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Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution

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Abstract

Drinking-water treatment sludge (DWTS) produced at water treatment plants is an inescapable by-product and has long been treated as a waste for landfill. In this study, a series of batch adsorption tests were conducted using a wide range of phosphorus (P) species to determine the adsorption capacities of freshly dewatered aluminium salt based DWTS. The adsorption process is highly dependant on the pH of the suspension and is good at low pHs with adsorption capacities in the order of orthophosphate>polyphosphate>organic phosphate when these three P species were simulated according to their level in typical municipal wastewater. At pH 4.0, the adsorption capacity for orthophosphate was 10.2 mg-PO₄³⁻/g DWTS, polyphosphate was 7.4 mg-PO₄³⁻/g DWTS and organic phosphate was 4.8 mg-PO₄³⁻/g DWTS. Subsequently, a continuous flow column test with dewatered Al-based DWTS as filter medium was conducted at a hydraulic loading of 2.79 m³/m².d and an extremely high P loading of 210.5 PO₄³⁻/m².d. The sludge bed remained stable and removed over 80% P in a 30 day period and the bed did not reach saturation point for over 60 days. This proves the potential of the sludge as a filter material in various forms of P immobilization, thus converting it from a waste to a useful material in pollutant control.

Keywords; Adsorption, aluminium, drinking water treatment sludge, phosphorus removal, reuse

1. INTRODUCTION

Drinking-water treatment sludge (DWTS) is a by-product generated during the production of drinking water where aluminium or iron based salts are used as coagulants to remove colour, turbidity and humic substances. Current legislation classifies DWTS as waste and usually it is chemically conditioned and mechanically dewatered before disposal in landfills. Although various alternative options for disposal, regeneration and beneficial reuse of DWTS have been explored in the past decade [1], the search for cost effective and eco-friendly disposal option(s) has become an urgent priority due to tighter environmental regulations, declining public acceptance of landfill solutions, increasing disposal costs and decrease in landfill capacity.

Aluminium or iron hydroxides are the important component of the sludge once it has been dewatered and this opens the possibility of reusing it to control pollutants such as phosphorus (P) since aluminium or iron ions can enhance their adsorption and chemical precipitation. Extensive studies have shown the effectiveness of DWTS for P immobilization in soils [2-5] and for preventing phosphorus runoff from agricultural land, holding phosphorus on the land until a crop uses it. Other recent studies explore the phosphorus adsorption ability of DWTS (especially aluminium based DWTS) and its use in other applications [6-10]. Ippolito et al. [11] reported a high phosphorus-binding capacity of approximately 12.5 g P/kg DWTS while Dayton and Basta [12] claimed a capacity ranging from 10.4 to 37.0 g P/kg DWTS by examining 18 DWTSs in the U.S. Leader et al. [13] reported a study of the use of lime and iron sludges as potential constructed wetland co-treatment substrates for both dairy and municipal wastewater treatment. Zhao et al. [14] also studied the reuse of dewatered Al-based sludge cake as the main substrate in a reed-bed system for P-enriched wastewater treatment. Chu [15] investigated the removal of dye from textile industry effluent using Al-based DWTS. Basibuyuk and Kalat [16] reported the use of waterworks sludge for the treatment of wastewater from a vegetable oil refinery. Guan et al. [17] studied the use of Al-

based DWTS for particulate removal in primary sewage treatment, using the large amount of insoluble aluminium hydroxides in the sludge as a coagulant in chemical coagulation/flocculation. More recently, the use of DWTS as a sorbent for perchlorate and arsenic removal was investigated by Makris et al. [18,19].

Although adsorption of P by DWTS has been well documented, P adsorption studies have concentrated predominately on the orthophosphate form and there is little information on the effectiveness of DWTS with other forms of P. Since phosphorus is a major influence on eutrophication in fresh waters, the study of P adsorption with a variety of species further the use of DWTS, converting it from a waste to a useful material, in accordance with the theme of environmental sustainability. Here, the adsorption by an Irish DWTS of three phosphate species (orthophosphate, polyphosphate and organic phosphate) was studied using laboratory batch and column tests with phosphate concentrations typical of municipal wastewater. The importance of this study lies in providing quantitative experimental evidence of the ability of DWTS to aid in P pollution control.

