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Transformation of beneficially reused aluminium sludge to potential P and Al resource after employing as P-trapping material for wastewater treatment in constructed wetland

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Abstract

The phosphorus (P)-saturated aluminium sludge used as substrate in constructed wetland (CW) for P-rich wastewater treatment was investigated to recover P and Al through chemical precipitations of the P-extraction leachate of the used aluminium sludge. pH plays a key role in such the precipitation processes. The obtained compounds were identified with XRD, FTIR and SEM analyses. The results showed that over 99% PO$_4^{3-}$ could be recovered as hydroxyapatite by adding calcium chloride at pH of 13. The remaining Al could be fully recovered as amorphous aluminium hydroxide at pH of 7.0 or alternatively as Tris(8-hydroxyquinolino)aluminium (Alq$_3$) by adding suitable quantity of 8-hydroxyquinoline. Although the purity, structure, characteristics and production control of the compounds are worthy for further investigation, this study successfully developed a post-treatment methodology for beneficially reused aluminium sludge. The significance of this study is not only transferring aluminium sludge from “waste” to potential P and Al resources but also reducing the environmental risk of final disposal of used aluminium sludge.

Keywords: P resource, aluminium sludge, P recovery, chemical precipitation
1. Introduction

Phosphorus (P) is essential to all living organisms since P is one of the vital components of the DNA and the key element of the energy supplier ATP [1]. For human being, P is a crucial contributor to human growth and metabolism, playing an important role in several functions such as transformation of energy, synthesis of amino acids and proteins, generation of vitamins and maintenance of bones and teeth etc. In modern society, there is a huge P consumption in agriculture, industry and human food. Undoubtedly, agriculture is by far the largest user of phosphate, accounting for 80-85% of total consumption. The consumption of phosphate as fertilizers to improve the food production is also rising largely. Moreover, it has been commonly recognized that the high quality reserves of P are being depleted expeditiously and that the prevailing management of phosphate, a finite non-renewable source, is not fully in accord with the principles of sustainability.

At the same time, the large amount of phosphate used worldwide leads to excess quantities of P released into various water bodies via discharge of industrial effluent, agriculture runoff, domestic wastewater etc., inducing eutrophication in surface waters and resulting in a high environmental risk [2]. Therefore, regarding the sustainable development, recovery P from wastewater has become a robust way in solving P pollution in waters and relieving P resource crisis at the same time. 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 quality of the waste sludges, 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 [3,4] or calcium phosphate [5,6] and ion exchange to achieve phosphoric acid [7,8] etc.
High strength animal farm wastewater with P-rich characteristics has been studied extensively at University College Dublin, Ireland, in incorporating dewatered alum sludge cakes (DASC) as substrate into constructed wetlands (CW) to enhance the P removal. DSAC is an inevitable and easily available by-product derived from the drinking water purification process with Al as main chemical component. The alum sludge-augmented constructed wetland system has demonstrated an excellent ability of organics and nutrients especially P removal/immobilization [9-11]. This pioneering development/investigation on the beneficial reuse of DASC for P-rich wastewater treatment is now underway for eventual field application [12].

However, recovery strategy of the immobilised P from the used/saturated DASC should be studied to further promote the beneficial reuse of DASC in CW technology. Actually, preliminary investigation has suggested a three-step procedure towards P recovery, which is: 1) P extraction from the used DASC, 2) decolouration of the P-extraction leachate and 3) precipitation of phosphate compounds. The step 1) and 2) have been previously studied [13,14]. Therefore, the objective of this study was to focus on the formation of phosphate compounds and related issues from the decoloured P-extraction leachate of the used DASC in CW system, thus transforming the used DASC to potential P resource.

2. Materials and methods

2.1 Decoloured P-extraction leachate

Used/saturated DASC in CW system was firstly subjected to P-extraction using H$_2$SO$_4$ [13]. The resultant P-extraction leachate was actually a red-brown sulphuric acid leachate (RSAL), which was then decoloured using a certain volume of H$_2$O$_2$ for oxidation. The product of the decolorized sulphuric acid leachate (DSAL) was used for P precipitation step [14]. The DSAL is a clear leachate with high concentrations of PO$_4^{3-}$, Al and SO$_4^{2-}$, as shown in Table 1.
It may be necessary to mention that the P-saturated DASC was obtained from a long-term operated laboratory scale CW system, which employed DASC as main substrate for a P-rich animal farm wastewater treatment trial with influent COD of 213 ± 127 mg/L; P of 28 ± 15 mg PO$_4$/$L$; SS of 72 ± 66 mg/L and pH of 6.8 ± 0.4. Originally, the DASC was collected directly from Ballymore-Eustace Water Treatment Plant in Southwest Dublin, Ireland, where aluminum sulphate was adopted as coagulant for reservoir water purification. After a long time of operation in the animal wastewater treatment system, the DASC (as substrate) was almost saturated with marginal P adsorption ability.

