Phosphorus recovery as $AlPO_4$ from beneficially reused aluminium-water treatment sludge

X.H. Zhao[a,b]*, Y.Q. Zhao[b] and P. Kearney[b]

[a] *School of Environmental Science & Engineering, Chang'an University, Xi'an, Shaanxi, China*

[b] *Centre for Water Resources Research, School of Civil, Structural & Environmental Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland*

Corresponding author: Tel.:+86-18702942034; E-mail:xiaohong.zhao@ucd.ie

ABSTRACT

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_2SO_4, 2) decolouration of extraction leachate via H_2O_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_2SO_4, 2) decolouration of extraction leachate via H_2O_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 PO_4/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 ($AlPO_4$). 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 H_2O_2 oxidation [10] and this solution was used for P precipitation step, i.e. the step 3).

Precipitation of $AlPO_4$ 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 $BaCl_2 \cdot 2H_2O$. 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_2SO_4, 98% w/w) (supplied by BDH), hydrogen peroxide solution (H_2O_2, 30% w/w) and barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) (supplied by Riedel-deHa ën 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 Kα radiation ($\lambda = 1.5406$), operated at 40 kV and 40mA. The XRD data were collected over the 2θ range of 15-80^o 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_2SO_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_2O_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_4^{3-} and Al^{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.

[Table 1]

[Figure 1]

3.2 Production of aluminium phosphate

By inspecting the data of Al^{3+} and PO_4^{3-} of the DSAL in Table 1, the molar ratio of P/Al is 0.47. It is expected that the precipitate of $AlPO_4$ 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 $AlPO_4$ precipitation. Although $AlPO_4$ 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 PO_4^{3-} needs one molar Al^{3+} to form $AlPO_4$, as described in Eq. (1). It implies that superfluous Al^{3+} could be co-precipitated as $Al(OH)_3$, as shown in Eq. (2), at the same time when $AlPO_4$ was formed. Therefore, the precipitates should be a mixture constituted with $AlPO_4$ and $Al(OH)_3$.

[Figure 2]

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \downarrow \quad (1)$$

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

Figure 3 shows the results of the two sets experiments to form the $AlPO_4$ (termed as AlP-1 and AlP-2) with experimental conditions/procedures and the concentrations of Al^{3+}, PO_4^{3-} and SO_4^{2-}. 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 SO_4^{2-} in DSAL using $BaCl_2 \cdot 2H_2O$ (Fig. 3b). It is clear that the large amount of SO_4^{2-} in DSAL did not affect the precipitation processes of Al^{3+} and PO_4^{3-} due to the fact that there is no change of SO_4^{2-} concentrations before and after precipitation. However, around 3.6% Al and 9.4% P were lost during the precipitation of $BaSO_4$.

[Figure 3]

From the mass balance calculation of Al^{3+}, PO_4^{3-} and SO_4^{2-}, 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_2O_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_2SO_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_2O_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.

Acknowlegments

The authors would like to acknowledge the research funding provided by the Irish state

Environmental Protection Agency through the Environmental Technologies Scheme (project no. 2005-ET-MS-38-M3) and Irish state Department of Agriculture, Fisheries and Food under the Research Stimulus Fund (project no. RSF 07-529). The first author wishes to thank University College Dublin for the *Ad Astra* scholarship. In particular, the authors appreciate the technical assistance provided by Guangzhou Institute of Geochemistry and Jinan University, Guangzhou, P.R. China during this study.

References

[1] P. Steen, Phosphorus availability in the 21st century, Phosphorus and Potassium. 217(Sep.-Oct.) (1998) 25-31.

[2] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Phosphorus recovery from wastewater by struvite crystallization: a review, Crit. Rev. Env. Sci. Tec. 39 (2009) 433-477.

[3] U. Berg, D. Donnert, P.G. Weidler, E. Kaschka, G. Knoll, R. Nüesch, Phosphorus removal and recovery from wastewater by tobermorite-seeded crystallisation of calcium phosphate, Water Sci. Technol. 53 (2006) 131-138.

[4] I. Midorikawa, H. Aoki, A. Omori, T. Shimizu, Y. Kawaguchi, K. Kassai, T. Murakami, Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high-speed adsorbent, Water Sci. Technol. 58 (2008) 1601-1607.

[5] Y.Q. Zhao, A.O. Babatunde, X.H .Zhao, W.C. Li, Development of alum sludge-based constructed wetland: An innovative and cost effective system for wastewater treatment, J. Environ. Sci. Heal. A. 44 (2009) 827-832.

[6] A.O. Babatunde, Y.Q. Zhao, A.M. Burke, M.A. Morris, J.P. Hanrahan, Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands, Environ. Pollut. 157 (2009) 2830-2836.