2. METHODOLOGY

2.1 Batch adsorption tests

Dewatered DWTS samples were collected from the dewatering unit of the Ballymore-Eustace Water Works located in Co. Kildare, South Dublin, Ireland where aluminium sulphate was employed for reservoir water flocculation. The large pieces of collected sludge cake were broken down to smaller fractions to pass a 2.36mm sieve. The moisture content (MC) of the sludge at the time of use was 74.5%. The major elemental components of the sludge were determined by ICP-analysis and 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 [10]. Three types of phosphate suspensions were prepared

separately; 14.7 mg- PO_4^{3-} /L orthophosphate (potassium dihydrogen phosphate: Riedel De Haen KH_2PO_4 , AnalaR grade), 10.8 mg- PO_4^{3-} /L polyphosphate (sodium hexametaphosphate: BDH $(\text{NaPO}_3)_6$, no grade) and 3.3 mg- PO_4^{3-} /L organic phosphate (adenosine monophosphate: Fluka $(\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P H}_2\text{O})$, AnalaR grade). The phosphate suspensions were prepared by dissolving pre-weighted salts in distilled water (pH 6.9-7.1) and the phosphate concentrations were typical of municipal wastewater [20].

Different masses of alum sludge ranging between 0.1g to 0.5 g and 100 ml of P suspension were poured into 150ml plastic bottles and the pH values of the suspensions were adjusted to 4.0, 5.5, 7.0 and 9.0 respectively by adding 0.1M sulphuric acid and 0.01M sodium hydroxide. The mixed samples were placed on a Stuart Orbital Shaker (SSL 1, Bibby Sterilin Ltd.) to agitate at 200 rpm for various durations up to 24 hours although different equilibration times of 17 hours [21], 24 hours [8, 11], 48 hours [10], 6 days [12] and up to 80 days [4] with initial P concentration ranged from 5.0 to 3,500 mg P/L were reported in similar studies. Then the samples were removed from the shaker and filtered using a 0.45 Millipore membrane filter to separate the solids from the liquid. The residual P concentration was determined according to method 8114 (HACH) using a HACA DR-2400 spectrophotometer. Phosphate that responds to colorimetric tests without any hydrolysis or oxidation digestion is called “reactive phosphorus”. Since colorimetric methods are only able to measure the concentration of reactive phosphorus, all other forms of phosphorus have to be converted/digested to the orthophosphate form first. In this study, orthophosphate was determined by the colorimetric method after reaction with vanadomolybdate reagent. The polyphosphate was digested to reactive phosphorus using the acid hydrolysis method by heating the sample at 105°C with sulphuric acid. The persulphate digestion method was used for the conversion of organic phosphate to reactive phosphate. The sample is heated to 105°C with sulphuric acid and potassium

persulphate salts. There was no control of temperature during the batch tests. However the room temperature was relative constant (21 ± 2 °) with no significant change.

2.2 Continuous flow test

A laboratory-scale continuous flow system as shown in Fig. 1 was set up using a 7.4 cm diameter Pyrex column (90cm long) filled with 500 g of prepared sludge (MC of 74.5%, sieved to pass a 2.36mm sieve) to form a packed sludge bed on top of a 10 cm supporting layer of gravel. A fine wire mesh is placed at the bottom of the column to prevent any loss of sludge. The artificial P-enriched solution was made up of a mixture of the three types of phosphate species used for the batch adsorption tests where the concentration of orthophosphate was 50.8 mg-PO₄³⁻/l, polyphosphate was 18.1 mg-PO₄³⁻/l and organic phosphate was 6.5 mg-PO₄³⁻/l which simulate the proportion of P species in typical municipal wastewater [20]. The pH of the artificial P-enriched solution is 6.8-7.2. This multi-P species solution was then fed into the top of the column by a peristaltic pump to pass through the sludge bed and the effluent was collected from the bottom of the column. The system was subjected to a high hydraulic loading and a P loading of 2.79 m³/m².d and 210.5 g-PO₄³⁻/m².d respectively for over 60 days. The influent and effluent samples were collected and phosphate concentrations were determined following the methodology described above. The effluent was also assessed for suspended solids (SS) from time to time to ensure that the system was not losing any sludge particles.