2.2 Precipitation methodology

2.2.1 Precipitation of calcium phosphate

Two series of 100 mL DSAL were adjusted by 10 M NaOH to pH range of 9-12 while CaCl$_2$·2H$_2$O (purchased from Riedel-deHaën Chemicals) was added with different molar ratio of Ca/P of 1.5 and 3, respectively. After reaction for 60 min, the precipitates were obtained and centrifuged at 3500 rpm for 15 min. The resultant precipitates were then washed by distilled water for at least three times before they were left for air-drying at room temperature for further characterization. The supernatant was analyzed for residual concentrations of P and Al. This allows optimising the reaction conditions for highest P precipitation efficiency.

Subsequently, two sets of 300 mL DSAL were used to conduct the precipitates tests to obtain the calcium phosphate at the particular pH of 13.0. In the first experimental set, calcium phosphates were formed in terms of CaP-1 while in the second experimental set, the large amount of sulphate ion (SO$_4^{2-}$) (in DSAL) was pre-immobilized by adding chemical equivalent quantity of BaCl$_2$·2H$_2$O (purchased from Riedel-deHaën Chemicals). The resultant precipitates of BaSO$_4$ were separated by centrifuging from the testing system. Thereafter, the remaining DSAL of set two experiment was subjected to calcium phosphate precipitation as the same as set one experiment by adding CaCl$_2$·2H$_2$O. The precipitates were termed as CaP-2, which were then washed and air-dried for further characterization.
2.2.2 Precipitation of aluminium compounds

Although P was recovered by forming precipitate of calcium phosphate, great deal of alum ion still remained in the DSAL. Subsequently, two methods were adopted to recover \( \text{Al}^{3+} \) as aluminium compounds. The first process generated aluminium trihydroxide (\( \text{Al(OH)}_3 \), ATH) simply by adjusting pH to 7. The second process was to obtain Tris(8-hydroxyquinolino)aluminium (\( \text{Alq}_3 \)) via addition of suitable quantity of 8-hydroxyquinoline (purchased from AlfaAesar Chemicals). In \( \text{Alq}_3 \) precipitation, 100 mL Al-rich solution/DSAL (in which P had been precipitated) was firstly adjusted by 10 M HCl to a pH range of 6.0-6.5. Thereafter, 50 mL 8-Hydroxyquinoline-absolute ethanol solution, which has a chemical equivalent quantity of 8-Hydroxyquinoline to aluminium, was added into the Al-rich solution. After mixed sufficiently in a beaker, the beaker was then carefully put into a water bath of 60-70°C and stirred for 30 min. The yellow precipitates were therefore observed, which can be separated by filtration. The resultant powder-like solids were washed by alcohol and distilled water, and then air-dried for analysis.

Unless otherwise stated, all the experiments were carried out at room temperature and replicated. The results were shown in average values. The entire precipitation experimental procedure is schematically illustrated in Fig. 1.

[Figure 1]

2.3 Analytical techniques

The concentrations of P, Al, \( \text{SO}_4^{2-} \) and Colour in 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

3.1 Precipitation of calcium phosphate

The results of initial P precipitation with CaCl\(_2\).2H\(_2\)O at pH of 9-12 are shown in Fig. 2. When the ratio of Ca/P is 1.5, over 98% P can be precipitated with calcium at the pH range tested. The maximum P precipitation efficiency of 99.4% appeared at the pH of 9 and a light decrease in efficiency was observed for higher pH values. However, it is interesting to see that the P precipitation efficiency increased with increasing pH when the ratio of Ca/P is 3, at which the maximum P precipitation of 99.9% can be obtained at pH 11. Comparing the cases of different molar ratios of Ca/P, it is clear that the high ratio of Ca/P is favorable to achieve the higher P precipitation efficiency. By inspecting the concentrations of residual Al, obviously, almost all the Al could be precipitated simultaneously with P precipitation at the pH of 9, but it reduced with increasing pH value. Interestingly, even at high pH of 12, 97.8% of Al at Ca/P ratio of 1.5 and 94.5% of Al at Ca/P ratio of 3 could still be co-precipitated, respectively, with the formation of calcium phosphate at the same time. Fig. 2 shows that the pH range of 9 to 12 seemed not suitable to obtain the relatively pure calcium phosphate due to the co-precipitation of Al. Thus, the subsequent experiments were carried out at higher pH condition of 13 and the molar ratio of Ca/P was set up to 3.

