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Chemical Engineering Journal 136 (2008) 108–115

Chemical Engineering Journal

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Reuse of dewatered aluminium-coagulated water treatment residual to immobilize phosphorus: Batch and column trials using a condensed phosphate

A.O. Babatunde, Y.Q. Zhao*, Y. Yang, P. Kearney

Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Earlsfort Terrace, Dublin 2, Ireland

Received 17 July 2006; received in revised form 21 February 2007; accepted 6 March 2007

Abstract

The aluminium content in dewatered aluminium-coagulated water treatment residual (DAC-WTR) can lead to a high phosphorus (P) removal capacity. Therefore, DAC-WTR has been used as adsorbent/soil amendment to remove P in several studies, focusing mostly on orthophosphates (ortho-P). This study is concerned with extending such reuse of DAC-WTR to remove P using a condensed phosphate as the model P source. Using a 48 h equilibration time and a 1.18 mm (mean particle size): (1) P removal was found to increase with increasing DAC-WTR dosage, but specific uptake of P per mass of DAC-WTR was decreased. (2) A maximum adsorption capacity of 4.52 mg-P/g of DAC-WTR was obtained at a pH of 4.0.

In the continuous flow test, P removal efficiency decreased from 90 to 30% when loading was increased from 3.9 to 16.5 g-P/m^2 day. An average 45% removal efficiency was obtained after an intentional P loading surge. At the end of the continuous flow test, an operating removal capacity of 2.66 mg-P/g of DAC-WTR was determined which was 83.3% of the adsorption maxima obtained in the batch tests. There was no excessive loss of solids during the continuous flow test and aluminium content in the effluent remained below 0.1 mg-Al^{3+}/l. These results have demonstrated that dewatered DAC-WTR can further be used as a low-cost adsorbent media for condensed phosphate removal.

Keywords: Adsorption; Aluminium-coagulated water treatment residual; Condensed phosphate; Disposal; Reuse; Wastewater treatment

1. Introduction

Phosphorus (P) is found in typical wastewaters from both domestic and industrial sources and it exists mainly as phosphates in dissolved or particulate form. The phosphates can be inorganic (including orthophosphates (ortho-P) and condensed phosphates (cond-P) or organic form (organically bound phosphates (org-P)). Typically, about 25% of the total P in settled sewage is present as ortho-P and is available for immediate biological metabolism [1]. However, in some cases such as agricultural and other industrial wastewaters, the form and concentration of the phosphate species present in the wastewater can be highly varied and particularly source-dependent. Each of the phosphate species can also significantly contribute to the total P load of a wastewater when present in substantial concentrations.

P in wastewater is a contributor of the essential nutrient P necessary for terrestrial and aquatic plants. P is particularly important due to its role in the binding of carbon in living organic matter (see Eq. (1)) [2,3]. From Eq. (1), the molar ratio of nitrogen, P and carbon necessary for biomass production is 16:1:106. Thus, very small increment in P concentration discharged to water bodies can result in algal bloom leading to eutrophication. It has been reported that even trace amounts of phosphate less than 1 ppm in treated wastewater from municipalities and industries can lead to eutrophication [4]:

$$106CO_2 + 16NO_3{}^- + HPO_4{}^{2-} + 122H_2O + 18H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2 \quad (1)$$

Therefore, the effective removal of P in wastewater is essential. Although during the processing of wastewater, total P removal is usually accounted for, it is the inorganic P concentration that is more important rather than the total P concentration as far as utilization both in the treatment plant, and subsequently in the receiving waters is concerned [1]. As stated earlier, the inor-

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* Corresponding author. Tel.: +353 1 7167356; fax: +353 1 7167399. *E-mail address:* yaqian.zhao@ucd.ie (Y.Q. Zhao).

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doi:10.1016/j.cej.2007.03.013

ganic P form, includes ortho-P and cond-P. While it is generally acknowledged that ortho-P is the dominant form of P in sewage, it is rather a position based on experiences with domestic sewage. In some other instances, e.g. industrial wastewaters, the form of P in the wastewaters can be widely varied and source- and process-dependent. P removal from wastewaters is accomplished mainly through chemical precipitation and/or incorporation into biological solids/microorganisms [5], but they are generally expensive processes. In addition, further costly treatment is often necessary to reduce P levels to acceptable limits. Several alternative techniques have therefore been explored as regards P removal and P adsorption using by-products appear to be gaining increasing attention. Accordingly, a number of materials, either natural or artificial, have been used as adsorbents to enhance P removal [6], while many more are still being explored.