[Fig. 1 here]

3 RESULTS

3.1 Batch adsorption tests

To identify the adsorption capacities of dewatered alum sludge, a series of batch tests were carried out as described above. Fig. 2 illustrates the residual P concentration with adsorption period at

varied DWTS dosage for the three P species. As shown in Fig. 2, the decrease in P concentration with adsorption period for all P species tested demonstrates that alum sludge has the ability to remove P through adsorption. Although the similar adsorption trend is observed, the dosing regime has affected the adsorption behaviour. More P is immobilized when 5 grams of sludge is used per litre of suspension compared to 1 gram. Similar results were obtained by Yang et al., [10]. It is apparent that the drop in P concentration is significant in the first 2 hours. The reduction was however more gradual thereafter and equilibrium was finally achieved after 24 hours of contact time except for the case of polyphosphate shown in Fig. 2b, indicating the variations of the P adsorption between the P species. This may be caused by the different initial concentrations of each of the prepared P species. However, varied P adsorption behaviour between P species was reported due to competitive adsorption even for the same initial concentration of the P species when aluminium hydroxide was employed as adsorbent [22].

[Fig. 2 here]

It has been illustrated in Fig. 3 that pH has an important impact on the mass of P adsorption. Greater P removal was observed when the pH of the suspension was within the acidic range while less adsorption occurred within the basic region for all P types analysed. P is adsorbed most when the pH of the suspension is 4.0 followed by 5.5, 7.0 and 9.0 for all three P species analysed. This is consistent with that reported by Kim et al., [8] and Yang et al., [10]. Both studies claimed that the P-adsorption by DWTS is favoured at acidic condition although orthophosphate was tested most.

[Fig. 3 here]

The maximum P adsorption capacities were determined using the linear form of the Langmuir isotherm as shown in Eq. (1)

$$\frac{C_e}{(x/m)} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \quad (1)$$

where x/m is the mass of P absorbed per unit mass of sludge at equilibrium, b is an empirical constant, Q_o is the maximum adsorption capacity (mg adsorbate/g adsorbent) and C_e is the equilibrium concentration of adsorbate in solution after adsorption. Q_o is determined as the reciprocal of the slope by plotting equilibrium test data of $C_e/(x/m)$ against C_e (see Eq. (1)).

Fig. 4 shows the adsorption capacities for orthophosphate, polyphosphate and organic phosphate at pH values of 4.0, 5.5, 7.0 and 9.0. The adsorption capacities vary for each phosphate type where orthophosphate has the highest adsorption capacities for all pH values tested while organic phosphate removal was the slowest. The adsorption capacity for orthophosphate was 10.2 mg-PO₄³⁻/g sludge, polyphosphate was 7.4 mg-PO₄³⁻/g sludge and organic phosphate was 4.8 mg-PO₄³⁻/g sludge, all at pH 4.0. Higher removal efficiencies were recorded at lower pH ranges while lower removal rates were observed at higher pHs. In comparison with the adsorption capacities obtained at pH 4.0, the adsorption capacities for orthophosphate, polyphosphate and organic phosphate at pH 9.0 was 6.3 mg-PO₄³⁻/g sludge, 3.2 mg-PO₄³⁻/g sludge and 2.6 mg-PO₄³⁻/g sludge respectively. Overall the adsorption capacities are in the following order: orthophosphate > polyphosphate > organic phosphate.