[7] A.O. Babatunde, Y.Q. Zhao, X.H. Zhao, Alum sludge-based constructed wetland system for enhance removal of P and OM from wastewater: Concept, design and performance analysis, Bioresource Technol. 101 (2010) 6576-6579.

[8] Y.Q. Zhao, A.O. Babatunde, Y.S. Hu, J.L.G. Kumar, X.H. Zhao, Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatmen, Process

Biochem. 46 (2011) 278-283.

[9] X.H. Zhao, Y.Q. Zhao, Investigation of phosphorus desorption from P-saturated alum sludge used as a substrate in constructed wetland, Sep. Purif. Technol. 66 (2009) 71-75.

[10] X.H. Zhao, Y.Q. Zhao, Decolouration of H_2SO_4 leachate from phosphorus-saturated alum sludge using H_2O_2 and advanced oxidation processes in phosphorus recovery strategy, J. Environ. Sci. Heal. A 44 (2009) 1557-1564.

[11] L.S. Burrell, C.T. Johnston, D. Schulze, J. Klein, J.L. White, S.L. Hem, Aluminium phosphate adjuvants prepared by precipitation at constant pH. Part I: compositon and structure, Vaccine 19 (2001) 275-281.

[12] S.Y. Venyaminov, F.G. Prendergast, Water (H_2O and D_2O) molar absorptivity in the 1000±4000 cm^{-1} range and quantitative IR spectroscopy of aqueous solutions, Anal. Biochem. 248 (1997) 234-245.

[13] T. Meher, A.K. Basu, S. Ghatak, Physicochemical characteristics of alumina gel in hydroxyhydrogel and normal form, Ceram. Int. 31 (2005) 831-838.

[14] M.M. Beppu, E. Oliveira, C. Lima, F. Galembeck, Aluminum phosphate particles containing closed pores: preparation, characterization, and use as a white pigment, J. Colloid Interf. Sci. 178 (1996) 93-103.

[15] D. Petruzzelli, N. Limoni, G. Tiravanti, R. Passino, Aluminum recovery from clarifier sludges by ion exchange: Comparison of strong and weak electrolyte cation resins performance. React. Funct. Polym. 38 (1998) 227-236.

[16] D. Petruzzelli, A. Volpe, N. Limoni, R. Passino, Coagulants removal and recovery from water clarifier sludge. Experience on a 50 L/d laboratory scale pilot plant. Wat. Res. 34 (2000) 2177-2182.

[17] J.E. Hyde, T.F. Morris, Phosphorus availability from phosphorus-amended water treatment residual, Commun. Soil Sci. Plan. 35 (2004) 1033-1046.

[18] G.K. Haustein, T.C. Daniel, D.M. Miller, Jr P.A. Moore, R.W. McNew, Aluminum-containing residuals influence high-P soils and runoff water quality. J. Environ. Qual. 29 (2000) 1954–1959.

Table 1 The characteristics of the RSAL and DSAL

	pH	Colour (Pt-Co units)	TOC (mg/L)	P (as PO_4^{3-}) (mg/L)	Al (mg/L)	SO_4^{2-} (mg/L)
RSAL	~2.1	4200	426	710	421	4100
DSAL	~1.9	0	94	680	414	4100

Figure captions:

Fig. 1. Close shot of RSAL and DSAL

Fig. 2. Effects of the pH on $AlPO_4$ precipitation (a) and P precipitation efficiency and concentration of residual Al at pH 6 and different reaction time (b)

Fig. 3. Precipitation of $AlPO_4$ in separated two sets experiments

Fig. 4. XRD pattern (a), FTIR spectra (b) and SEM (c) and visible photograph (d)of $AlPO_4$