[Figure 2]
The processes and results of the calcium phosphate formation at pH of 13 are illustrated in Fig. 3. Here, Al\(^{3+}\) was well separated from PO\(_4^{3-}\) by adjusting pH to 13 with only 10% of Al\(^{3+}\) mass loss (on average) being recorded. Two calcium phosphates in terms of CaP-1 and CaP-2, respectively, were obtained. Clearly, SO\(_4^{2-}\) is also irrespective to the formation of calcium phosphate and the main components of CaP-1 and CaP-2 should be the same which were unveiled by XRD and FTIR analyses, as shown in Fig. 4a and Fig. 4b, respectively.

[Figure 3]

[Figure 4]

In XRD spectra, the characteristic peaks (at 2\(\theta\)) appear at 26° and 32° which are almost identical to those in stoichiometric microcrystalline hydroxyapatite (Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\), HAP) [15]. But the level of crystallization of powder is low due to the weak intensity of peaks. The FTIR spectrum shows characteristic peaks at 560-610 and 1000-1100 cm\(^{-1}\), being assigned to PO\(_4^{3-}\) groups in the HAP resulting from P-O symmetric and asymmetric stretching and 3500 cm\(^{-1}\) correspond to the vibration of OH [16].

The microstructure of the powder CaP-2 was examined by SEM and is shown in Fig. 4c. As it can be seen from the morphologies of the particles, there is a distribution of small particles which show an approximatively lamellar structure, and large agglomerates consisting of fine particles. From visible photograph, the HAP obtained here is white powders, as shown in Fig. 4d.

3.2 Precipitation of aluminium compounds

In both the approaches of Al precipitation to form either Al(OH)\(_3\) (ATH) or Alq\(_3\), over 99% of the Al precipitation efficiency can be achieved, indicating that these two methods are effective. XRD pattern and FTIR spectrum of the ATH powders are shown in Fig. 5a and b. The diffuse peaks indicate that the product is amorphous. The characteristic peaks at 400-770 cm\(^{-1}\) belong to the vibration of Al-O group and those at 1068 and 1157 cm\(^{-1}\) imply the
stretching of O-H [17].

[Figure 5]

The SEM observation of ATH in Fig. 5c shows that the ATH samples consisted of small particles and large agglomerates. From visible photograph shown in Fig. 5d, the ATH samples look like white solid gel.

XRD pattern and FTIR of Alq₃ are shown in Fig. 6. From XRD, the main characteristic peaks of Alq₃ at 2θ of 9.09, 10.34, 13.45, 15.53 and 24.16° were observed and the high level crystallization appeared due to the high intensity of diffraction. Compared with other compounds, the FTIR spectrum of Alq₃ is very complex but in accord with the reference [18].

[Figure 6]

From the observation of SEM (Fig. 6c) and visible photograph (Fig. 6d) of Alq₃, the Alq₃ is yellow needle-like solids and the SEM microphoto indicates that the microstructure of Alq₃ is cube pillar with diameter around 10 μm.

4. Discussion

4.1 P recovery process

The main purpose of the current study was to explore an efficient and practically operated methodology to recover P from DSAL. Since DSAL is a solution characterized with a great deal of Al³⁺, PO₄³⁻, SO₄²⁻ and low pH value, the wet chemical method of precipitation should be considered as the first choice. As is known, most of the phosphates are insoluble in aqueous solution, such as aluminium, ferric and calcium phosphates. Therefore, considering the fact that there still has large amount of Al³⁺ in DSAL, the attempt of forming AlPO₄ precipitation has been carried out firstly and reported elsewhere [19]. Although P can be recovered as AlPO₄ from solution only through pH adjustment by adding alkali, through
Inspecting the mass balance, it should be pointed out that the resultant precipitation is a mixture mainly consisted of amorphous AlPO$_4$ and Al(OH)$_3$ due to the surplus Al in the system [19]. The excess Al should be co-precipitated with AlPO$_4$ by forming Al(OH)$_3$ at the pH of 6. For this reason, precipitation of calcium phosphates was considered.

