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Two strategies for phosphorus removal from reject water of municipal wastewater treatment plant using alum sludge

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Abstract
In view of the well recognized need of reject water treatment in MWWTP (municipal wastewater treatment plant), this paper outlines two strategies for P removal from reject water using alum sludge, which is produced as by-product in drinking water treatment plant when aluminium sulphate is used for flocculating raw waters. One strategy is the use of the alum sludge in liquid form for co-conditioning and dewatering with the anaerobically digested activated sludge in MWWTP. The other strategy involves the use of the dewatered alum sludge cakes in a fixed bed for P immobilization from the reject water that refers to the mixture of the supernatant of the sludge thickening process and the supernatant of the anaerobically digested sludge. Experimental trials have demonstrated that the alum sludge can efficiently reduce P level in reject water. The co-conditioning strategy could reduce P from 597-675 mg P/L to 0.14-3.20 mg P/L in the supernatant of the sewage sludge while the organic polymer dosage for the conditioning of the mixed sludges would also be significantly reduced. The second strategy of reject water filtration with alum sludge bed has shown a good performance of P reduction. The alum sludge has P-adsorption capacity of 31 mg-P/g-sludge, which was tested under filtration velocity of 1.0 m/h. The two strategies highlight the beneficial utilization of alum sludge in wastewater treatment process in MWWTP, thus converting the alum sludge as a useful material, rather than a waste for landfill.

Keywords
Alum sludge; reject water; reuse; phosphorus; municipal wastewater treatment plant

INTRODUCTION
Up till now, the removal of phosphorus (P) is one of the major targets in municipal wastewater treatment plant (MWWTP). In MWWTP employing biological phosphorus removal (BPR) process, the removal of P consists of its conversion from the influent into the activated sludge followed by the removal of the P-rich excess activated sludge from the main treatment stream. However, during the ensuing sludge treatment stage, generally including thickening to reduce its volume and then anaerobic digestion to stabilize the sludge, it is believed that the P is released to the supernatant (Jardin and Popel, 1994). This waste stream is termed as reject water (other terms are return liquor, sewage sludge filtrate or centrifugate) and it is normally recycled back to the main wastewater stream due to its poor quality which makes it unacceptable for direct discharge. Although the flow of reject water is only 2% of the raw wastewater flow (Janus and Roest, 1997), the concentration of P in reject water is up to 130 mg/L (Pitman, 1999). Consequently, the recycling of such P-rich reject water can contribute from 10% to 80% of P load on the activated sludge tank (van Loosdrecht and Salem, 2006), leading to a considerable negative impact on entire BPR process (Tchobanoglous et al., 2003). Therefore, the removal of P from reject water can significantly reduce the P load to the main stream of the MWWTP.

Regarding the P removal in reject water, emphasis is being placed on seeking the cost effective methods and materials with enhanced P removal/immobilization ability although separated biological treatment method has been applied (van Loosdrecht and Salem, 2006). It is noted that the studies on the reuse of “alum sludge” for the removal of a wide range of P species have demonstrated the considerable ability of such “novel material” as a promising adsorbent for strong P sorption affinity (Huang and Chiswell, 2000; Kim et al., 2002; Ippolito et al., 2003; Makris et al., 2005; DeWolfe, 2006; Yang et al., 2006; Razali et al., 2007; Babatunde et al., 2008). Alum sludge is a resultant inevitable by-product of the drinking water treatment plant when aluminium salt is
added as a coagulant. It is historically reviewed that alum sludge is a “waste” with marginal effect for reuse and has to be disposed for landfill. However, intensive studies particularly in recent years have revealed that alum sludge possesses P adsorption capacity of up to 37.0 g P/kg alum sludge (Dayton and Basta, 2005).

Alum sludge, either in liquid phase or in solid phase (after dewatering), can be easily obtained from the sludge treatment process of the drinking water treatment plant. Attempts have been made to beneficially re-use of such forms in civil and environmental engineering (Babatunde and Zhao, 2007). Recent report of direct reuse of alum sludge in MWWTP has demonstrated a good ability of the alum sludge in enhancing particulate pollutant removal in primary sedimentation tank due to a large portion of insoluble aluminum hydroxides in the sludge as a coagulant in chemical coagulation/flocculation (Guan et al., 2005). Mortula and Gagnon (2007) studied the P removal from the secondary municipal effluent using oven-dried alum sludge and the results indicated that oven-dried alum sludges have potential to provide a low cost technological solution for P removal for small- and medium-sized municipalities.

