Tang et al. (2008), P removal in columns  
440 was examined using four different substrate materials. The  $r^2$  values obtained ranged from  
441 0.00 to 0.92 and the  $k$  values for all the substrates were found to increase with an increase  
442 in the HRT, although the increases were reported to be marginal. The authors therefore  
443 concluded that the increase of the HRT prolonged the contact time between the substrates  
444 and P added to the columns, and improved the substrate adsorption performance.

445

[INSERT TABLE 4 HERE]

446

447

448 The maximum P adsorption capacity as determined by the Langmuir equation of the  
449 Al-WTR used in the study range from 10.2 to 31.9 mg-P g<sup>-1</sup>, compared to an adsorption  
450 capacity range of 0.09 to 0.62 mg-P g<sup>-1</sup> obtained for the four substrates in the study by Tang  
451 et al. (2008). In our previous studies (Yang et al., 2006), we have shown that the driving  
452 force of P removal by the Al-WTR is considered to be the abundant aluminium ions in its  
453 matrix and this is also in agreement with other authors (Ippolito et al., 2003; Makris et al.,  
454 2005). The abundant aluminium ions in the Al-WTR greatly influence its adsorption  
455 behaviour and capacity through the ligand exchange mechanism. Furthermore, the Al-WTR  
456 has a greater capacity for P adsorption than most of the other substrates based on the  
457 evaluation of the maximum P adsorption capacity using the Langmuir model (see section  
458 3.3.1). This would therefore facilitate rapid P removal in the systems. The greater k values  
459 obtained in the current study and the comparatively greater Al-WTR adsorption capacity  
460 suggest its use in engineered wetlands systems as a very promising and practical solution to  
461 remove P from P-rich wastewaters.

462

## 463 **Conclusions**

464 Aluminium-based water treatment residual (Al-WTR), a by-product of water treatment  
465 facilities that use aluminium sulphate as coagulant is shown to have suitable physico-  
466 chemical characteristics for use as substrate in engineered wetlands. The Al-WTR has a  
467 significant phosphorus (P) adsorption capacity, ranging from 10.2 mg-P g<sup>-1</sup> to 31.9 mg-P g<sup>-1</sup>  
468 due to being predominantly composed of amorphous aluminium species. It has an ideal

469 surface for biofilm growth and attachment with specific surface area ranging from 28.0 m<sup>2</sup>  
470 g<sup>-1</sup> to 41.4 m<sup>2</sup> g<sup>-1</sup>. The pH and the electrical conductivity of the AI-WTR both showed that it  
471 should suitably support plant growth while chemical analysis also indicate that there is no  
472 component of the AI-WTR that should significantly preclude its use as substrate in  
473 engineered wetlands. Significant P removal was achieved in the long-term column  
474 experiments and the results further suggested that P removal was not improved by  
475 increasing the hydraulic retention time from 0.125 d to 0.17 d. This was thought to be due  
476 to the significant P adsorption capacity of the AI-WTR which facilitated rapid P removal at  
477 the instant of P contact with the AI-WTR. The potential use of the AI-WTR as substrate in  
478 engineered wetlands would represent a novel and practical method that can be applied for  
479 the treatment of P containing wastewater in engineered wetland systems. The concept is  
480 also sustainable as the objective of its utilization is not merely to dispose the AI-WTR, but  
481 to beneficially reuse it for enhancing wastewater treatment. Such development comes at a  
482 time when landfills spaces are decreasing and alternatives to AI-WTR disposal are being  
483 sought.

484

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489

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Fig. 2: Surface images of the Al-WTR using SEM-EDX (top) and SEM (bottom).

Fig. 3: Kinetics of P removal as a function of adsorbent dosage (Al-WTR = 5, 10, 15 and 20 g L<sup>-1</sup>) using an initial P concentration of 5 mg L<sup>-1</sup> (error bars denote mean ± S.D)

Fig. 4: P uptake plotted alongside P removal (%) using an initial P concentration of 5 mg L<sup>-1</sup> (error bars denote mean ± S.D).

Fig. 5: Removal efficiency of (a) RP and (b) SRP in the experimental columns as a function of pore volumes (1-5 refers to the respective columns)

Table 1 Configuration and design of the experimental columns

	Column number				
	1	2	3	4	5
<sup>a</sup> substrate layout (cm)					
Sand	0	0	0	0	10
Pea gravel	0	10	20	30	10
Al-WTR	50	40	30	20	30
Gravel support	10	10	10	10	10
% Al-WTR	100	80	60	40	60
Design					
Flow type	Batch	Batch	Batch	Batch	Batch
HLR (m <sup>3</sup> m <sup>-2</sup> d <sup>-1</sup> )	1.86	1.75	1.69	1.63	1.69
<sup>b</sup> HRT (d)	0.125	0.125	0.125	0.125	0.125

<sup>a</sup> from the top surface of the substrate bed and in the direction of flow, <sup>b</sup>HRT = initial hydraulic retention time. All substrates arranged in layers

Table 2 Major elemental chemical composition of the aluminum-based water treatment residual compared to other water treatment residual and potential wetland media