PO$_4^{3-}$ can be precipitated by Ca$^{2+}$ under alkaline condition to form calcium phosphates which could be expressed in Eq. (1) and (2).

$$3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 \downarrow$$  (1)

$$10 \text{Ca}^{2+} + 6 \text{PO}_4^{3-} + 2 \text{OH}^- \rightarrow \text{Ca}_{10}((\text{PO}_4)_6(\text{OH})_2) \downarrow$$  (2)

Low pH benefits precipitation of Ca$_3$(PO$_4$)$_2$, whereas the formation of hydroxyapatite is dominant as long as the pH value is higher than 10 [20]. In current study, however, if pH value is adjusted to 9-12, most of Al$^{3+}$ can be precipitated as Al(OH)$_3$, leading to a negative effect on the purity of hydroxyapatite. Therefore, a further increase of pH up to 13 was proposed, in which Al(OH)$_3$ can be dissolved to AlO$_2^{-}$. As a result, considerably pure hydroxyapatite was obtained which has been identified by XRD and FTIR analyses (see Fig. 4).

Accordingly, the Ca/P ration is 1.67. Normally, calcium phosphates were widely used as a long-term fertilizer. Bioactive calcium phosphate ceramics such as hydroxyapatite and tricalcium phosphate have been widely used as bone graft materials. That is the reason of more attentions having been paid to their syntheses, characterization and application [21,22].

After immobilizing PO$_4^{3-}$ under pH 13, aluminium can be precipitated as Al(OH)$_3$ by adjusting the pH to 7 according to the reaction showing in Eq. (3).

$$\text{AlO}_2^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 \downarrow$$  (3)

It can be seen from the XRD pattern (see Fig. 5) that, even though most of the Al(OH)$_3$ are amorphous, a small portion the bayerite (α-Al(OH)$_3$) phase can still be recognized by their major diffraction peaks at 2θ = 20.14° and 40.34°, respectively, although they are weak and broad. This result is accordant with other study reported from the literature [23].

Al(OH)$_3$ is a common source for producing aluminum oxides which have wide applications in catalysts, ceramics, capacitors, and substrates for integrate circuits etc. The
resultant powder from this study may be potentially used as a raw industrial material.

Alternatively, Alq\textsubscript{3} can be formed in the DSAL solution after PO\textsubscript{4}\textsuperscript{3-} is immobilized. Alq\textsubscript{3} is an organic electronic material and could be used as an efficient electroluminescent material [24] for OLED use in the next generation of display [25,26]. It can be produced by the reaction of Al\textsuperscript{3+} and 8-hydroxyquinoline (C\textsubscript{9}H\textsubscript{7}NO) (see Eq. (4)) under the pH range of 4.2-9.8 [18].

\[ 3 \text{C}_9\text{H}_7\text{NO} + \text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{C}_{27}\text{H}_{18}\text{AlN}_3\text{O}_3 \downarrow + 3 \text{H}_2\text{O} \quad (4) \]

The spatial framework and the molecular structure of Alq\textsubscript{3} are illustrated in Fig. 7 [27]. Obviously, the structure is such that the central Al atom is surrounded by the three quinolate ligands in a pseudooctahedral configuration with the A- and C-quinolate nitrogens and the B- and C-quinolate oxygen trans to each other. Because of complication of its structure, large numbers of sharp absorption peaks appeared in FTIR spectra which are contributed with vibration C=C, C-N, C-O, C-H, Al-O, -OH and the ring of quinoline etc. (see Fig. 6).

[Figure 7]

The results shown in Fig. 3 indicated that the SO\textsubscript{4}\textsuperscript{2-} has no negative effect on the formation of calcium phosphates. Therefore, considering the economic issue and the simplification of operation, there is no requirement to remove SO\textsubscript{4}\textsuperscript{2-} first. Overall, through easy-handling chemical reactions, the main components, P and Al, of used DASC in CW system could be recovered successfully as different compounds such as aluminum phosphate, hydroxyapatite, aluminum hydroxide, and Alq\textsubscript{3}.

**4.2 Significance of this study**

Regarding P elimination in constructed wetland system, the performance mainly depends on the adsorption ability of substrate. Since the generally employed substrates, i.e. gravel, sand or soil, have low capacity for P trapping, prominent research goals of CW has being focused on seeking specialized substrates with conductive physicochemical characteristics to
improved P removal. A great variety of different novel types of materials, including natural products such as Laterite [28] and peat [29], industrial by-products like slag [30], coal fly ashes [31] and man-made products like LECA [32] and Filtra P [33], have been reported in literatures.

