Dewatered alum sludge: A potential adsorbent for phosphorus removal

Y. Yang*, D. Tomlinson, S. Kennedy and Y.Q. Zhao

Centre for Water Resources Research, Department of Civil Engineering, University College Dublin, National University of Ireland, Earlsfort Terrace, Dublin 2, Ireland
(E-mail: *yongzhe.yang@ucd.ie*; *DaveyTomlinson@gmail.com*; *Skennedy6@hotmail.com*; *yaqian.zhao@ucd.ie*)

Abstract
Alum sludge refers to the by-product from the processing of drinking water in Water Treatment Works. In this study, groups of batch experiments were designed to identify the characteristics of dewatered alum sludge for phosphorus adsorption. Air-dried alum sludge (moisture content 10.2%), which was collected from a Water Treatment Works in Dublin, was subjected for artificial P-rich wastewater adsorption tests using KH_2PO_4 as a model P source. Adsorption behaviours were investigated as a function of amount and particle size of alum sludge; pH of solution; and adsorption time. The results have shown that pH plays a major role not only in the adsorption process but also in the adsorption capacity. With regard to adsorption capacity, this study reveals the Langmuir adsorption isotherm being the best fit with experimental data (R^2=0.98-0.99). The maximum adsorption capacities range from 0.7 to 3.5mg-P/g when the pH of the synthetic P solution was varied from 9.0 to 4.3, accordingly. The outcome of this study indicated that alum sludge is suitable for use as an adsorbent for removal of phosphate from wastewater.

Keywords
Adsorption; alum sludge; phosphorus; reuse; wastewater treatment

INTRODUCTION

Wastewater containing phosphate should be treated before discharge to eliminate the possible danger of causing eutrophication of receiving waters. With regard to phosphorus removal technologies, the most important removal processes are chemical removals including phosphorus precipitation with aluminium, calcium and iron salts (de-Bashan and Bashan, 2004). However, the cost associated with the use of metal salts may hinder the widespread application of the chemical removal technologies. Therefore, seeking the low-cost adsorbents remains the active research topic for phosphorus removal. To date, a number of “materials” have been tested as adsorbents in their natural and modified features. For example, activated red mud (Pradhan, *et al*., 1998), slag (Lee, *et al*., 1997), sand (Arias, *et al.*, 2001, Bubba, *et al.*, 2003;), fly ash (Ugurlu, *et al*., 1998), iron oxide tailing (Zeng, *et al*., 2004), activated aluminium oxide and granulated ferric hydroxide (Genz, *et al*., 2004) were all reported for phosphorus adsorption in recent years. It is noted from the literature that alum sludge has also been preliminarily investigated for use in this type of process with varying degrees of success (Kim, *et al*., 2003).

Alum sludge refers to the by-product from the processing of drinking water in Water Treatment Works when aluminium sulfate is used as coagulant. In Ireland, alum sludge is dewatered and then disposed of as waste to a landfill site since alum sludge contains a high level of aluminium, which has been shown to be toxic to aquatic life and relatively inert, providing marginal benefits to soil fertility. However, the abundant amorphous aluminium ions in dewatered alum sludge can become valuable for phosphorus removal in wastewaters since the ions enhance processes of adsorption and chemical precipitation (Sujana, *et al*. 1998; Huang and Chiswell, 2000; Chu, 2001). Moreover, the reuse of alum sludge will be environmentally and economically beneficial. Although management of alum sludge is receiving much attention in recent years, its use for phosphorus removal as an adsorbent remains in the infant stage.

The purpose of this study is to test the adsorption behaviour of dewatered Irish alum sludge for phosphorus removal in an artificial solution. Groups of experiments were designed to investigate the effects of amount and particle size of dewatered alum sludge, as well as pH on phosphorus adsorption rate. Adsorption capacity was then studied. Finally, the possible application of this kind of research towards the reuse or final disposal of dewatered alum sludge is highlighted.

MATERIAL AND METHODS

Alum sludge and phosphorus solution

Dewatered alum sludge was collected from Ballymore Eustace Water Treatment Works in Southwest Dublin, where a filter press was used for dewatering and the moisture content of the dewatered sludge cake is 72-75%. After collection, the sludge cakes were subjected for air-drying in room temperature and the moisture content became 10.2% at the time of being used. This air-dried sludge was then ground and sieved to provide the testing sludge (adsorbent) with different range of particle sizes. By using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Advantage), TOC-V CSH (Shimadzu) and FT-IR Spectrophotometer (EQUINOX-55), the characteristics of the sludge in this study are illustrated in Table 1.