An industrial by product that can potentially be used to enhance P removal is dewatered aluminium-coagulated water treatment residual (DAC-WTR) commonly referred to as “alum sludge”. DAC-WTR is a product obtained as a result of the water treatment processes (including coagulation, flocculation, clarification and filtration) followed by dewatering processes in the treatment of raw water, using aluminium sulphate as the primary coagulant. Chemical coagulants are added to raw waters during potable water treatment processes to remove particles, colour and impurities particularly from high turbidity raw waters. The impurities aggregate into a flocculated mass and together with the chemical coagulant used, they are then separated from the water, becoming a residual requiring further treatment before final disposal.

Aluminium sulphate is the most widely used coagulant in water treatment works around the world with over 2 million tonnes of DAC-WTR generated daily from water treatment plants in the United States alone [7]. Typically, the DAC-WTR generated in most cases is disposed off via landfilling or through land application, but both options including others are now faced with close scrutiny. The increasing generation of DAC-WTR coupled with environmental restraint on its current disposal outlets has therefore necessitated increased research towards its reuse. There are now over 11 ways in which DAC-WTR is being reused, and most have included its use in building and construction, coagulant recovery, land applications and incorporation into the activated sludge process [8].

It has also been noted that the aluminium content in DAC-WTR can become valuable in the removal of P from aqueous solutions [9], and this has been demonstrated in several studies [10,11]. Almost all the studies have focused on ortho-P removal, using laboratory scale batch experiments and/or short or long term column experiments. Ortho-P have been widely researched because of the fact that it is acknowledged to be the most commonly found P species in wastewaters, while lab-scale batch and column experiments are usually employed in such studies to serve as a primer for large-scale tests and/or field applications. However, ortho-P is not necessarily the only or the major P species in all wastewaters and there is often a competitive effect for removal when other species are present [12]. Therefore, in assessing the P removal capacity of potential adsorbents especially on a laboratory scale, it is worthwhile considering their capacity for removing other phosphate species as well.

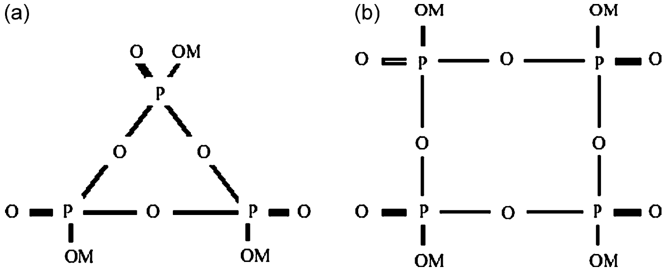

Fig. 1. Structures of condensed metaphosphates: (a) cyclotriphosphate and (b) cyclotetraphosphate (M is H^+ or a monovalent metal cation) [14].

The DAC-WTR used in this study has been demonstrated to have a comparable capacity to adsorb ortho-P [13], and its use is now extended to the removal of cond-P. Cond-P are chains of two or more ortho-P groups that are linked together with a general P–O–P bond. Forms of cond-P include metaphosphates (cyclic bonded), pyrophosphate and polyphosphate (linearly bonded). Figs. 1 and 2 show the structure of two forms of cond-P [14]. Small amounts of some cond-P are added to some water supplies during treatment to prevent corrosion and some are also used extensively in the treatment of boiler waters. Larger quantities of these compounds can be found in laundering and commercial cleaning fluids. However, polyphosphates being basic constituents of detergents and water softeners are the most common inorganic cond-P in municipal wastewater. Cond-P is also widely used as fertilizers in the soil and in 1996, it was reported that about 750,000 tonnes of cond-P were used worldwide and eventually discharged into wastewater treatment plants [15]. It has also been reported that biologically treated sewage was found to contain cond-P which was released from dead bacterial cells [15]. Cond-P undergo hydrolysis in aqueous solution and revert into ortho-P and this makes them available for immediate biological uptake. Thus their removal during wastewater treatment is equally important. In separate studies, Kim et al. [16] examined P adsorption by a DAC-WTR collected from a water clarification plant in Chungju, Korea and showed that the DAC-WTR could adsorb cond-P from aqueous solution while Altundogan and Tumen [17] examined cond-P adsorption by bauxite and also showed that bauxite can be a good adsorbent for cond-P in solution as well. Using sodium hexametaphosphate as the model cond-P, Galarneau and Gehr [18] showed that

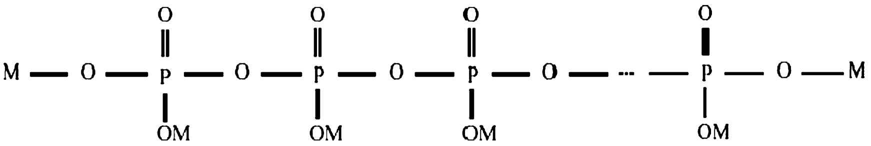

Fig. 2. Structure of a linear condensed phosphate (polyphosphate) (M is H^+ or a monovalent metal cation) [14].

