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

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Abstract

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

Capsule:

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

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

1. Introduction

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

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

A low-cost material that can enhance P removal is aluminium-based water treatment residual (Al-WTR), a by-product of water treatment facilities that use aluminium salts as coagulant. It is the most widely generated water treatment residual (WTR) worldwide, and is mostly landfilled at huge costs since it is regarded as a by-product of little known reuse value. However, the chemical composition of Al-WTR gives it a highly reactive surface and a strong affinity for P (Elliot et al., 2002; Ippolito et al., 2003; Makris et al., 2005; Babatunde and Zhao, 2007). In addition, Al-WTR is an easily available by-product in towns, cities and metropolis regions worldwide that utilize surface waters as a drinking water source. And since Al-WTR is derived from residual of treatment of raw water which contains mainly turbidity, colour, suspended clays and humic substances, it is unlikely to contain a substantial quantity of toxic substances. Knowledge of its physicochemical characteristics and P adsorption capacity would be very useful for practical guidance in utilizing its P adsorption capacity and gaining future acceptance for Al-WTR based engineered wetland system.

2. Materials and methods

2.1 Al-WTR

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

2.2 Physical and chemical properties

2.2.1 Physical properties

The Al-WTR was air-dried and ground to pass a 2-mm mesh sieve. Thereafter, specific physical properties were determined as follows. Porosity was determined from the amount of water needed to saturate a known volume of the Al-WTR while bulk density was determined from the volume of water displaced by a known mass of the Al-WTR sample (n=5). Surface area was measured using nitrogen Brunauer Emmett Teller (BET) isotherms on a Micromeritics Gemini 2375 volumetric analyzer. Total pore volume was calculated from the amount of vapour absorbed at a relative pressure (P/P^o, where P is the equilibrium pressure and P^o is the saturation pressure of the adsorbate) close to unity. Micropore volume of the Al-WTR was calculated using the Dubinin-Radushkevich (DR) model of micropore filling, which is based on the Polanyi's concept of characteristic curve to describe adsorption into micropores (Gregg and Sing, 1982). The characteristic curve can be expressed as in Eq. (1).

$$\frac{V}{V^0} = \exp\left(-\frac{A}{\varepsilon\beta}\right)^2 \qquad \text{Eq. (1)}$$

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

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

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

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

As a first approximation, the micropore volume can be determined directly from the BET-N_2 adsorption isotherm, and it corresponds to the volume of gas adsorbed at P/P^o of 0.15 (Gregg, 1982). However, from Eq. (2), a graph of log V against $\log^2$ (P^o/P) will give micropore volume of the Al-WTR, V^o, 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 µm. 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 CuKa radiation, operating at 40 kV and 30 mA, from 3^o to 75^o 2Θ, with a scanning step of 0.02^o at 1^o per minute while the FTIR spectra was measured using the KBr wafer technique in a FTIR spectrometer (Excalibur series).

2.2.2 Chemical properties

Chemical properties were determined as follows: pH was taken as the pH of a 0.01 M $CaCl_2$ solution of the Al-WTR (McLean, 1982) (particle size < 2 mm, Al-WTR: solution ratio of 1:10). Loss of ignition (LOI) was determined in accordance with standards (British Standards Institution, 1990). Electrical conductivity (EC) was measured at 25°C using a Radiometer CDM83 electrical conductivity meter (Smith and Doran, 1996). The elemental metal composition was carried out by carefully weighing ca. 0.025 g of the air-dried Al-WTR samples (particle size < 2 mm) into clean TMF vessels followed by addition of 4 ml HNO_3 + 200 µl HF + 4 ml H_2O. Samples were then digested using a low volume microwave digestion technique (Sandroni et al., 2003), and the digestates analysed for dissolved metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Specific anions (Cl^-, SO_4^{2-}, SiO_4^{2-}) and humic acid (expressed as total organic carbon (TOC)) of the Al-WTR were determined separately as described in Yang et al. (2006).

