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<th>Phosphorus recovery as AlPO 4 from beneficially reused aluminium sludge arising from water treatment</th>
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The purpose of this study was to develop an efficient and possible practically operated methodology to recover phosphorus (P) from P-saturated dewatered aluminium sludge cakes (DASC), which has been beneficially reused as constructed wetlands substrate for P-rich wastewater treatment. A three-step procedure of 1) P extraction by H$_2$SO$_4$, 2) decolouration of extraction leachate via H$_2$O$_2$ oxidation, and 3) AlPO$_4$ precipitation by pH adjustment, has been explored. The optimal conditions to form the precipitates of AlPO$_4$ can be obtained with 97% of P and 99% of Al being recovered. The obtained compounds were identified by XRD, FTIR and SEM analyses. Although the purity, structure, characteristics and production control of the compounds are worthy for further investigation, this study provides a showcase of a “close loop” on beneficial reuse of a “waste” and recovery of useful elements after the reuse.

**Key words:** P resource, aluminium sludge, P recovery, chemical precipitation, AlPO$_4$

1. **Introduction**

It has been generally agreed that the wiser wastewater treatment should consider the resource recovery especially the phosphorus (P) since it is one of the vital components of the DNA and the key element of the energy supplier ATP [1]. In particular, P is a non-replaced resource
with limited source in nature. In general, conventional P removal techniques in wastewater treatment are based on the phosphate precipitation as iron or alum salt or fixation in activated sludge through biological P removal. Unfortunately, huge amounts of the resultant water-rich sludge including chemical sludge and/or activated sludge were generated during these processes, leading to increasing costs for conditioning, dewatering and disposal of these sludges. In addition, due to high water content and the low stability of the waste sludges derived from the activated sludge process, reuse of P is not an economic attractive option. Thus, in recent year, some advanced alternative techniques have been developed and applied to recover P from wastewater as P-contained products which can be reused as resource. These include crystallization to obtain struvite [2] or calcium phosphate [3] and ion exchange to achieve phosphoric acid [4] etc.

At University College Dublin, Ireland, several research projects have strived to incorporate dewatered aluminium sludge cakes (DASC) (an inevitable by-product derived from the drinking water treatment process when aluminium sulphate is used as raw water coagulant) as wetland substrate into constructed wetlands (CW) to enhance the immobilization/removal of P. The aluminium sludge-augmented constructed wetland system has demonstrated an excellent ability of organics and nutrients especially P removal/immobilization [5-7]. This pioneering development/investigation on the beneficial reuse of DASC for P-rich wastewater treatment is now underway for eventual field application [8].

However, there is a big concern about the used or saturated DASC, which is full of immobilized P. Once saturated, DASC will stop adsorbing P and may become a P source if physicochemical conditions change. Can this P be recovered? The objective of this study was to explore a technique to recover P from used DASC as P-contained products, thus transforming the used DASC to potential P resource after employing it as P trapping material for wastewater treatment in CW system.

A three-step procedure of 1) P extraction from the used DASC by H$_2$SO$_4$, 2) decolouration of extraction leachate via H$_2$O$_2$ oxidation, and 3) AlPO$_4$ precipitation by pH adjustment, has been explored. As the step 1) and 2) have been reported previously [9,10], this paper is focused on the step 3), i.e. the recovery and purification of AlPO$_4$. 
2. Materials and methods

2.1 Materials

The P-saturated DASC was obtained from a long-term (750 days) operated laboratory-scale CW system, which employed wet DASC as sole wetland substrate without mixture with other conventionally used wetland substrates (such as soil, sand and gravel) for a P-rich animal farm wastewater treatment trial with influent COD 213 ± 127 mg/L; P 28 ± 15 mg PO₄₃⁻/L; SS 72 ± 66 mg/L and pH 6.8 ± 0.4. Originally, the DASC was collected directly from Ballymore-Eustace Water Treatment Plant in Southwest Dublin, Ireland, where aluminium sulphate was adopted as coagulant for reservoir water purification.

After 750 days’ operation of the laboratory-scale CW system, the DASC (as substrate) was significantly saturated with marginal P adsorption ability. The used DASC samples in this study were then taken from the CW system and dried at room temperature. It was followed by grinding and sieving to diameter <0.3 mm to provide the test samples in this study. The characteristics of the prepared P-saturated DASC and air-dried fresh DASC before use (for comparative purpose) were shown in detail in Zhao and Zhao (2009) [9]. The significant change is the P content in fresh DASC (154 mg/kg dry mass) and P-saturated DASC (38,590 mg/kg dry mass).