aluminium hydroxide has a significant and comparable removal capacity for cond-P as much as for ortho-P while the removal capacity for cond-P was noted to be higher than that for org-P. However, in most of these studies, the adsorption capacity was not determined. This study addressed the adsorption trend and adsorption capacity of a DAC-WTR for cond-P in batch and continuous modes. Continuous phosphate removal under increasing hydraulic load and recovery from shock loading in a lab-scale column test were also investigated. Scanning electron micrograph (SEM) images were also taken to examine changes to the surfaces of the DAC-WTR particles before and after the continuous flow tests.

2. Materials and methods

2.1. DAC-WTR and P-rich solution

DAC-WTR (with moisture content of 78.2%) was obtained from the Ballymore-Eustace water treatment works Co. Kildare, Ireland. The plant produces about 230,000 m^3 of potable water daily for the city of Dublin. The raw water with a colour of 105 Hazens flows through a series of tunnels under gravity from the Poulaphuca reservoir, 1.5 km away from the works. Aluminium sulphate is used as the primary chemical coagulant at a dose of 42–60 mg/l. The major elemental components of the dewatered DAC-WTR used in this study as determined by ICP analysis were 46% aluminium (as Al_2O_3), 1.2% iron (as Fe_2O_3), 1.2% calcium (as CaO) and 10% humic acids classified as TOC [13]. The collected DAC-WTR cakes were ground and sieved to prepare the testing DAC-WTR samples (hereafter referred to as the adsorbent) with a mean particle size of 1.18 mm. Artificial P-rich solution was prepared in the laboratory by dissolving known amount of sodium hexametaphosphate ($(NaPO_3)_{12–13}\cdot Na_2O$, Fluka 71600) in distilled water to give a concentration of 5.4 mg-P/l.

2.2. Batch tests

P removal by the adsorbent as a function of adsorbent dosage was studied using a batch equilibration technique. Different masses of the adsorbent ranging from 0.1 to 3.0 g were equilibrated with 100 ml of the working P solution (5.4 mg/l) for 48 h on a rotary shaker (48 h was previously determined to be sufficient for equilibrium). After 48 h, samples were withdrawn, filtered through a 0.45 μm Millipore membrane filter and analysed for residual P. The amount of P adsorbed or P uptake, q_e (mg/g), was determined from the difference between the initial concentration, C_0 (mg/l), and the final P concentrations, C_e (mg/l), at equilibrium using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where V is the solution volume (l) and m is the adsorbent mass (g). Adsorption capacity was determined by contacting the adsorbent with 100 ml of the working P solution (5.4 mg/l) on a rotary shaker for 48 h. The adsorbent dosage range used was 1–5 g/l. Further tests were done to examine the effect of initial solution pH on the P adsorption capacity of the DAC-WTR. A pH range of 4.0–9.0 was used and sample pH was adjusted as necessary using 0.1 M sulphuric acid and 0.01 M sodium hydroxide.

A cond-P solution of 5.4 mg/l was used in this study for the following reasons: (1) To reflect as close as possible the possible concentration of cond-P types in typical raw domestic wastewaters, with approximate concentrations in the range of 1–3 mg-P/l [19]. (2) It has been noted that although the maximum P adsorption capacity of a material may be underestimated from isotherms derived at low concentrations [20], such capacities are often exceeded when higher concentration are used [21] and may thus be unrealistic and inapplicable to wastewater treatment. Therefore, laboratory P adsorption capacity values derived from isotherms using concentration found in real wastewaters would be more relevant.

2.3. Continuous flow test

Continuous flow testing was carried out using a perspex column (1 m long and 7.4 cm in diameter) packed with approximately 1 kg of the adsorbent to a height of 50 cm with 10 cm of washed gravel at the base to act as support. A basic schematic diagram of the experimental column is shown in Fig. 3. Bed porosity was determined before the start of the experiment by noting the volume of solution needed just to submerge the adsorbent in the column using an upward flow. The porosity was then computed from both the volumetric flow rate and the volume of the column itself and the volume decrease in the feed tank. Synthetic P-rich solution was percolated through the bed at an initial flow rate of 2.32 m^3/m^2 day corresponding to an initial residence time of 3 h (computed using Eq. (3)) and a P loading rate of 3.9 g-P/m^2 day:

$$T_{\text{rave}} = \frac{\pi r^2 h \Phi}{Q_{\text{ave}}} \tag{3}$$

where T_{rave} is the average residence time in (h), Q_{ave} the average computed flow rate (cm^3/h), r the radius of the column (cm), h