This paper outlines the two strategies for P removal from reject water using alum sludge. One strategy was the use of the alum sludge in liquid phase for co-conditioning and dewatering with the anaerobically digested sludge in MWWTP. It is expected that the alum sludge will be a potential adsorbent for P removal from the supernatant of the anaerobically digested sludge (Yang et al., 2007). The other strategy involves the use of dewatered alum sludge cakes in a fixed bed for P immobilization from the mixed waste streams generated from the sludge thickening process and the sludge dewatering process in a MWWTP. Both the strategies can be separately employed for P control in reject water of MWWTP, thus highlighting the novel reuse of the alum sludge and its integration into a municipal wastewater treatment process.

OUTLINES OF THE TWO STRATEGIES

The strategy of co-conditioning of the anaerobic digested sludge of a MWWTP with alum sludge is shown in Fig. 1. The aluminium-coagulated drinking water treatment sludge in its liquid form obtained from a water treatment plant was introduced to the anaerobically digested sludge treatment process of a MWWTP. The liquid alum sludge is then mixed in a proper ratio with anaerobic digested sludge for a joint conditioning using an organic polymer as conditioner. It is expected that the involvement of alum sludge in such co-conditioning may result in: (1) the P reduction in reject water after dewatering since the alum sludge will enhance the P immobilization; (2) reduction of the polymer (a widely used conditioner to promote sludge dewatering) dosage required to achieve good dewaterbility since the alum sludge may act as a skeleton builder in the mixed sludges and thus has beneficial effect in the dewatering process (Lai and Liu, 2004).

The strategy of the use of dewatered solids alum sludge in a fixed bed for P immobilization from the reject water that is the mixture of the supernatant of the sludge thickening unit and the sludge dewatering unit in a MWWTP is illustrated in Fig. 2. The reject water was subjected to filtration in a fixed bed, which was filled with dewatered solids alum sludge as filter medium. Since the previously removed P from the influent via BPR process in phosphate accumulating organisms can be released when bacteria that contain stored phosphorus (i.e. phosphate accumulating organisms) are subjected to anaerobic conditions, the supernatant of the anaerobically digested sludge is a P rich stream (Pitman, 1999). It is expected that the dewatered solids alum sludge can serve as a low cost adsorbent in the filtration bed to adsorb P from the supernatant onto the alum sludge, thus significantly reducing the P level in the supernatant. Accordingly, P in reject water is removed and the P load to the main stream of the MWWTP is reduced.
EXPERIMENTAL APPROACHES

**Digested activated sludge and supernatant.** The anaerobically digested sludge was collected from the anaerobic digestion unit of a MWWTP located in northeast Dublin, Ireland. The MWWTP employs an anaerobic/anoxic/aerobic (A²/O) process for municipal wastewater treatment. The primary sludge (from the primary sedimentation tank) and the excess activated sludge (from the secondary sedimentation tank) were both thickened and thereafter mixed together before being fed to the anaerobic digestion unit. The water content of the anaerobic digested sludge ranged from 96.95% to 98.21% with an average of 97.89%. The capillary suction time (CST) of the anaerobic digested sludge ranged from 451 seconds to 474 seconds while the specific resistance to filtration (SRF) ranged from $40.0 \times 10^{13}$ m/kg to $65.4 \times 10^{13}$ m/kg. The P concentration in the supernatant of the anaerobic digested sludge ranged from 597.3 to 674.5 mg-P/L with an average of 600.0 mg-P/L.

**Alum sludge.** The liquid alum sludge with moisture content of 95.2% was collected from the holding tank of the sludge dewatering unit of a water treatment plant in southwest Dublin, Ireland where aluminium sulphate is used as principal coagulant for treating a nearby reservoir water. Characterization of the alum sludge was done by examining its physical and chemical properties and the results has been reported elsewhere (Yang et al., 2007). In its principal form, the alum sludge contained 0.93% aluminium in 1 g of liquid alum sludge. The liquid alum sludge contains 4.8% of suspended solid while the water content is 95.2%. The other principal chemical component is natural organic matter (NOM), expressed as TOC, which is 118.4 mg-C/g-sludge. The dewatered alum sludge cakes were collected from the filter press plate of the same water treatment plant. The
moisture content of the alum sludge cakes was 72-75%. After collection, the sludge was air-dried (with moisture content 23.47 to 25.19% at the time of use) and then milled and sieved into different particle sizes ranged from 0.425 to 2.36mm. The prepared sludges were then used in the fixed sludge bed trial. The aluminium content (expressed as Al₂O₃) in the alum sludge tested by ICP-AES (inductively coupled plasma-atomic emission spectrometry, IRIS Advantage, Thermo Elemental, Franklin, Massachusetts, USA) ranged from 24.7-46.3%, depending on the seasonal dosage of aluminium sulphate.