2.3 P adsorption

2.3.1 Adsorption isotherm experiments

P adsorption behavior and maxima, and effects of adsorbent dosage, equilibration time and initial P concentration on P adsorption were investigated. For determining equilibrium adsorption time, different masses of Al-WTR (0.5, 1.0, 1.5 and 2.0 g) were shaken with 100 ml each of P solutions (5, 30 and 120 mg-P L^{-1}) contained in 250ml bottles for 1 to 120 hours using a rotary shaker. For the optimal dosage determination, a wide range of 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 each of four P solutions (5, 30, 120 and 360 mg L^{-1}) contained in 250 ml bottles for 48 hours (predetermined equilibration time) using a rotary shaker. Finally, batch experiments were conducted to determine the P adsorption capacity and adsorption parameters. 1.0 g of the Al-WTR was equilibrated with 100 ml of varying P concentrations ranging from 0 to 360 mg-P L^{-1} for 48 hours at different pH levels (pH 4, 7 and 9). Data obtained were analyzed using the Langmuir and Freundlich models to determine the relevant adsorption parameters. In all cases, P solutions were made up from stock standard KH_2PO_4 solution while P analysis was carried out using a HACH DR/2400 spectrophotometer according to standard operating procedures.

2.3.2 Column experiments

Five columns using different proportions of Al-WTR as substrate were set up as shown in Fig.1 (only one representative unit shown). The substrate layout and design of all the columns is presented in Table 1. The columns were used to simulate sub-surface vertical flow engineered wetland systems. Similar configuration utilizing columns to depict laboratory scale wetland systems are used in such laboratory scale studies (Sun et al., 2005 and Lee and Scholz, 2006). The columns were fed with wastewater collected periodically from the secondary holding tank of an animal research farm, and it had a P-PO_4^{3-} concentration of about 48-90 mg-P L^{-1}. On being brought to the laboratory, the wastewater was allowed to settle overnight and the supernatant was then collected and used. However, the supernatant was sometimes diluted with tap water or spiked with artificial P solution to give a range of P concentrations used to examine the response and individual P removal behaviour of the columns. Accordingly, influent P concentration into the system ranged from 18.1 to 346.1 mg-P L^{-1}. This range was chosen to accommodate possible levels of P in both domestic and industrial wastewaters as well as a worst case scenario. Inflow and outflow were regulated by peristaltic pumps and samples were collected over a period of 25 weeks. Only the analysis for reactive P (RP, conducted on unfiltered samples) and soluble reactive P (SRP, conducted on filtered samples using a 0.45 μm membrane filter) are presented and discussed. RP is a measure of reactive orthophosphate present in the wastewater and which is either soluble or attached to suspended solids while SRP is a measure of soluble orthophosphate, the filterable (soluble, inorganic) fraction of phosphorus and the form directly taken up by plant cells. SRP can thus be viewed as the soluble component of the RP. It is necessary to distinguish between these two analytical forms of P so as to point out the role of the Al-WTR in the systems. In the systems, RP can be removed by both filtration and/or adsorption on the Al-WTR (i.e. filtration of RP attached to the solid particles and adsorption of the soluble component of the RP which is the SRP), whereas SRP would be solely removed by adsorption on the Al-WTR. Therefore, the contribution of the Al-WTR to the overall P removal in the systems can be determined. P removal efficiency data were plotted as a function of the pore volumes to reduce the effect of flow variation if the data is plotted as a function of time. The plot was also used to examine individual P removal in the systems.

[INSERT FIG 1 HERE]

[INSERT TABLE 1 HERE]