Element (mg g <sup>-1</sup> )	Water treatment residual				Other potential media	
	a	b	c	d	e	f
Al	42.67	38.3 - 125.4	15 - 300	297	nd	0.065 - 0.084
Fe	3.336	16.3 - 26.1	5 - 66	102	nd	21.9 - 45.8
Ca	0.820	4.5 - 54.6	3 - 50	29	nd	12.1 - 34
P	0.123	0.5 - 4.4	0.2 - 4.4	3.5	nd	nd
As	0.034	0.007 - 0.04	nd	nd	0.001 - 0.07	nd
Pb	0.005	0.005 - 0.032	nd	0.04	0.03 - 11.69	nd
Mg	0.237	0.054 - 0.142	nd	8.9	nd	6.5 - 27.1
Mn	0.270	0.036 - 2.688	nd	nd	nd	0.39 - 0.846
Ti	0.099	nd	nd	nd	nd	nd
Zn	0.03	0.05 - 0.0017	nd	0.03	0.07 - 7.89	nd
*Cl-	16.1	nd	nd	nd	nd	nd
*SO <sub>4</sub> <sup>2-</sup>	8.3	nd	nd	nd	nd	nd
*SiO <sub>4</sub> <sup>2-</sup>	11.2	nd	nd	nd	nd	nd
*TOC	97.5	nd	8.5-225**	nd	nd	nd

<sup>a</sup>This study, <sup>b</sup>James DeWolfe (22), <sup>c</sup>Makris and O'Connor, (20), <sup>d</sup>Babatunde and Zhao (6), <sup>e</sup>EPA (Ireland) (23)

<sup>f</sup>Kvarnstrom, et al. (24), \*mean values obtained from Yang et al. (14), nd no data, \*\* total carbon. Determination were carried out on air-dried aluminum-based water treatment residual with particle sizes <2mm.

Table 3 Adsorption isotherm model equations and corresponding linear forms, and adsorption model constant parameters, adsorption capacity and  $R^2$  at different pH values

Model equation	Linear plot	Parameters	pH		
			4	7	9
<b>Langmuir</b>					
$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{a_L}{K_L} C_e + \frac{1}{K_L}$	$Q_0$ (mg g <sup>-1</sup> )	31.9	23.0	10.2
		$b$ (L mg <sup>-1</sup> )	0.027	0.025	0.024
		$R^2$	0.98	0.97	0.97
<b>Freundlich</b>					
$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$k_f$ (L g <sup>-1</sup> )	0.67	0.53	0.41
		$n^{-1}$	0.89	0.81	0.81
		$R^2$	0.91	0.93	0.88

$Q_0$  and  $b$  are Langmuir's maximum adsorption capacity ( mg g<sup>-1</sup>) and adsorption constant ( L mg<sup>-1</sup>) respectively, while  $k_f$  and  $n^{-1}$  are Freundlich's and heterogeneity factor respectively.  $q_e$  is the mass of P adsorbed on the Al-WTR ( mg g<sup>-1</sup>) at equilibrium and  $C_e$  is the equilibrium concentration of P in solution (mg L<sup>-1</sup>). For the Langmuir model,  $b = a_L$  and  $Q_0 = K_L/a_L$ .

Table 4 Relationship between influent and effluent concentrations at different HRT's and mean values of phosphorus removal constant,  $k$  (m d<sup>-1</sup>)

System	HRT = 0.125d						HRT = 0.17d					
	RP			SRP			RP			SRP		
	Empirical eqn.	$r^2$	$k$	Empirical eqn.	$r^2$	$k$	Empirical eqn.	$r^2$	$k$	Empirical eqn.	$r^2$	$k$
1	$C_e = 0.3603C_i - 4.52$	0.75	7.8	$C_e = 0.0183C_i - 0.53$	0.08	11.7	$C_e = 0.1171C_i - 1.86$	0.76	6.9	$C_e = 0.108C_i - 3.04$	0.71	8.3
2	$C_e = 0.2869C_i - 3.49$	0.84	8.3	$C_e = 0.0365C_i + 0.16$	0.50	12.2	$C_e = 0.141C_i - 3.87$	0.73	6.8	$C_e = 0.1697C_i - 6.5$	0.50	8.0
3	$C_e = 0.3269C_i - 4.04$	0.80	8.0	$C_e = 0.0596C_i - 0.05$	0.59	11.7	$C_e = 0.4861C_i - 27.4$	0.79	4.6	$C_e = 0.5245C_i - 20.78$	0.82	4.8
4	$C_e = 0.541C_i - 7.55$	0.90	6.8	$C_e = 0.2123C_i - 1.27$	0.60	9.4	$C_e = 0.4873C_i - 15.12$	0.79	3.3	$C_e = 0.4975C_i - 3.96$	0.73	2.6
5	$C_e = 0.2684C_i - 3.43$	0.83	9.0	$C_e = 0.0546C_i - 0.07$	0.65	12.3	$C_e = 0.2649C_i - 17.03$	0.70	6.5	$C_e = 0.2754C_i - 14.32$	0.66	7.7