As an inevitable and huge output by-product of drinking water treatment plants, the expense for disposing DASC to landfill site increases gradually. Therefore, employment of DASC as main substrate for P trapping has a remarkable significance of transferring a “waste” to raw material which could be combined with CW to enhance the capacity of P retention, making alum sludge-based CW system served like a P sink. The results obtained from the current study demonstrated that a large amount of P in used/saturated DASC could be recovered as P compounds through some chemical processes, developing a suitable and effective methods for used DASC post-treatment in which not only P compounds could be achieved but also the environment risk for used DASC final disposal could be reduced as well. Additionally, without a doubt, the usefulness of recovered P compounds can be justified as raw materials used in many areas.

It should be noted that commercial phosphates are mainly produced from natural phosphate rock. Even though the price of the natural phosphate rock has an increasing tend, for example the price of phosphate rock from Morocco remained below 50 US $/ton up to 2006 and went up to more than 300 US $/ton by 2008 with peaks around 1,000 US $/ton [34]. The recovered P is even more expensive. Balmél [35] calculated the costs of about 3,600 euro/ton P for a P recovery from wastewater in combination with P elimination. For P recovery from sewage sludge, the costs could be about 8,800 euro/ton P. From the calculation based on this laboratory scale P recovery study, the chemical investment can be 0.68 euro/g P. However, for practical use the chemical cost could be low. Nevertheless, it should be noted that the P recovery is an expensive process.

Although the purity, structure, characteristics and production control of the compounds are worthy for further investigation, this work successfully explored the methodology to transformation of the used DSAC in CW system as potential resource for P recovery after
employment of DASC as P trapping material for wastewater treatment.

5. Conclusions

Chemical precipitation was adopted to separate $\text{Al}^{3+}$, $\text{PO}_4^{3-}$ and $\text{SO}_4^{2-}$ from DSAL. pH is the key factor for such the precipitation process. When pH of the DSAL is adjusted to 13, $\text{Al}^{3+}$ turns to $\text{AlO}_2^-$ and $\text{Al(OH)}_3$ cannot be formed. Therefore, over 99% $\text{PO}_4^{3-}$ could be recovered as hydroxyapatite by adding calcium chloride. Thereafter, aluminium remained in the solution could be precipitated as $\text{Al(OH)}_3$ gel after adjusting the pH to 7. Alternatively, aluminium remained in the solution could be precipitated as $\text{Alq}_3$ by adding suitable quantity of 8-hydroxyquinoline. Although $\text{SO}_4^{2-}$ has no adverse effect on the precipitation process of either aluminium phosphate or hydroxyapatite, it could be immobilized by barium salt. To characterize all the precipitations obtained, XRD and FTIR analyses and SEM and visible photograph were employed to assistant the identification of the various precipitations. Overall, this study explored and developed an effective and consistent methodology to recover P and Al as potential P and Al resources from DASC after employment as substrate in CWs for wastewater treatment.

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References


**Figure Caption**

**Fig. 1** Schematic illustration of P recovery processes

**Fig. 2** Effect of pH and the ratio of Ca/P on the precipitation process of calcium phosphate

**Fig. 3** Calcium phosphate formation with and without SO$_4^{2-}$

**Fig. 4** XRD pattern (a), FTIR spectra (b), SEM (c) and visible photograph (d) of resultant calcium phosphate

**Fig. 5** XRD pattern (a), FTIR spectra (b), SEM (c) and visible photograph (d) of aluminium hydroxide (ATH)

**Fig. 6** XRD pattern (a), FTIR spectra (b), SEM (c) and visible photograph (d) of Alq$_3$

**Fig. 7** The geometry of mer-Alq$_3$ with labels A–C for three quinolate ligands (a) and The molecular structure of Alq$_3$ (b)
Adjusting pH to 13.0 using 10 M NaOH & adding CaCl₂·2H₂O, stirring for 30 min.

**Fig. 1** Schematic illustration of P recovery processes
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Fig. 3 Calcium phosphate formation with and without SO$_4^{2-}$.
Fig. 4 XRD pattern (a), FTIR spectra (b), SEM (c) and visible photograph (d) of resultant calcium phosphate
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Fig. 6 XRD pattern (a), FTIR spectra (b), SEM (c) and visible photograph (d) of Alq₃.
The geometry of mer-Alq3 with labels A–C for three quinolate ligands (a) and the molecular structure of Alq3 (b) [27].
Table 1 The characteristics of DSAL

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