2.3.3 Modelling P removal in subsurface flow system

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

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

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

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

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

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

3. Results and discussion

3.1 Physical properties

The Al-WTR had a bulk density of 1.18 ± 0.11 g cm^{-3} and a porosity of 45%, both of which are comparable to values of 0.7 to 1.83 g cm^{-3} (bulk density) and 30 to 54.4% (porosity) reported in literature for potential candidate materials for wetland systems (Roger, 2000; Drizo et al., 1999; Del Bubba et al., 2003). From the PSD, the values of d_{10} and d_{60} and UC were computed to be 0.5, 1.8 and 3.6 respectively and these are consistent with several guidelines for securing adequate hydraulic conductivity and minimizing risk of clogging (Vymazal, 1998; IWA, 2000). Qualitative assessment of the elemental distribution on the surface of the Al-WTR by the SEM-EDX showed the predominance of aluminium and this was expected to highly influence its P adsorption ability (See Fig. 2 (top)). Ippolito et al. (2003) found similar results using SEM-EDX. The microstructure of the Al-WTR as examined by SEM (Fig. 2 (bottom)) suggests a ‘rough’ surface that would be ideal for biofilm growth and in particular, the presence of 2 µm pores. Roger (2000) noted that biofilms bacteria need a potential environment typically 1-3 µm. The samples were further analyzed using N_2 adsorption. The N_2 adsorption isotherm plot obtained beared a strong resemblance to the IUPAC type IV isotherm, with a H_2 type of hysteresis loop. The specific surface area (SSA) ranged from 28.0 to 41.4 m^2g^{-1}. Makris et al. (2004) found that WTRs can have SSA up to 105 m^2 g^{-1}. Furthermore, the SSA of the Al-WTR was found to increase with increasing particle size suggesting large inner porosity in the grains.

[INSERT FIG 2 HERE]

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

3.2 Chemical properties

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

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

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

[INSERT TABLE 2 HERE]

The aluminium content is also quite high when compared with some other potential wetland filters as reported by Kvarnstrom et al. (2004), but the calcium and iron levels in the Al-WTR are comparatively low. Aluminium (expressed as Al_2O_3) accounted for 8.1% by composition of the sampled Al-WTR. Aluminium is known to play a key role in P adsorption/precipitation by solid matrices via ligand exchange by phosphate ion reactions with aluminium oxides forming inner-sphere complexes (Ippolito et al., 2003; Yang et al., 2006). Hence, substrates that are particularly rich in aluminium can effectively remove P by adsorption and/or precipitation of chemically stable phosphate phases. Table 2 further shows that the concentration of the major constituents in the Al-WTR are within the typical ranges as reported in literature for WTRs (DeWolfe, 2006; Babatunde and Zhao, 2007; Makris and O'Connor, 2007) although a wide variability amongst samples is observed. The arsenic concentration in the Al-WTR is however much greater than the mean value of 0.0113 mg g^{-1} reported for five Al-WTRs as reported by Makris and O'Connor (2007) while levels of lead and zinc in the Al-WTR are below their typical levels in uncontaminated soils (Babatunde, 2007).

3.3 P adsorption tests

3.3.1 Batch tests- P adsorption behavior and determination of adsorption isotherm constants

The P uptake kinetic profile at an initial P concentration of 5 mg-P L^{-1} is shown in Fig. 3 with results indicating the process to be initially rapid. The same trend was observed for all the initial P concentrations used, therefore, only the plot of initial P concentration of 5 mg-P L^{-1} is shown to illustrate the general trend. However, in all cases, the initial rapid rate of adsorption decreased with time, giving way to a very slow rate of approach to equilibrium, and equilibrium concentrations were generally reached within 6 to 24h depending on dosage and initial P concentration. Accordingly, an equilibrium time of 48 hours was adopted. The biphasic pattern of P adsorption suggests that the initial fast rate is due to characteristic P retention on highly accessible surfaces like particle exteriors and macropores, while the slower stage is characterized as P adsorption via intraparticle diffusion in meso- and micropores and/or diffusion within the organic matter (Axe and Trivedi, 2002; Makris et al., 2004).

[INSERT FIG 3 HERE]

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

[INSERT FIG 4 HERE]

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

[INSERT TABLE 3 HERE]

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

3.3.2 Column tests

Fig. 5 shows a plot of the removal efficiency for RP and SRP in the five systems as a function of pore volumes. Note that all the columns have different substrate configuration as listed in Table 1. A clear influence of the proportion of Al-WTR can be observed in the pattern of the removal efficiencies. All the columns removed P effectively particularly over the first 100 pore volumes during which average influent P was 18.5 mg-P L^{-1} (RP) and 10.0 mg-P L^{-1} (SRP). During this period, average removal efficiencies for the columns were 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 1-5 respectively. Columns began to lose the P adsorptive capacity after variable lengths of time. This was particularly evident in column 4, which had the least proportion of the Al-WTR in composition (40%).