Table 1. The chemical components of alum sludge

Chemical composition	Unit	Amount
Aluminum (as Al_2O_3)	mg/g	458-463
Iron (as Fe_2O_3)	mg/g	11.9-12.3
Calcium (as CaO)	mg/g	11.6-11.7
Magnesium (as MgO)	mg/g	7.4-7.6
Humic acid (as TOC)	mg/g	96.4-98.5
Cl^-	mg/g	16.0-16.2
SO_4^{2-}	mg/g	8.2-8.4
SiO_4^{2-}	mg/g	10.6-11.8
H_2O at 105℃ (moisture content)	%	10.2
H_2O at 1000℃	mg/g	260-270

The phosphorus solution was prepared artificially by dissolving the pre-weighed potassium dihydrogen phosphate (KH_2PO_4) in distilled water. This solution was then incubated in laboratory at 20±2℃ and maintained airtight to prevent the CO_2 from affecting the pH of the solution.

Experimental procedure

Adsorption experiments were conducted in 250 ml flasks. Defined amounts (50, 100, 150, 200, 250, 500mg) of alum sludge were added to 50ml distilled water in a series of flasks. The flasks were then introduced with 50 ml aliquots of phosphate solution, which has the concentration of 10mg-P/l, to obtain initial phosphate concentration of 5 mg-P/l and concentration of alum sludge 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 g/l, respectively. Prepared flasks were placed on an orbital shaker (SSL1, Bibby Sterilin LTD, UK.) at 200 rpm for a certain adsorption period. After completing the adsorption test the suspensions in flasks were filtered through 0.45μm millipore filter paper to separate the sludge and the liquid. The phosphate and pH of the liquid were respectively monitored using a Hach spectrophotometer (DR/2400) and a pH meter (WTW, pH 325, Germany). Effect of pH on adsorption was conducted by series adsorption tests at fixed amount of sludge addition with different pH of suspension from 4.3 to 9.0 adjusted by either sulfuric acid (0.01 M) or sodium hydroxide (0.1M). Adsorption tests were also conducted with the same amount of sludge addition but varied particle size.

RESULTS

To identify the adsorption ability of dewatered alum sludge, series bottle adsorption tests were carried out with different amounts of sludge (adsorbent) addition. Adsorption behaviour was monitored by measuring the residual phosphorus against the adsorption period till the equilibrium concentration was reached. The results are illustrated in Fig. 1. It is evident from Fig. 1 that the dewatered alum sludge has the ability to be an adsorbent for phosphorus removal. Although the different amount of sludge shows the same trend of adsorption behaviour, it is clear that increasing the adsorbent, results in an increase in phosphorus removal. In addition, the sharp drop of the phosphorus in suspension in 2 hours shown in Fig. 1 indicates the instant at which the adsorption process takes place.

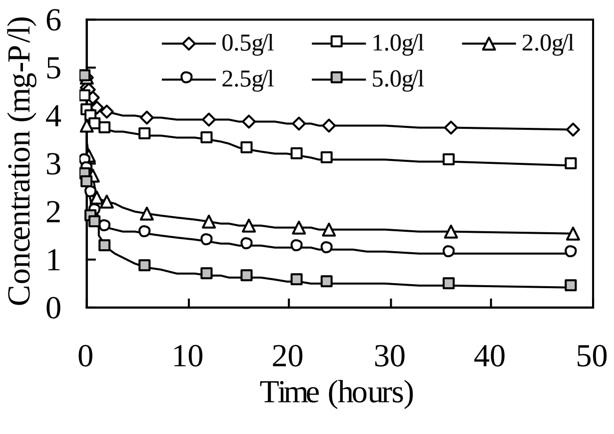


Fig. 1 Residual phosphorus concentration with adsorption period at varied sludge amount (sludge particle size of 0.063 mm, pH at 6.8-7.2)

Fig. 2 presents the effect of sludge particle size on adsorption behaviour. It is observed clearly that the fine grain of sludge will bring about a better adsorption process, which leads to not only the rapid reduction of phosphorus in suspension but also the lower equilibrium concentration, indicating the extent of phosphorus removal.