**Co-conditioning procedure.** Sludge conditioning tests were conducted using the anaerobic digested sludge and the mixed sludge (the mixed sludge refers to the mixture of the anaerobic digested sludge and alum sludge at a mixing ratio of 2:1; v/v, anaerobic digested sludge: alum sludge). The 2:1 mixing ratio was determined as the optimal mixing ratio that ensures the lowest P concentration in the supernatant with the least amount of alum sludge addition (Yang et al., 2007). A cationic polyelectrolyte named Superfloc C2260 (CYTEC, Netherlands), which is a high molecular weight polymer with a charge density of 40%, was employed as chemical conditioner. The conditioning tests were performed using a jar-stirring device where the sludge was mixed with the various polymer doses at a mean velocity gradient \( \bar{G} \) value of 500 s⁻¹ for 20 s, followed by a reaction process which was at a \( \bar{G} \) value of 34 s⁻¹ for 294 s. This provides a \( \bar{G}T \) value of 10000, which is considered as the most critical determinant factor to ensure the shear conditions. The dewaterability of the sludge was evaluated using the CST and SRF.

**Reject water filtration with alum sludge bed.** Continuous flow testing was conducted on-site at the MWWTP located in northeast Dublin, Ireland. The experimental setup consists of a Perspex column (1.0 m long and 94 mm in-diameter) packed with 3.3 kg of prepared dewatered alum sludge to a height of 65 cm with 10 cm of gravel at the base to act as support layer. The reject water, which is a mixture of the supernatant from a gravity belt thickener (GBT) (the excess activated sludge thickening unit) and the supernatant from a centrifuge (anaerobic digested sludge dewatering unit), with average P concentration of 113.5mg-P/L was passed through the bed from the top of the bed at a filtration velocity of 1.0 m/h.

**Analyses.** In the sludge co-conditioning strategy CST, SRF, P and pH were monitored. The CST was determined using a Triton CST Apparatus (Triton WPRL, Type 130) with a CST paper of size 7x9cm. The SRF tests were performed using a standard Buchner funnel with a Whatman No. 1 qualitative filter paper (Ø70mm). A 50 kpa of vacuum suction was applied. For P measurement samples were filtered using 0.45 \( \mu \)m millipore filter membrane (Millipore) before measurement. It was followed by P analysis using inductively coupled plasma - mass spectrometry (ICP-MS) (X series, Thermo Elemental, Franklin, Massachusetts, USA) (for P concentration less than 0.05 mg-P/L) and the stannous chloride method (4500-P D, APHA, 1992) (for P concentration higher than 0.05 mg-P/L). The pH of samples was determined via a pH meter (pH 325, WTW). In reject water filtration strategy, samples of influent and effluent from the alum sludge bed were subjected for P measurement with the same procedure as described above.

**RESULTS**

**Co-conditioning of anaerobic digested sludge with alum sludge.** The major properties of the mixed sludges at ratio of 2:1 (anaerobic digested sludge : alum sludge, v/v) are shown in Table 1. The 2:1 mix ratio was predetermined in a previous study reported elsewhere (Yang et al., 2007). It is clear that, compared with the raw anaerobically digested sludge, the addition of alum sludge into anaerobically digested sludge could lead to the improvement of the sludge dewaterability as gauged by CST and SRF. More significantly, the P concentration in the supernatant of the mixed sludge is
tremendously reduced due to the adsorption by alum sludge (Yang et al., 2006; Zhao et al., 2007). It is noted that the TOC and pH of the supernatant of the mixed sludge are increased, and this may be caused by the release of TOC from the alum sludge during P adsorption (Yang et al., 2006).