2.2 Experimental methodology

According to the preliminary studies [9,10], the P recovery procedure was designed as three steps: 1) P extraction from the used DASC, 2) decolouration of the P-extraction leachate and 3) precipitation of aluminium phosphate (AlPO₄₃⁻). In the first step, a red-brown sulphuric acid leachate (RSAL) was obtained under the optimal condition for P extraction from P-saturated DASC [9]. Subsequently, the decolorized sulphuric acid leachate (DSAL) was obtained by using H₂O₂ oxidation [10] and this solution was used for P precipitation step, i.e. the step 3).

Precipitation of AlPO₄₃⁻ was conducted in a series of 100 mL DSAL. The DSAL was adjusted by 4 M NaOH to pH range of 4-10.5 and stirred for 30 min, while the precipitate of
AlPO$_4$ was obtained and centrifuged at 3500 rpm for 15 min. The resultant precipitates were washed by distilled water completely, and then left for air-dried at room temperature for further characterization. The supernatant was analyzed for P and Al residual concentrations. To investigate the effect of reaction time on P precipitation, another series of 100 mL DSAL was adjusted by 4 M NaOH to the optimal pH value determined from the previous experiment and stirred for 5, 15, 30, 60 and 120 min, respectively. The precipitates were separated by centrifuge and the supernatants were analyzed for P and Al residual concentrations.

Finally, two sets of 300 mL DSAL were used to conduct the precipitates tests under the optimal conditions. The difference between the two sets experiments is that the large amount of sulphate ion (SO$_4^{2-}$) (in DSAL) in one set experiment was pre-removed by adding BaCl$_2$·2H$_2$O. Thereafter, the remaining DSAL of set one experiment was subjected to pH adjustment as the same as set two experiment. The resultant precipitates were obtained at optimal pH and reaction time, and then washed and air-dried for further characterization.

The chemicals used in this study are sodium hydroxide (NaOH) (supplied by Merck KGaA), hydrochloric acid (HCl, 36% w/w) and sulphuric acid (H$_2$SO$_4$, 98% w/w) (supplied by BDH), hydrogen peroxide solution (H$_2$O$_2$, 30% w/w) and barium chloride dihydrate (BaCl$_2$·2H$_2$O) (supplied by Riedel-deHaën Chemicals). All chemicals are in analytical grade.

2.3 Analytical techniques

The concentrations of P, Al and SO$_4^{2-}$ in solution and colour of solution were analyzed using a Hach spectrophotometer (DR/2800) according to the standard method. The pH was measured by pH meter (ATI ORION, model 720A). The phase composition of the resultant compound powder was determined on a X-ray diffraction (XRD) patterns using a Bruker D8 Advance diffractometer (Germany) with Cu K$_\alpha$ radiation ($\lambda = 1.5406$), operated at 40 kV and 40mA. The XRD data were collected over the 20 range of 15-80° at a scan speed of 1.5 min$^{-1}$ with an increment of 0.01. The spectra of the precipitates were measured by a Bruker Vector 70 Fourier-transform infrared spectrometer (FTIR) (Germany) to indentify the nature of the bondings. The data was collected from the scan range of 4000-370 cm$^{-1}$. Samples were prepared by mixing powders of the composites with KBr. Pure KBr was used as a background. The morphological structure and particle size of precipitates
were examined with Scanning Electron Microscope (SEM, JEOL JSM-T 300, Japan).

3. Results and discussion

3.1 P extraction and decolouration of RSAL

The characteristics of the achieved RSAL and DSAL were listed in Table 1. According to the calculation of mass balance, around 98% P and 100% Al were released to RSAL. Whereas, most of organics, which was derived from the source water and transferred to the sludge during the water purification processes (such as flocculation, sedimentation and filtration), were extracted into RSAL by H\textsubscript{2}SO\textsubscript{4} as well, resulting in high concentration of TOC and red-brown colour of solution. Without a doubt, such high colour has to be removed if the pure P compound is expected to be formed as a consequence of P recovery process. Therefore, H\textsubscript{2}O\textsubscript{2} oxidation was employed to decolorize the RSAL. After decolouration, near 78% TOC and 100% colour were eliminated and there was little mass loss of PO\textsubscript{4}\textsuperscript{3-} and Al\textsuperscript{3+} in DSAL compared with RSAL. Fig. 1 shows the photograph of RSAL and DSAL, which provides visible evidence on P extraction leachate and decolouration of RSAL.