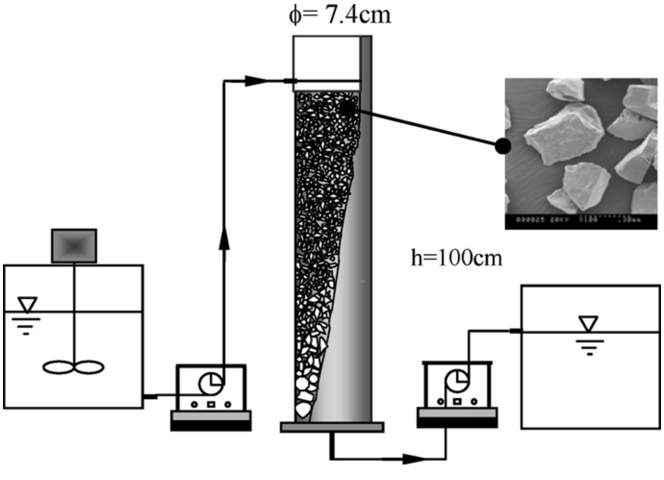

Fig. 3. Schematic diagram of the lab-scale continuous flow test with the DAC-WTR shown in the inset.

the combined height of the sludge and gravel in the column (cm) and Φ is the bed porosity.

The bed was kept submerged at all times in the influent solution which was set at a predetermined level above the surface of the adsorbent in the column and variation from that level monitored over time. Samples of influent and effluents were collected three times a week and analysed for P, pH and suspended solids (SS). The aluminium (Al^{3+}) content of the effluent was also measured to monitor possible release of aluminium from the sludge. P, aluminium and suspended solids were analysed using a Hach DR/2400 spectrophotometer according to standard operating procedures. Total-P was determined after sample digestion following the APHA standard methods [22]. The P analysis was carried out by first digesting the samples to convert them to reactive P (ortho-P). Samples were then reacted with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. In the presence of vanadium, yellow molybdovanadophosphoric acid is formed whose colour intensity is proportional to the reactive P concentration. The P concentration is then determined using the HACH DR-2400 spectrophotometer. pH was measured using a pH meter (WTW, pH 325, Germany) with a two point calibration of the electrode. At the end of the fourth month, the bed was subjected to shock loading by increasing the P loading seven times and the recovery response was monitored. On completion of the experiments, the final porosity was determined by measuring the total volume of solution drained from the bed.

2.4. SEM imaging

Samples of both the fresh unused DAC-WTR particles and those that have been subjected to column testing were naturally dried and their surfaces were observed under a scanning electron microscope (SEM) (JEOL-4519). Samples were mounted on aluminium stubs layered with conductive carbon cement to ensure adherence to the stub. After air drying for 24 h, the samples were coated with a thin layer of gold to make the specimen conductive and emit secondary electrons. Samples were thereafter observed using the SEM.

3. Results and discussion

3.1. Batch tests

3.1.1. Effect of adsorbent dosage

Fig. 4 shows the percentage removal of P by the fresh adsorbent plotted alongside P uptake for the range of adsorbent dosage used. It can be seen that the percentage of P removal increased with an increase in amount of adsorbent up to 5 g/l. At dosages beyond 5 g/l, the increase in % P removal became marginal. The uptake of P (as determined using Eq. (2)) however decreased with an increase in the adsorbent dosage. At an adsorbent dosage greater than 5 g/l, P removal in percentage terms was fairly constant with a continuing decrease in specific P uptake. This suggests that an increase in the adsorbent dosage beyond 5 g/l would decrease its effectiveness. Thus the adsorbent dosage was limited to 5 g/l in subsequent experiments.

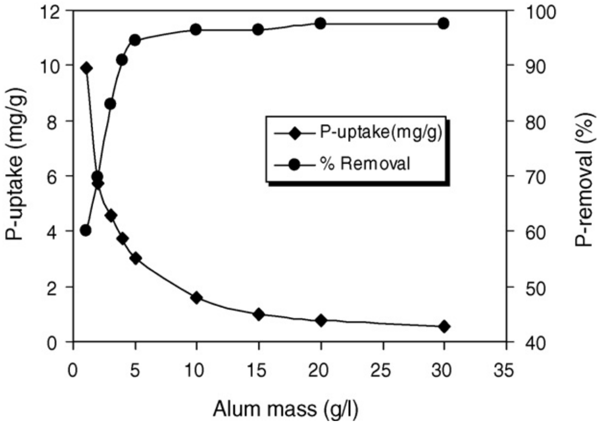

Fig. 4. Effect of adsorbent dosage on P uptake and percentage removal.