Table 1 Results of the co-conditioning of the anaerobic digested sludge with alum sludge

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<th>Parameter</th>
<th>Anaerobic digested sludge</th>
<th>Mixed sludge with ratio of 2:1 (anaerobic sludge : alum sludge)</th>
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<tr>
<td>CST (s)</td>
<td>451</td>
<td>380</td>
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<tr>
<td>SRF ($\times 10^{13}$, m/kg)</td>
<td>48.3</td>
<td>28.1</td>
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<tr>
<td>Supernatant P (mg P/L)</td>
<td>597-675</td>
<td>0.14-3.20</td>
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<tr>
<td>Supernatant TOC (mg/L)</td>
<td>77-118</td>
<td>190-320</td>
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<tr>
<td>pH</td>
<td>6.8-7.1</td>
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The results of the conditioning of the mixed sludge (at ratio of 2:1) by a cationic polyacrylamide Superfloc C2260 are illustrated in Fig. 3. The P concentration in the supernatant of the mixed sludge during the conditioning process is also jointly illustrated in the figure. The results show that the polymer conditioning results in a significant improvement of the mixed sludge dewaterability as evaluated by CST and SRF. The values of CST and SRF decreased from 421 to 33.9 seconds and from $30.01 \times 10^{13}$ to $2.74 \times 10^{13}$ m/kg, respectively, while polymer dose was increased from 0 to 15 mg/L. The optimal polymer dose for the mixed sludge conditioning was determined to be 15 mg/L since further increase of polymer dose beyond that value did not bring about any further decrease of SRF or CST as shown in Fig. 3. In addition, Fig. 3 shows that the phosphate concentration in the supernatant was very low at all the different polymer doses, ranging from 0.15 to 3.1 mg-P/L.

![Fig. 3 Polymer (Superfloc C2260) conditioning of the mixed sludge (ratio=2:1) and the P concentration in the supernatant](image)

To reflect the benefit of the co-conditioning of anaerobic digested sludge with alum sludge, Fig. 4 illustrates the changes of SRF and CST with various dosages of polymer (Superfloc C2260) for the digested sludge only. The values of SRF decreased from $44.65 \times 10^{13}$ to $3.21 \times 10^{13}$ m/kg and CST decreased from 484 to 25 seconds with increasing polymer dose up to 120 mg/L. However, it is interesting to note that large amount of polymer was added and the optimal dose was 120 mg/L, which corresponds to the lowest SRF and CST values as illustrated in Fig. 4. Also in Fig. 4, the results show that the initial P concentration in the supernatant of the anaerobic digested sludge ranged from 601 to 615 mg-P/L, exhibiting a minor change across the wide range of polymer doses. However, by comparing Fig. 3 & 4, it can be seen that the P in the aqueous phase of the sludges was
significantly reduced by the addition of the alum sludge and the polymer dosing did not contribute to P removal from the aqueous phase of the sludges.

![Graph showing P concentration vs. Polymer dose](image)

**Fig. 4** Polymer (Superfloc C2260) conditioning of the anaerobic digested sludge and the P concentration in the supernatant

**Reject water filtration with alum sludge bed.** Fig. 5 illustrates the behaviour of the reject water filtration with alum sludge bed. This on-site trial of the P removal system from reject water has demonstrated the feasibility of the novel use of dewatered alum sludge bed for P control in reject water. The P concentration of the reject water varied from 81 to 116 mg-P/L and the pH of the reject water ranged from 7.8 to 8.1. The filtration bed was run in continuous mode and the P reduction from the alum sludge bed was monitored. Before setting-up the on-site trial, groups of batch experiments were designed to identify the characteristics of dewatered alum sludge for P adsorption. Factors influencing the adsorption capacity including pH, initial P concentration and equilibration time were examined using KH$_2$PO$_4$ as a model P source. Of these, pH and initial P concentration have significant effects on adsorption capacity. A pH increase from 4.3 to 9.0 decreased the P adsorption capacity (measured at initial P concentration of 100 mg-P/L) from 23.9 to 1.1 mg-P/g-sludge, suggesting that the adsorption capacity was significantly influenced by the pH of the aqueous solution. This is due to the fact that P adsorption onto alum sludge is through ligand exchange and coupled with a release of OH ions (Yang et al., 2006). The P adsorption capacity (using a pH 7.0 and equilibration time of 28 days) significantly increased from 3.1 to 14.3 mg-P/g-sludge when the initial P concentration was increased from 5 to 100 mg-P/L. The results of the continuous flow filtration trial showed that the average P concentration in the reject water was reduced from 113 mg-P/L to < 0.008 mg-P/L. At the designed breakthrough concentration of 1.0 mg-P/L, the breakthrough adsorption capacity was calculated to be 16 mg-P/g-sludge while the exhaustion adsorption capacity was 31 mg-P/g-sludge, as illustrated in Fig. 5. Such the P adsorption capacity can be used as a guide for design purpose when further trial and large application are proposed.