3.2 Production of aluminium phosphate

By inspecting the data of Al\textsuperscript{3+} and PO\textsubscript{4}\textsuperscript{3-} of the DSAL in Table 1, the molar ratio of P/Al is 0.47. It is expected that the precipitate of AlPO\textsubscript{4} could be formed through adjusting pH of the solution using NaOH. The results of P precipitation efficiency by pH adjustment of the DSAL and the mass of precipitate are illustrated in Fig. 2a. The results of the effect of reaction time on P precipitation under fixed pH value of 6 are shown in Fig. 2b. It is clearly indicated that the pH is the most important factor for precipitate formation. The suitable pH range is 5 to 6, at which over 98% P can be deposited. Many studies have reported that the pH served as the
key parameter for AlPO₄ precipitation. Although AlPO₄ has a wide pH range of precipitation from 3 to 9, the optimal pH value is 5-6 in this study, which is consistent with the results of other studies [11]. The reaction of P precipitation seems prompt since over 99.9% P can be precipitated in 5 min. There is no observation of the significant difference regarding P precipitation efficiency with different reaction time. Residual Al after P precipitation also exhibited the same level with little difference in prolonged reaction time. According to stoichiometry, one molar PO₄³⁻ needs one molar Al³⁺ to form AlPO₄, as described in Eq. (1). It implies that superfluous Al³⁺ could be co-precipitated as Al(OH)₃, as shown in Eq. (2), at the same time when AlPO₄ was formed. Therefore, the precipitates should be a mixture constituted with AlPO₄ and Al(OH)₃.

**[Figure 2]**

\[
\text{Al}^{3+} + \text{PO}_4^{3-} \rightarrow \text{AlPO}_4 \downarrow \quad (1)
\]

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \downarrow \quad (2)
\]

Figure 3 shows the results of the two sets experiments to form the AlPO₄ (termed as AlP-1 and AlP-2) with experimental conditions/procedures and the concentrations of Al³⁺, PO₄³⁻ and SO₄²⁻. AlP-1 was obtained by adjusting pH of DSAL to 6 using 10 M NaOH directly (Fig. 3a), whereas AlP-2 was obtained after firstly immobilizing SO₄²⁻ in DSAL using BaCl₂·2H₂O (Fig. 3b). It is clear that the large amount of SO₄²⁻ in DSAL did not affect the precipitation processes of Al³⁺ and PO₄³⁻ due to the fact that there is no change of SO₄²⁻ concentrations before and after precipitation. However, around 3.6% Al and 9.4% P were lost during the precipitation of BaSO₄.

**[Figure 3]**

From the mass balance calculation of Al³⁺, PO₄³⁻ and SO₄²⁻, the precipitates of AlP-1 and AlP-2 should be the same which can be confirmed by XRD and FTIR analyses (Fig. 4a). Either XRD patterns or FTIR spectra of AlP-1 and AlP-2 are highly similar. As shown in Fig. 4b, the diffuse peaks in XRD pattern indicate the formation of the amorphous aluminium compounds. In FTIR curves of AlP-1 and AlP-2, the most prominent feature is the strong
band in the 1000-1200 cm\(^{-1}\) region which corresponds to the P-O stretch of the structural PO\(_4\) groups [11]. The H-O-H bending vibration was observed at around 1650 cm\(^{-1}\) which is close to its value in bulk water [12]. The broad and smooth absorption bands in range of 400-800 and 2700-3700 cm\(^{-1}\) relate respectively to the Al-O and O-H stretching vibration [13]. A SEM micrograph of the AlPO\(_4\) is shown in Fig. 4c. It is clear that the particles of the resultant AlPO\(_4\) exhibited the non-uniform shape and size. The sizes generally range from 2-40 μm. The visible photograph of the AlPO\(_4\) is shown in Fig. 4d. It reveals that the precipitate is a kind of white powders. AlPO\(_4\) is a valuable product which has been widely used as adsorbents, catalyst carrier, catalysts and white pigment [14]. However, it should be pointed out that the white powder obtained here is a mixture mainly consisted of amorphous AlPO\(_4\) and Al(OH)\(_3\) due to the surplus Al in the system. The suitable ratio of P/Al to form AlPO\(_4\) has been proved to be over 1 [14]. Obviously, the ratio of P/Al studied is quite lower and the excess Al should be co-precipitated with AlPO\(_4\) by forming Al(OH)\(_3\) at the pH of 6. As a result, it is interesting to make further efforts to obtain more pure and high quality AlPO\(_4\).