To a limited extent, it could be reasoned that the amount of available sites for P adsorption on the sludge may bear some indirect proportion with the mass concentration of the alum sludge used and therefore increasing the adsorbent mass would increase the extent of P removal up to some point. It has been reported that the concentration of surface hydroxyl groups is related to the alum sludge concentration through surface site density [23]. It was therefore suggested that the percent of adsorption would expectedly increase with increased alum sludge dose, albeit with a decrease in the loading capacity [23]. It is however desirable to determine the effective mass concentration of adsorbent to be used.

Data on the kinetics of cond-P adsorption by the DAC-WTR (not shown) indicates a biphasic nature of adsorption characterized by an initial fast reaction and a second stage characterized by a slow reaction. This is the same trend exhibited and reported in the case of ortho-P adsorption using the DAC-WTR [24]. This biphasic nature of P adsorption has been well published and attributed to: (1) the initial instant of physical adsorption as phosphate ions are adsorbed onto the available adsorption sites and (2) a second slower stage probably due to the diffusive migration of adsorbed P inside the adsorbing surface and or precipitation on the surface followed by occlusion [25].

3.1.2. P adsorption capacity as a function of pH

An adsorption isotherm was constructed using the Langmuir adsorption isotherm equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{4}$$

where q_e is the mass of P adsorbed per unit mass of sludge (mg-P/g-sludge), b an empirical constant related to the entropy with units of inverse of concentration (mg^{-1}), Q_0 the adsorption capacity (mg-P/g-sludge) and C_e is the equilibrium P concentration (mg-P/l). A linearized form of the Langmuir adsorption isotherm (Eq. (5)) was fitted to experimental data to obtain the adsorption maxima (Q_0) and the empirical constant (b):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

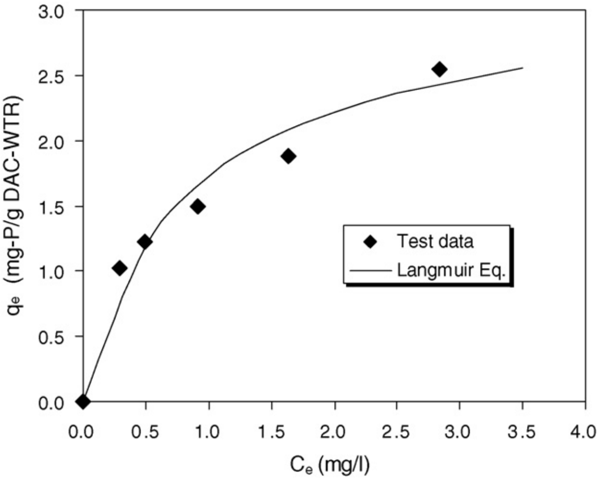

Fig. 5. Plots of Langmuir adsorption isotherm and test data for P adsorption onto alum DAC-WTR (pH 7.0).

A plot of the Langmuir isotherm and one set of test data is shown in Fig. 5. The plot indicates that as more adsorptive sites are occupied on the adsorbent, there is a decreasing probability for P ions to bind to a vacant site on the adsorbent. A maximum capacity for adsorption is thus reached at which the adsorbent becomes saturated.

The Langmuir dimensionless constant called the equilibrium parameter, R_L was then determined as defined by

$$R_L = \frac{1}{1 + bC_0} \qquad (6)$$

where b is as defined before and C_0 is the initial P concentration (mg/l). The R_L values indicate the type of isotherm as shown below [26]:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The regression values and the constants obtained at the different pH are shown in Table 1. From Table 1, the adsorption of P by the DAC-WTR can be described as favourable with R_L values increasing with increasing pH but well within the range of favourable adsorption. It can also be inferred that P adsorption in the acidic region is the most favourable and the least reversible across the pH range studied. Correspondingly, the maximum adsorption capacity values obtained decreased with increasing solution pH, with the highest adsorption capacity obtained at pH 4.0 in this study. This agrees with the findings of Kim et al. [16] that indicates a pH range of 4.0–7.0 for the maximum adsorption of inorganic phosphates and also the works of Altundogan and Tumen [17] and Galarneau and Gehr [18] that have both shown that maximum removal of cond-P occurs at slightly acidic conditions. A variation of the adsorption and adsorption maxima with pH could possibly be attributed to the change of surface potential of the adsorbent particles and the combined effects of phosphate speciation and pH on the adsorbent particles and in solution. In particular, the pH at the point of zero charge referred to as pH_{pzc} plays an important role in the adsorption phenomenon. In our previous study [13], the DAC-WTR exhibited a trend of decreasing surface charge with increasing pH and the measured pH_{pzc} was 8.5. 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 abundantly positively charged surface. However, as pH rises above the pH_{pzc}, the surface becomes predominantly negatively charged and phosphate adsorption decreases. More detailed investigation into the mechanisms and trends of P (ortho-P) adsorption onto the DAC-WTR (revealing the ligand exchange mechanism involved and the inner sphere complex formed) could be found in our previous publication [13]. Moreover, it has also been shown that the mechanism of cond-P adsorption on aluminium hydroxide similarly involves the inner sphere complexation [15]. Kim et al. [16] reported that both ortho-P and cond-P showed a similar trend in the adsorption pattern while Altundogan and Tumen [17] in a similar study on cond-P removal using bauxite noted that the adsorption mechanism of condensed phosphate can be explained in terms of the basic principles suggested for ortho-P adsorption.