The outcome of the trial of the alum sludge filtration bed indicated that dewatered alum sludge is suitable for use as a low-cost adsorbent for P rich reject water treatment. Such reuse of dewatered alum sludge as adsorbent for P removal from the reject water can therefore eliminate the P loading to wastewater treatment process.

**DISCUSSION**

Treatment of reject water has gained international attention in recent years since the high strength P in such the reject water brings about significant P loading of the main wastewater treatment process.
of a MWWTP. Alum sludge derived from the waste stream of the drinking water treatment process has been proposed for P immobilization in the reject water treatment. Utilization of alum sludge can be in the liquid form, which is the original nature, or in solids form, which is the dewatered form in most of the water treatment plants worldwide. Studies on some natural and man-made products and some industrial by-products have showed that their P-removal capacity varied from 0.025 to 32 mg-P/g (Lena, 2006). In comparison, the dewatered alum sludge used herein can be seen to have a significant and comparable P adsorption capacity (see Fig. 5) due to the abundant Al and its strong affinity with P (Ippolito et al., 2003; Makris et al., 2005; DeWolfe, 2006). In particular, compared with other P immobilization materials, alum sludge is a locally, easily and hugely available material with nature of free of charge for the moment. Beneficial reuse of the alum sludge falls into the theme of environmental sustainability which encourages “reduce, reuse and recycle”.

![Diagram of P removal and adsorption capacity](image)

**Fig. 5** Continuous operation of P rich reject water filtration with alum sludge bed

The two strategies tested in this study have demonstrated their role in P removal in reject water from a MWWTP. Although co-conditioning of sewage sludge with alum sludge has been previously studied (Lai and Liu, 2004), emphasis of co-conditioning of the two kinds of sludges regarding P reduction in reject water has not been reported from the literature except for the authors’ previous report (Yang et al., 2007). It is noted from Table 1 and Fig. 3 & 4 that the advantages of the co-conditioning strategy are both the P immobilization and the dosage saving of the organic polymer. However, it should be borne in mind that such the co-conditioning could be hindered by the difficulty of the alum sludge transportation especially in liquid form due to the fact that the MWWTP and the drinking water treatment plant are not normally located close to each other.

Beneficial reuse of the alum sludge in the form of solids might be a good example in practice. Significant immobilization of P in reject water via a dewatered alum sludge bed tested in this study provides evidence to show that the dewatered alum sludge (solids) can be a novel and low cost
adsorbent and also a cost effective solution for P removal in reject water in MWWTP. Due to the fact that alum sludge is currently treated as a waste for landfill, the reuse of such sludge jointly in MWWTP will be reasonably recognised as a sustainable approach regarding alum sludge management. However, it should be pointed out that further study and large scale trial should be conducted before practical application can be made. Pre-treatment of the reject water may be necessary and optimising design of the alum sludge bed should also be studied. In addition, possible clogging of the bed and potential release of some elements from the alum sludge when it is used as adsorbent in the filtration bed should be equally investigated.

CONCLUSIONS
One of the most effective ways to decrease P concentration in the effluent of MWWTP could be removal of P from reject water (termed alternatively as return liquor, sewage sludge filtrate or centrifugate), which is the mixture of the supernatants generated from the sludge thickening process and the anaerobic digestion process or the liquid fraction produced after dewatering of anaerobically digested activated sludge. Two strategies of using both liquid alum sludge and dewatered alum sludge for P control in reject water have demonstrated their advantages as cost-effective approaches in main wastewater treatment process in MWWTP for eliminating P. Since the alum sludge is treated as a “waste” for landfilling, such application of the waste sludge would thus transform the alum sludge from a ‘waste’ material into useful material in terms of ‘using waste for wastewater treatment’.

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