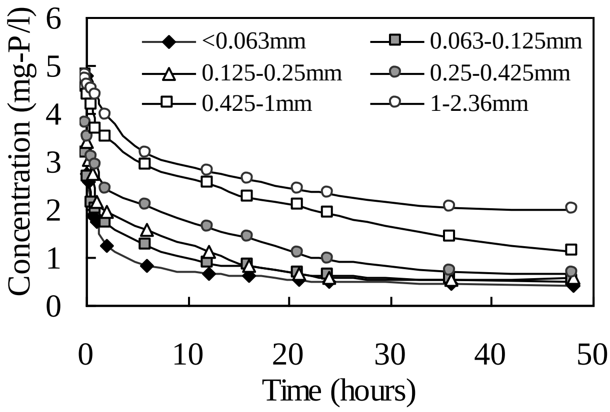


Fig. 2 Effects of particle size on adsorption behaviour (sludge amount of 5 g/l, pH at 7.0)

The effect of pH on adsorption behaviour was examined and the results are shown in Fig. 3. By inspecting the diagram, it is noted that the greater amounts of phosphorus are captured in acid environment while the reduced adsorption of phosphorus occurs in alkaline environment. Thus the adsorption capacity of alum sludge is strongly pH dependent. The period to reach the equilibrium concentration can be identified as 48 hours as noted from Fig. 3.

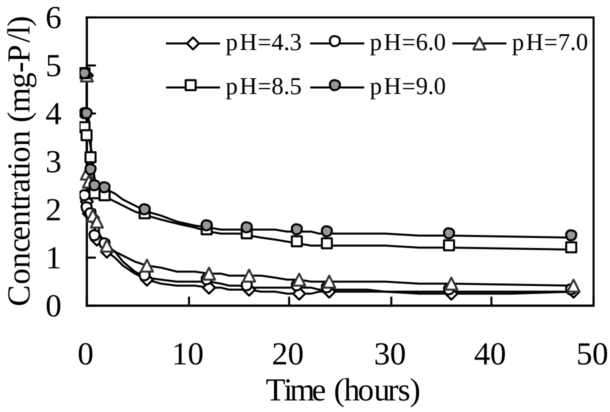


Fig. 3 Effects of pH on adsorption behaviour (sludge amount of 5 g/l, particle size of 0.063 mm)

Fig. 4 shows the adsorption capacity in terms of Q_0 (mg-P/g-sludge) as a function of pH of phosphorus suspension. Here, the adsorption capacity was determined experimentally and the data were computed using the Langmuir isotherm in the linear form of

$$\frac{C_e}{(x/m)} = \frac{1}{Q_0}C_e + \frac{1}{Q_0 b} \qquad \text{Eq. (1)}$$

where *x/m* is the mass of phosphorus adsorbed per unit mass of sludge; *b* is a constant related to the energy of the adsorption-desorption process; Q_0 is the maximum adsorption capacity (mg-P/g-sludge); and C_e is the equilibrium concentration of phosphorus (mg-P/l) in suspension after adsorption. It is seen from Fig. 4 that the adsorption capacity decreases from 3.5 to 0.7mg-P/g-sludge when the pH of the phosphate suspension increases from 4.3 to 9.0.

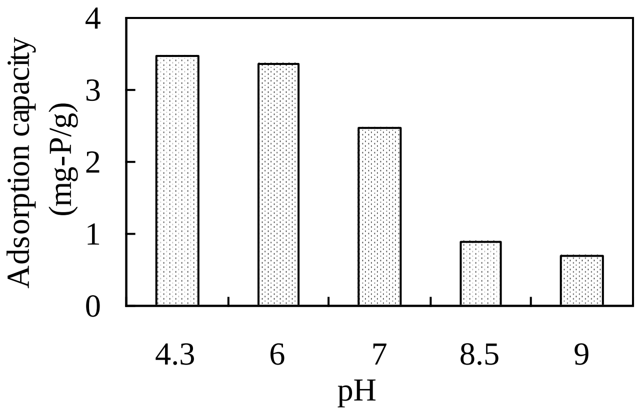


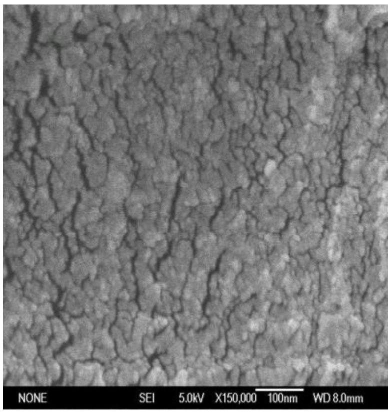
Fig. 4 The adsorption capacity of alum sludge at different pH of suspensions