Table 1
Langmuir isotherm coefficients for P adsorption at different pH

pH	Q_0 (mg-P/g)	b	R_L	R^2
4.0	4.52	1.75	0.096	0.997
6.0	4.05	0.96	0.162	0.964
7.0	3.12	1.24	0.131	0.959
8.0	1.96	1.28	0.127	0.969
9.0	1.74	1.11	0.143	0.970

3.2. Continuous flow test

3.2.1. Normal operation

Table 2 shows the column operating conditions for the different periods and the corresponding percentages of P removal including results of SS and Al^{3+} monitoring in the effluents. As can be seen in Table 2, the hydraulic loading rate was increased gradually to four times the initial loading rate at the end of the fifth period (period ‘e’). The average computed residence time of the synthetic wastewater in the column (determined using Eq. (3)) was decreased from the initial 3.0 h during the first period (period ‘a’) to 0.5 h at the end of the fifth period. During the first period of the experiments, corresponding to an initial P load of 3.9 g-P/m^2 day and hydraulic loading rate of 2.32 m^3/m^2 day, excellent P removal was obtained with an average 91.5% of the influent P load removed. The excellent P removal efficiency obtained during this period further corroborates the observed trend in the batch tests during which the bulk of phosphate in solution was removed at the instant of contact with the adsorbent.

It can be reasoned that P adsorption onto the adsorbent surface is an instantaneous process characterized by a diffusive migration of the phosphate species in solution onto the adsorptive sites on the adsorbent and this could be expected to proceed as long as a concentration gradient exists. With time and given the increases in the hydraulic and P loadings, the efficiency obviously began to decline. At the end of the fifth period with a total

Table 2
Summary of operating conditions in the column at different periods

Parameter	Operating period				
	a	b	c	d	e
Duration (days)	32	30	31	15	15
Computed residence time (h)	3.0	2.0	1.5	0.8	0.5
Hydraulic loading rate (m^3/m^2 day)	2.32	3.48	4.64	6.96	9.28
P loading rate (g-P/m^2 day)	3.9 ± 0.2	5.9 ± 0.6	7.0 ± 0.7	11.7 ± 0.4	16.5 ± 0.5
Average P removal (%)	91.5 ± 3.6	85.6 ± 6.0	74.5 ± 7.3	45.6 ± 2.3	25.5 ± 6.0
Suspended solids (mg/l) (effluent)	5.6 ± 3.7	2.4 ± 1.1	2.2 ± 1.3	2.2 ± 0.8	1.4 ± 0.9
Aluminium (mg-Al^{3+}/l) (effluent)	0.06 ± 0.04	0.07 ± 0.01	0.09 ± 0.07	0.05 ± 0.03	0.02 ± 0.01

cumulative P load of 3.99 mg-P/g of sludge, the removal efficiency had declined to about 25.5 at.% a retention time of 0.5 h. The levels of SS and aluminium monitored in the effluents were consistently low and do not pose any serious concern at this stage. In a similar study using an aluminium-coagulated water treatment residual, it was suggested that at slightly acidic or circumneutral pH conditions, P can be efficiently removed with very low release of aluminium [16]. However, very low levels of soluble aluminium was found in an aluminium-coagulated water treatment residual reuse tests [27]. It can be expected that since aluminium in the DAC-WTR exists as an insoluble form of aluminium oxide, it is unlikely to be released, at least within the pH range of aluminium insolubility.