[Fig. 4 here]

3.2 Continuous flow test

Phosphate breakthrough curves were used to quantify P adsorption under continuous loading. The ratio of effluent concentration (C_e) to influent concentration (C_o) was plotted against the column operation time (with a constant daily flow rate), as shown in Fig. 5. The breakthrough curves showed a slow increase from the beginning till 30days' operation, indicating that the DWTS bed poses efficient P immobilisation ability for all three P species regardless of the extremely high phosphorus and hydraulic loadings. Initially orthophosphate removal efficiencies remained over

80% for 28 days, but the ratio of C_e/C_0 increased more rapidly compared to polyphosphate and organic phosphate after 30 days. Consequently, C_e/C_0 of orthophosphate reached 0.92 at 62th day when the experiment was ended. This implied the approach of saturation point of orthophosphate adsorption. In contrast, the increases of C_e/C_0 of polyphosphate and organic phosphate were relative slow in spite of the fluctuated pattern shown in Fig. 5. At the end of the experiment, the ratio of C_e/C_0 was recorded as 0.43 and 0.45 for polyphosphate and organic phosphate respectively, corresponding to a lowest removal efficiency of 57.3% (for polyphosphate) and 54.6% (organic phosphate).

[Fig. 5 here]

Fig. 6 illustrates the mass of phosphate species in and out during entire continuous column testing. Substantial P immobilization can be observed despite the difference in influent concentrations of P species. According to Fig. 6, calculated mass of immobilized P per mass of DWTS for orthophosphate, polyphosphate and organic phosphate is 50.7, 23.5 and 8.6 mg-PO₄³⁻/g DWTS, respectively.

[Fig. 6 here]

4 DISCUSSION

4.1 Batch adsorption tests

It was evident from this study that P adsorption by an Al-based DWTS was affected by a number of factors (Figs. 2 and 3). By increasing the quantity of sludge, although the P adsorption per mass of DWTS could be decreased since more adsorption sites become available, the total mass of P adsorbed would increase. Thus, the residual P concentration when a larger quantity of sludge was added into the P suspension was much lower compared to when only a small amount of sludge was

used. Faster P removal occurred when available sites were more abundant than available P [23]. Other studies also reported the same effect [6, 10].

Adsorption is believed to be a physicochemical process that is highly dependant on pH [8, 10, 24]. Adsorption favours a low pH medium as adsorption is coupled with the release of OH^- ions [25]. Minimal P removal took place within the alkaline ranges due to more OH^- ions in the suspension occupying the active sites on the surface of the alum sludge, forming a counter ion layer that reduces P adsorption. OH^- ions compete strongly with phosphates for available sites when the suspension is within the alkaline ranges [26]. Past studies [8, 24, 27] have proven that aluminium solubility is highly dependant on pH. Yang et al. [26] reported that the surface charge of Al-based DWTS sludge showed a variation from +75.8 mV to -33.7 mV that corresponds to a pH change from 4.3 to 9.0. A positive surface charge when the pH of the suspension is low would indicate the presence of unsatisfied surface charge that is neutralised by the phosphate ions.

Al-based DWTS adsorbed inorganic phosphate to a greater extent than organic phosphate for all pH values tested (Fig. 4). Similar findings were reported by Kim et al. [8] and Galarneau and Gehr [24]. The difference in adsorption capacities suggests that different mechanisms are responsible for the removal of inorganic and organic phosphates. Apart from that, the phosphate structure and the structure of the complexes formed between phosphate and the sludge add to the difference [22]. Orthophosphate occupies the adsorbent surface more rapidly since it has a greater diffusion rate due to its smaller molecular weight [22]. The maximum adsorption capacities derived in this study differ from those obtained in other studies, Table 1. This difference could be attributed to the nature of the alum sludge and the phosphate suspensions used as well as the testing conditions. The properties of DWTS are highly variable depending on the source of the raw water as well as the chemical used during raw water treatment [4, 5]. More importantly, Dayton and Basta [12] reported

a significant effect of experimental conditions including particle size, initial P concentration and equilibration time on maximum adsorption capacity (Q_0). According to their study, a mean increase of Q_0 of 2.46-fold was obtained when particle size of DWTS was reduced from <2mm to <150 μm while a increase of 5.83-fold on Q_0 was gained after prolonging shaking time from 17 hours to 6 days with corresponding of the particle size of <2mm and <150 μm being used (Table 1).