[INSERT FIG 5 HERE]

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

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

3.3.3 HRT influence on phosphorus removal and determination of k values

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

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

[INSERT TABLE 4 HERE]

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

Conclusions

Aluminium-based water treatment residual (Al-WTR), a by-product of water treatment facilities that use aluminium sulphate as coagulant is shown to have suitable physico-chemical characteristics for use as substrate in engineered wetlands. The Al-WTR has a significant phosphorus (P) adsorption capacity, ranging from 10.2 mg-P g^{-1} to 31.9 mg-P g^{-1} due to being predominantly composed of amorphous aluminium species. It has an ideal surface for biofilm growth and attachment with specific surface area ranging from 28.0 m^2 g^{-1} to 41.4 m^2 g^{-1}. The pH and the electrical conductivity of the Al-WTR both showed that it should suitably support plant growth while chemical analysis also indicate that there is no component of the Al-WTR that should significantly preclude its use as substrate in engineered wetlands. Significant P removal was achieved in the long-term column experiments and the results further suggested that P removal was not improved by increasing the hydraulic retention time from 0.125 d to 0.17 d. This was thought to be due to the significant P adsorption capacity of the Al-WTR which facilitated rapid P removal at the instant of P contact with the Al-WTR. The potential use of the Al-WTR as substrate in engineered wetlands would represent a novel and practical method that can be applied for the treatment of P containing wastewater in engineered wetland systems. The concept is also sustainable as the objective of its utilization is not merely to dispose the Al-WTR, but to beneficially reuse it for enhancing wastewater treatment. Such development comes at a time when landfills spaces are decreasing and alternatives to Al-WTR disposal are being sought.

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Fig. 1: Schematic layout of a single unit of the experimental columns

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^{-1}) using an initial P concentration of 5 mg L^{-1} (error bars denote mean ± S.D)

Fig. 4: P uptake plotted alongside P removal (%) using an initial P concentration of 5 mg L^{-1} (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
[a] 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 ($m^3 m^{-2} d^{-1}$)	1.86	1.75	1.69	1.63	1.69
[b]HRT (d)	0.125	0.125	0.125	0.125	0.125

[a] from the top surface of the substrate bed and in the direction of flow, [b]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^{-1})	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_4^{2-}	8.3	nd	nd	nd	nd	nd
*SiO_4^{2-}	11.2	nd	nd	nd	nd	nd
*TOC	97.5	nd	8.5-225**	nd	nd	nd

[a]This study, [b]James DeWolfe (22), [c]Makris and O'Connor, (20), [d]Babatunde and Zhao (6), [e]EPA (Ireland) (23) [f]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
Langmuir					
$q_e = \frac{Q_0 b C_e}{1 + bC_e}$	$\frac{C_e}{q_e} = \frac{a_L}{K_L} C_e + \frac{1}{K_L}$	Q_o (mg g^{-1})	31.9	23.0	10.2
		b (L mg^{-1})	0.027	0.025	0.024
		R^2	0.98	0.97	0.97
Freundlich					
$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	k_f (L g^{-1})	0.67	0.53	0.41
		n^{-1}	0.89	0.81	0.81
		R^2	0.91	0.93	0.88

Q_o and b are Langmuir's maximum adsorption capacity (mg g^{-1}) and adsorption constant (L mg^{-1}) 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^{-1}) at equilibrium and C_e is the equilibrium concentration of P in solution (mg L^{-1}). For the Langmuir model, $b = a_L$ and $Q_o = K_L/a_L$.

Table 4 Relationship between influent and effluent concentrations at different HRT's and mean values of phosphorus removal constant, k (m d^{-1})

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