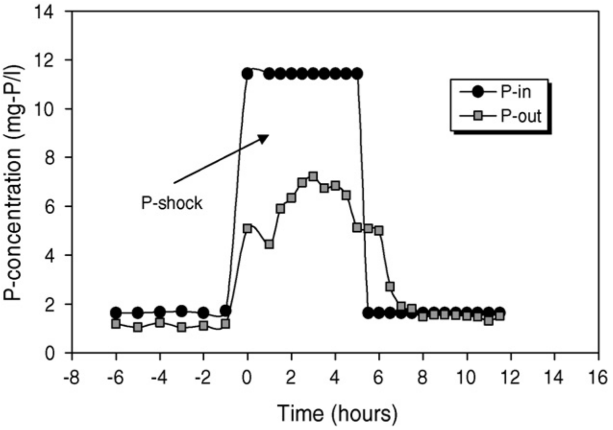

Fig. 6. Effect of shock loading on P removal.

3.2.2. Shock loading and response

At the end of the fifth period, the system was subjected to a shock loading by maintaining the hydraulic loading rate at 9.28 m^3/m^2 day (four times the initial loading rate during the first period) and increasing the influent P concentration seven times, i.e. P loading of 106.2 g-P/m^2 day. The recovery and response of the system was monitored. This was done to simulate possible occurrence in practice and examine the response and recovery of the DAC-WTR. A high loading of 83.4 g-P/m^2 was used in a similar column study on P removal [28]. The primary objective of the applied P shock in this test was to assess the response and recovery of the DAC-WTR after such loads and determine the operating capacity of the system.

The deliberate P shock loading lasted for 5 h and the effluent P concentration was monitored every half hour. Initial operating conditions were resumed after the shock loading and terminated after 10 days. The effect of the shock load on the P removal in the "alum sludge bed" is shown in Fig. 6. It can be seen from Fig. 4 that despite the very high P loading and the near saturation of the adsorbent (with P removal declined to about 25.5% prior to the application of the P shock), an improved P removal efficiency (45%) was obtained. When influent P concentration dropped back to the pre-shock level, the effluent P concentration returned to the pre-shock level after about 3 h. But removal efficiency declined further after a few days to less than 10%. Two interesting points can be noted here: (1) The significant amount of P adsorbed during the shock test may suggest that although the residence time is important in ensuring sufficient contact time for P removal in the column, it appears the P loading rate had more effect on the removal process. For instance, in the period preceding the shock load corresponding to a loading rate of 16.5 g-P/m^2 day and an average residence time of 0.5 h, the average removal efficiency was about 26% whereas during the immediate shock period with the same retention time but at an extremely high loading of 106.2 g-P/m^2 day, the efficiency was increased to about 45%. (2) It can also be suggested that the adsorption of P in the column is diffusion controlled as the high concentration of P in the influent might have initiated a concentration gradient, which further drives the phosphate in solution to the adsorptive sites on the adsorbent up to saturation. This suggests that as long as the operating capacity is not reached,

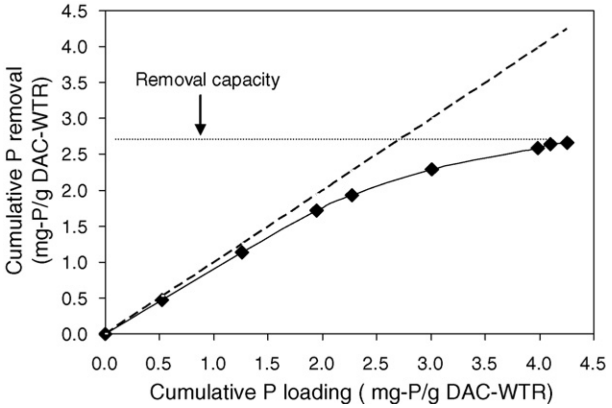

Fig. 7. Plot of cumulative P removed against cumulative P loaded in the DAC-WTR column. (The long dashed line represents points corresponding to 100% removal.)

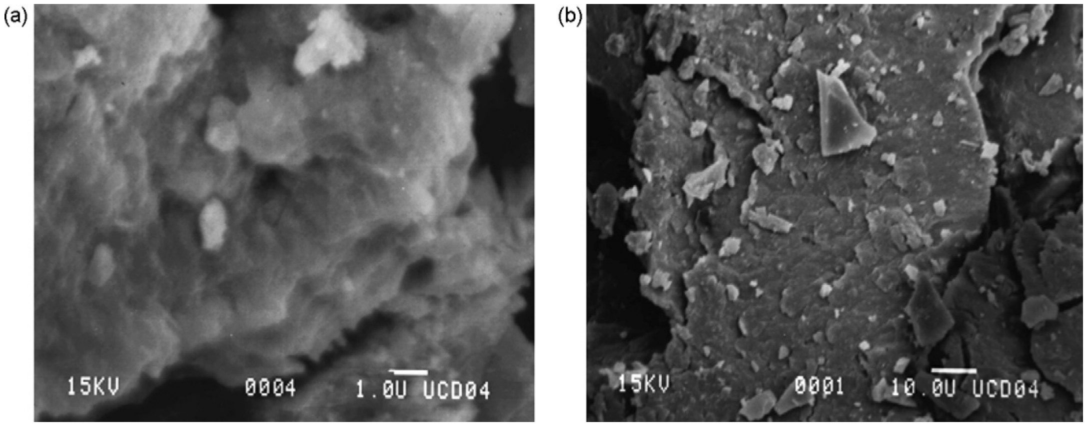

Fig. 8. SEM images (magnification, 3000×) of surfaces of (a) fresh and unused DAC-WTR and (b) DAC-WTR loaded with P for 140 days.