[Table 1 here]

4.2 Continuous flow tests

Fig. 5 provides the evidence that Al-based DWTS in a fixed bed can serve as an adsorption material for efficient immobilization of a wide range of P species. When compared with limited data in the literature, the packed DWTS bed in this study performed well under high hydraulic ($2.79 \text{ m}^3/\text{m}^2.\text{d}$) and phosphate ($210.5 \text{ g-PO}_4^{3-}/\text{m}^2.\text{d}$) loadings. The concentration of orthophosphate accounts for 67% of the total phosphate concentration (three P species mixed together) in the influent while the concentration of polyphosphate and organic phosphate makes up the remaining 24% and 9%. This simulates the proportions of P species found in municipal wastewater [20]. Due to the high P loadings, the removal efficiency decreases rapidly over time especially after 30 days operation (see Fig. 5). One of the objectives of this study was to explore the feasibility of using dewatered Al-based DWTS as a potential material for P adsorption/removal. For this reason, we used a higher P loading than is usually encountered in wastewater practice, especially in domestic and municipal wastewaters. It is reasonable to believe that the packed DWTS bed should be operated longer if a lower P loading applied. Due to the different concentrations of P species in influent, direct comparison of adsorption behaviour from P breakthrough curves is questionable. However, one of the important outcomes of the continuous operation is the measurement of the mass of trapped P per mass of the DWTS used. Computed masses of $50.7 \text{ mg-PO}_4^{3-}/\text{g}$ (Ortho-P), $23.5 \text{ mg-PO}_4^{3-}/\text{g}$ (Poly-P) and $8.6 \text{ mg-PO}_4^{3-}/\text{g}$ (Organic-P) were obtained during the entire continuous operation period. This

is at variance with the maximum adsorption capacities shown in Fig. 4. The reason could be multi-derived. However, the use of an equilibrium time of 24 hours in estimating maximum adsorption capacity in this study may be inadequate, leading to the underestimation of the capacity since the P adsorption equilibrium by DWTS can be a long time. Makris et al., [4] conducted a long-term test of up to 80 days adsorption with four Al-based DWTS collected from different locations in the U.S. They claimed that the Langumir-based P sorption maxima were not determined as the isotherm did not reach an obvious plateau. Makris et al., [28] also established an intraparticle P diffusion model to help predicting long-term adsorption behaviour of DWTS. Dong et al. [29] and Arias and Brix [30] also reported the disagreements between batch test and continuous test in maximum adsorption capacity. They suggest that the theoretical batch-test estimation of adsorption capacity may lead to a biased result when applied to a real treatment system like reed beds. Obviously, relevant further study is needed and dynamic modelling is desirable to develop a better understanding of operation characteristics.

Fig. 5 indicates that the decrease in removal efficiency of orthophosphate after 30 days operation is more significant than that of other two P species. The reason may be related to the competition for adsorption among the P species. It has been proven that certain adsorption sites on metal hydroxide surfaces may favour orthophosphate while others may be specific for other phosphate species [31]. When the concentration of orthophosphate is high, the orthophosphate specific adsorption sites may become exhausted leading to competition between orthophosphate ions and other phosphate species for common surface sites [22].

During the continuous column testing, a closing observation and time to time measurement of effluent SS were made to explore the possible loss by dissolving of alum sludge. This issue is critically important as any SS in the effluent would possibly signify both the loss of sludge material

and adsorptive sites, making the proposed practical reuse of alum sludge impossible. However, the SS monitoring suggest that there was no significant loss of sludge during the testing period. However, some compaction of the sludge particles was observed as indicated by the decrease in height of the packed sludge column. A direct consequence of the sludge compaction is a reduction in the hydraulically active pore volume, and this may lead to the clogging of the bed during long term operation. However, this is beyond the scope of the current study.