[Figure 4]

It has been noted in the literature that recovery of aluminium in water clarifier sludge (alum sludge) has been well studied [15,16]. Therefore, the achieved compound (mixture of AlPO\(_4\) and Al(OH)\(_3\) ) in this study could be regarded as a non-conventional case, focusing on P recovery, rather than Al. Considering non-replacement of P element in nature, recovered product serving as potential P resource probably makes more sense. However, as mentioned above, pure AlPO\(_4\) could be obtained under P/Al ratio >1. AlPO\(_4\) applied as a slow release fertilizer with low toxicity of Al for plants has been well demonstrated [17,18]. Hence obtained product containing AlPO\(_4\) and Al(OH)\(_3\) could be severed as potential fertilizer for crop growth in practice. On the contrary, if considering AlPO\(_4\) for the purpose of landscaping related use (such as grass land, garden use etc), there is no need to decolour the RSAL, thus cost can be reduced for AlPO\(_4\) recovery.

3.3 Practical implementation

Although the purity, structure, characteristics and the production control of the formed
compounds (AlPO$_4$ and Al(OH)$_3$) are worthy for further investigation, this study successfully explored the technical principle to transformation of the beneficially reused DASC as potential P resource after its employment as P trapping material for wastewater treatment in CW system. It should be noted that the large application of the technique in practice is not yet ready based on this laboratory scale trial. Some presaged suggestions and concerns can be made and discussed.

It is unnecessary to dry the used DASC during the P recovery procedure if it is implemented in practice. This will significantly save the cost of the recovery process. Decolouration process of RSAL using H$_2$O$_2$ would be unnecessary unless special case of commercial P product is required. For the purpose of agricultural application of used DASC as P slow-release fertilizer, direct use of DASC after saturated wetland would be satisfactory. In addition, it is proposed and wiser to conduct a cost-effective analysis before any investment is made to implement practical scale P recovery from the reused DASC in CW system. Nevertheless, this study provides a good reference for beneficial reuse of DASC and P recovery in practice.

4. Conclusions

Through H$_2$SO$_4$ extraction, around 97% P and 99% Al in beneficially reused DASC could be released into RSAL. Then, 100% color derived from some organics and 78% TOC could be reduced by H$_2$O$_2$ oxidation, resulting in clear DSAL. Chemical precipitation was adopted to separate Al$^{3+}$, PO$_4^{3-}$ and SO$_4^{2-}$ from DSAL. pH is the key factor for such a precipitation process. Through adjusting the pH of DSAL to 6, Al$^{3+}$ and PO$_4^{3-}$ could be completely co-precipitated as a white mixture of amorphous AlPO$_4$ and Al(OH)$_3$. Large amount of SO$_4^{2-}$ has been demonstrated no adverse effect on the precipitation process of AlPO$_4$. To characterize all the precipitations obtained, XRD and FTIR analyses augmented with SEM and visible photograph have identified the formed precipitates.

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<th>TOC (mg/L)</th>
<th>P (as PO$_4^{3-}$) (mg/L)</th>
<th>Al (mg/L)</th>
<th>SO$_4^{2-}$ (mg/L)</th>
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<td>RSAL</td>
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<td>426</td>
<td>710</td>
<td>421</td>
<td>4100</td>
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<tr>
<td>DSAL</td>
<td>~1.9</td>
<td>0</td>
<td>94</td>
<td>680</td>
<td>414</td>
<td>4100</td>
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Figure captions:

Fig. 1. Close shot of RSAL and DSAL

Fig. 2. Effects of the pH on AlPO₄ precipitation (a) and P precipitation efficiency and concentration of residual Al at pH 6 and different reaction time (b)

Fig. 3. Precipitation of AlPO₄ in separated two sets experiments

Fig. 4. XRD pattern (a), FTIR spectra (b) and SEM (c) and visible photograph (d) of AlPO₄
Fig. 1.
Fig. 2.
After adjusting pH to 6, stirred 15 min

After adding 3.13g BaCl2, stirred 30 min

Fig. 3.
Fig. 4.