the “alum sludge bed” is able to sustain P reduction in influent load even at high incidental increases.

3.2.3. Estimation of operating capacity

Operating capacity of the system was determined as the capacity obtained when the adsorbent is exhausted and the effluent equals the influent concentration. This has been appropriately used and referred to in other column adsorption studies [29]. The pH value during the period of investigation ranged between 6.55 and 7.35. By taking into account the total P loaded onto the DAC-WTR including the shock load and the cumulative P removed, an operating capacity of 2.66 mg-P/g was determined as illustrated in Fig. 7, and this is about 83.3% of the value obtained for adsorption capacity at pH 7.0 in the batch kinetic tests (Table 1).

The adsorption capacity obtained at pH 7.0 (Table 1) would suggest that 1 kg of the adsorbent used in this study would remove 3.12 kg of P from the solution. Therefore, at the initial conditions of the column test corresponding to a load of 16.34 mg-P/day, and assuming 100% removal, the operating capacity of the system should span about 7 months. However, as shown in Fig. 5, at the end of the test (approximately 5 months) including the shock and recovery period, an operating capacity of 2.66 mg-P/g was achieved, which is 83.3% of the value obtained during the batch tests.

Therefore, the results of this study would indicate that the adsorption capacity obtained in the batch test could give an idea of the total amount of P that can be removed by the substrate material but the system P loading would determine the operating time. Therefore, when evaluating the long term removal capacity of a P adsorbent, the loading and concentration should be carefully chosen. As stated earlier, although the removal of P by the DAC-WTR is a finite process, it is more important to realise that a significant amount of P can be immobilized by the DAC-WTR up to saturation, while the P-saturated DAC-WTR may further be used as a soil improver.

3.2.4. SEM examination of sludge surface

SEM examination of the sludge before and after the continuous P adsorption in the column is shown in Fig. 8. SEM is a qualitative method used to investigate the material's surface. Fig. 8 clearly shows the difference between the two alum sludge surfaces. Before the adsorption (Fig. 8a) the sludge particles have a porous structure, relating to the potential to adsorb P ions from the aquatic solution. However, following the adsorption for 140 days, the particle surface (Fig. 8b) becomes much smoother than that of the original particles.

4. Conclusions

Based on the results of this investigation,the following conclusions can be made:

- The dewatered DAC-WTR has a significant adsorption capacity for the removal/immobilization of condensed phosphate (using sodium hexametaphosphate as model) in aqueous solution. The capacity is pH-dependent and ranges from 4.52 mg-P/g (DAC-WTR) at pH 4.0 to 1.74 mg-P/g (DAC-WTR) at pH 9.0 when evaluated by the Langmuir isotherm equation.
- Continuous flow testing reveals that substantial amount of phosphate was removed from the solution over a period of 140 days. Under a continually increased P loading from 3.9 to 16.5 g-P/m^2 day, P removal rate decreased from 90 to 30%. Overall, an operating capacity of 2.66 mg-P/g of sludge was determined for the system. This represents 83.3% of the value obtained in the batch tests.
- There was no significant loss of sludge or release of aluminium during the continuous flow test. This indicates that the dewatered DAC-WTR is a suitable material for this reuse. However, there was decrease in column porosity after the test probably due to the disintegration of the sludge into finer particles.
- Results of the high reactivity of the DAC-WTR and its effectiveness in immobilizing condensed phosphate provides a basis for a multi-prong approach to sustainable development as the DAC-WTR is converted from a waste to landfill material into a resource for the removal of P from wastewater.

Acknowledgements

This study was partially supported by the Irish Environmental Protection Agency under the Environmental Technologies

Research Awards (grant no.: 2005-ET-S-7-M3). Dublin City Council Water Treatment Works, Ballymore-Eustace, and FH Wetland Systems Ltd. Co., Cork, Ireland are thanked for their assistance during the project. University College Dublin is also acknowledged for financial support awarded to the first author of this paper through the open postgraduate scholarship. Authors also wish to sincerely acknowledge the stimulating questions and remarks of the anonymous reviewers.

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