DISCUSSION

The main objective of this paper is to identify the ability of the Irish dewatered alum sludge for phosphorus adsorption. Thus, a series of adsorption tests with varied amounts of sludge addition was conducted. It seems quite obvious to predict, without experimental demonstration, that the greater amount of phosphorus can be captured by increased amounts of adsorbent. However, it is better to have the trends of adsorption behaviour with different quantities of adsorbent to confirm the existence of adsorption ability (Fig. 1). More significantly, this study identified the adsorption capacity of 3.5 and 0.7mg-P/g-sludge corresponding to the pH of 4.3 and 9.0, respectively. This result is in good agreement with that reported by Huang and Chiswell (2000) who claimed the adsorption of 0.30-0.33 mg phosphate per 1 gram of air-dried spent alum sludge. However, Kim *et al*. (2003) reported a much higher adsorption capacity of 25mg-P/g-sludge. The disagreement may be attributed to the characteristics of alum sludge derived from different raw waters since the properties of alum sludge are highly variable and dependent upon the characteristics of the raw waters.

With regard to the factors affecting the adsorption behaviour, this study demonstrated that the sludge grain size significantly affect the adsorption process (see Fig. 2). This is believed to have something linked with the surface area on where the phosphorus is adsorbed. However, Huang and Chiswell (2000) concluded that the particle size does not appear to be important in the rate of uptake of phosphorus. In this study, pH has been approved as the vital factor to affect the adsorption process (see Fig. 3). It is believed that the adsorption is a physicochemical process which is highly dependent in appearance on pH, but actually on both the species of orthophosphate and the aluminium hydroxide in the suspension. Nevertheless, the result of this study agreed with that reported by Kim *et al*. (2003) on the effect of pH, claiming a lower pH being positive to phosphorus adsorption. However, Karageorgiou *et al*. (2005) provided evidence to support that the best adsorption of phosphorus by calcite occurred at the pH of 12 during the test of pH from 7.6 to 12. Obviously, more research work should be carried out on this aspect.

Although the adsorption mechanism is out of the scope of this paper, the principle of the phosphorus adsorption by alum sludge is considered to be the abundant aluminium ions in dewatered alum sludge (Sujana, *et al*. 1998; Chu, 2001). Table 1 shows that 458-463 mg aluminium (as Al_2O_3) out of 1 g alum sludge is in dewatered Irish alum sludge. However, the alum in the sludge is virtually amorphous, having no distinct shape or form, when examined morphologically by a scanning electron microscope (SEM) (see Fig. 5 (left)), rather than pure aluminium hydroxide (Fluka, 11033, α -$Al(OH)_3$) in a pattern of a regular crystalline structure (see Fig, 5 (right)). Moreover, FT-IR results from this study show that the alum sludge contains some humic acid and the amount given in terms of total organic carbon (TOC) is 96-99 mg/g-sludge (see table 1).



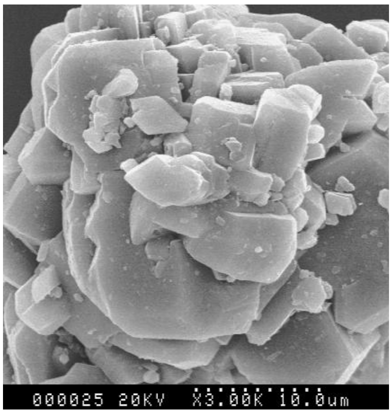


Fig. 5 SEM observation of dewatered alum sludge (left) and aluminum hydroxide (Fluka, 11033, α-$Al(OH)_3$) (right) (JSM-6700F, Field Emission Scanning Electron Microscope, JEOL Ltd)

The chemical composition, the morphological structure and the surface characteristics of alum sludge may affect the adsorption mechanisms and should be considered regarding the research in understanding the adsorption mechanism. Further study will involve the investigation on the adsorption mechanisms that will provide the understanding of adsorption behaviour.