5 CONCLUSIONS

This study has demonstrated that dewatered Al-based DWTS has the potential to be used as raw material for a wide range of P species removal in simulated P-enriched wastewater. Considerable amounts of P can be adsorbed onto a relatively low mass of DWTS. The adsorption capacities obtained from the Langmuir isotherm vary for the different types of P species as well as the pH of the P suspension. The highest adsorption capacity is obtained for orthophosphate (say, KH_2PO_4), followed by polyphosphate (say $(\text{NaPO}_3)_6$) and finally organic phosphate (say $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P} \cdot \text{H}_2\text{O}$). P adsorption favours acidic suspensions rather than alkaline suspensions for all the three P species tested. In a continuous flow test, a simulated Al-based DWTS bed received a high hydraulic loading of $2.79 \text{ m}^3/\text{m}^2\cdot\text{d}$ and an extremely high P loading of $210.5 \text{ PO}_4^{3-}/\text{m}^2\cdot\text{d}$. Results show that the dewatered Al-based DWTS bed removed more than 80% of P regardless of the P species in 30 days and the bed did not reach saturation point for continuous operation after 60 days. Thus Al-based DWTS has proven its utility as a filter material or adsorbent in P immobilization. Therefore, this study quantifies the benefits of reusing such sludge to remove P in real wastewater treatment engineering, such as constructed treatment wetland. Reusing Al-based DWTS as a P adsorbent is not only effective but also a potentially cheap approach to remove P. The findings of this study could revolutionise the handling of such kind of sludge in Ireland in the future for the reuse of it as

a low-cost material, rather than as a waste requiring costly disposal, in accordance with the concept of sustainable development.

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FIGURES

Fig. 1 Schematic of continuous flow test

Fig. 2 Effects of DWTS dosing regime on P adsorption at pH 4 for (a) orthophosphate, (b) polyphosphate and (c) organic phosphate

Fig. 3 Effects of pH on P adsorption at DWTS dose of 5g/L for (a) orthophosphate, (b) polyphosphate and (c) organic phosphate

Fig. 4 Adsorption capacities for orthophosphate, polyphosphate and organic phosphate

Fig. 5 Breakthrough curves of phosphate species in continuous column testing

Fig. 6 Mass of phosphate species in and out during continuous column testing

TABLES

Table 1 Comparison of maximum adsorption capacities of this study with that reported from the literature

Test conditions	Maximum adsorption capacity Q_0 (mg PO_4^{3-} /g DWTS)			Reference
	Ortho-P	Poly-P	Organic-P	
Particle size <2.36 mm pH 4.0 Equilibration time 1 day	10.2 (Initial P concentration 14.7mg PO_4^{3-} /l)	7.4 (Initial P concentration 10.8mg PO_4^{3-} /l)	4.8 (Initial P concentration 3.3 mg PO_4^{3-} /l)	This study
Particle size <2 mm Initial P concentration up to 4,000 mg PO_4^{3-} /l pH 7.1 Equilibration time overnight	25.0	14.3	12.5	[8]
Particle size 0.063-2.36 mm Initial P concentration 15.3 mg PO_4^{3-} /l pH 4.3	10.5	≐	≐	[10]
NS*	0.30-0.33	≐	≐	[7]
Particle size 0.1-0.3 mm Initial P concentration 918 mg PO_4^{3-} /l Equilibration time 1 day	38.3	≐	≐	[11]
Particle size <2 mm Initial P concentration 10.7g PO_4^{3-} /l Equilibration time 17 hrs	2.02-50.49	≐	≐	[21]
Particle size <150 μm Initial P concentration 0-10.7 g PO_4^{3-} /l	5.63-90.27 (Equilibration time 17 hrs) 31.82-113.22 (Equilibration time 6 days)	≐	≐	[12]
Particle size <2 mm Initial P loading 30.6 mg PO_4^{3-} /g sludge Equilibration time 10 days	22.95-30.60 (four kinds of alum sludge tested)	≐	≐	[4]

NS*: not specified