This study reveals some of the potential uses of dewatered alum sludge. For example: Dewater alum sludge could be used as a medium in constructed wetlands for wastewater treatment, especially for phosphorus-rich effluent. Dewatered alum sludge could be used in civil engineering as paving material to assist in runoff water pollution control. Dewatered alum sludge could also be used to build agricultural dams for agricultural wastewater pre-treatment etc. Use of alum dewatered sludge in these and perhaps unexplored-ways would thus transform the alum sludge from a ‘waste’ material into useful material in terms of ‘using waste for waste treatment’; thus complying with the theme of sustainable development. Extensive experiments and further research plans towards future applications of dewatered alum sludge are currently under way at University College Dublin (UCD).

CONCLUSION

The results of this study on phosphate adsorption by using alum sludge as adsorbent support the following conclusions.

- It has been demonstrated in this study that the Irish dewatered alum sludge has the adsorption ability for phosphorus removal. Its adsorption capacity is identified experimentally to be 0.7 to 3.5 mg-P/g-sludge depending on pH of the phosphorus solutions.
- Many factors may affect the adsorption rate and adsorption capacity. The results have shown that the pH plays a key role in adsorption process. Alum sludge has a higher phosphate

adsorption capacity in acid pH region than in alkaline pH region.

- Amount and particle size of alum sludge have the important effects on adsorption behaviour. Large quantity and fine grain of sludge will lead to the enhanced adsorption process for phosphorus removal.
- The utility of phosphorus adsorption ability of the Irish dewatered alum sludge will bring about some potential applications of the sludge to wastewater treatment engineering.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the University College Dublin, National University of Ireland for financial support and Xi'an University of Architecture and Technology (Xi'an, China) for technical support. Mr. Patrick Kearney, a senior technical staff in Water and Effluent Laboratory, University College Dublin, is thanked for his invaluable technical assistance during this study.

REFERENCES

Arias C. A., Bubba M. D. and Brix H. (2001). Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Wat. Res*., **35**(5), 1159-1168.

Bubba M. D., Arias C. A. and Brix H. (2003). Phosphorus adsorption maximum of sands for use media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Wat. Res*., **37**(14), 3390-3400.

Chu, W. (2001). Dye removal from textile dye wastewater using recycled alum sludge. *Wat. Res.*, **35**(13), 3147-3152.

de-Bashan. L. E. and Bashan Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Wat. Res*., **38**(19), 4222-4246.

Genz A., Kornmuller A. and Jekel M. (2004). Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminum oxide and granulated ferric hydroxide. *Wat. Res*., **38**(16), 3523-3530.

Huang, S. H. and Chiswell, B. (2000). Phosphate removal from wastewater using spent alum sludge. *Water Sci. & Technol*., **42**(3-4), 295-300.

Karageorgiou K., Paschalis M. and Anastassakis G. N. (2005). Removal of phosphate species from solution by adsorption on to calcite used as natural adsorbent. 1st International Conference On Engineering for Waste Treatment-Benefical Use of Waste and by-Products, France.

Kim J. G., Kim J. H., Moon H., Chon C. and Ahn J.S. (2003). Removal capacity of water plant alum sludge for phosphorus in aqueous solution. *Chemical Speciation and Bioavailability*, **14**, 67-73.

Lee S. H., Vigneswaran S. and Moon H. (1997). Adsorption of phosphorus in saturated media columns. *Separation and Purification Technology*, **12**(2), 109-118.

Pradhan J., Das P., Das S. and Thakur R. S. (1998). Adsorption of phosphate from aqueous solution using activated red mud. *Journal of Colloid and Interface Science*, **204**(1), 169-172.

Sujana, M. G., Thakur, R. S. and Rao S. B. (1998). Removal of fluoride from aqueous solution by using alum sludge. *Journal of Colloid and Interface Science*, **206**(1), 94-101.

Ugurlu, A. and Salman, B. (1998). Phosphorus removal by fly ash**.** *Environment International*, **24**(8), 911-918.

Zeng L., Li X. and Liu J. (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Wat. Res*., **38**(5), 1318-1326.