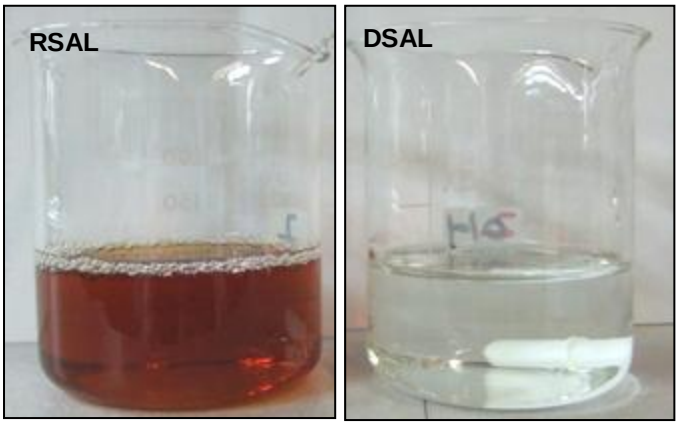
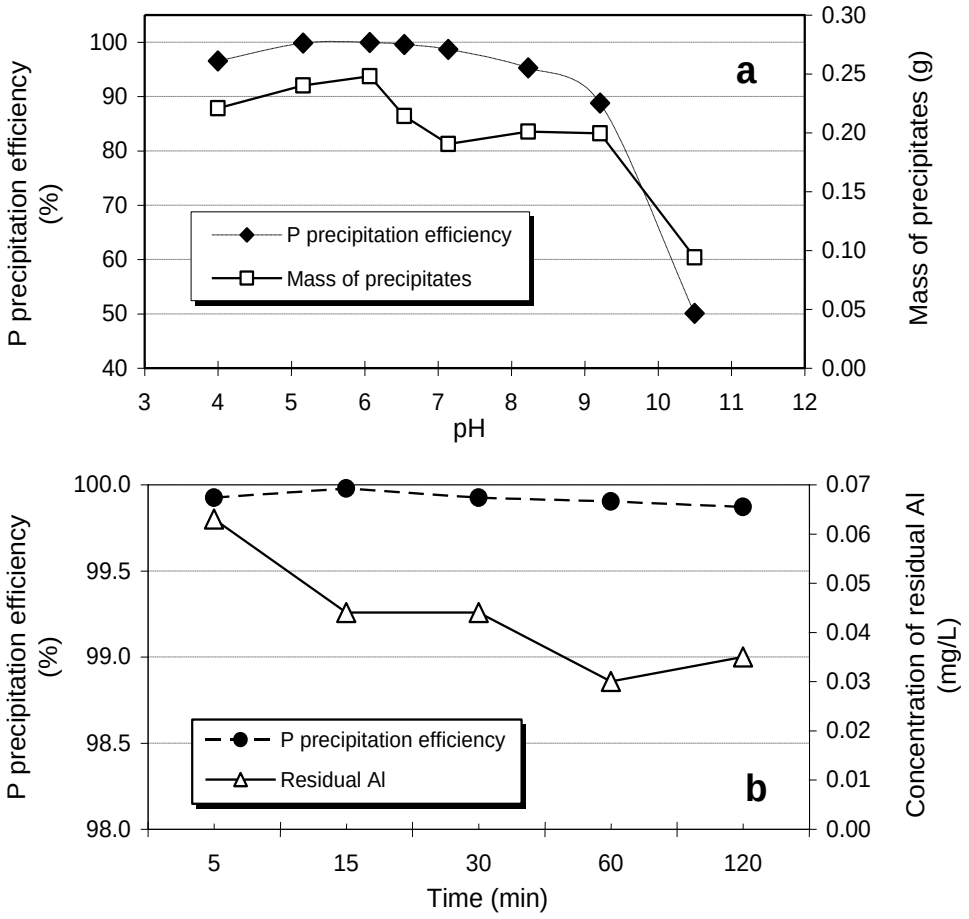


Fig. 1.



342

343 **Fig. 2.**

344

345

346

347

348

349

350

351

352

353

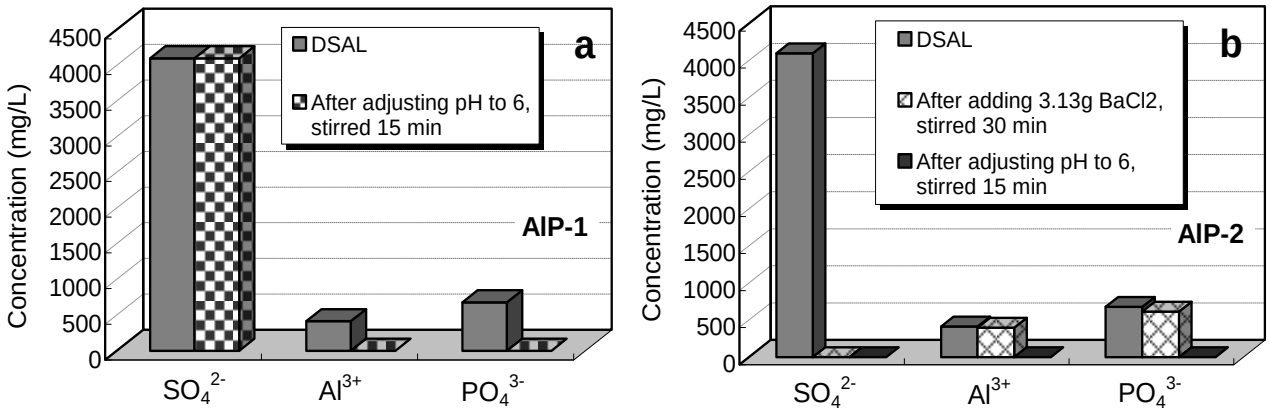
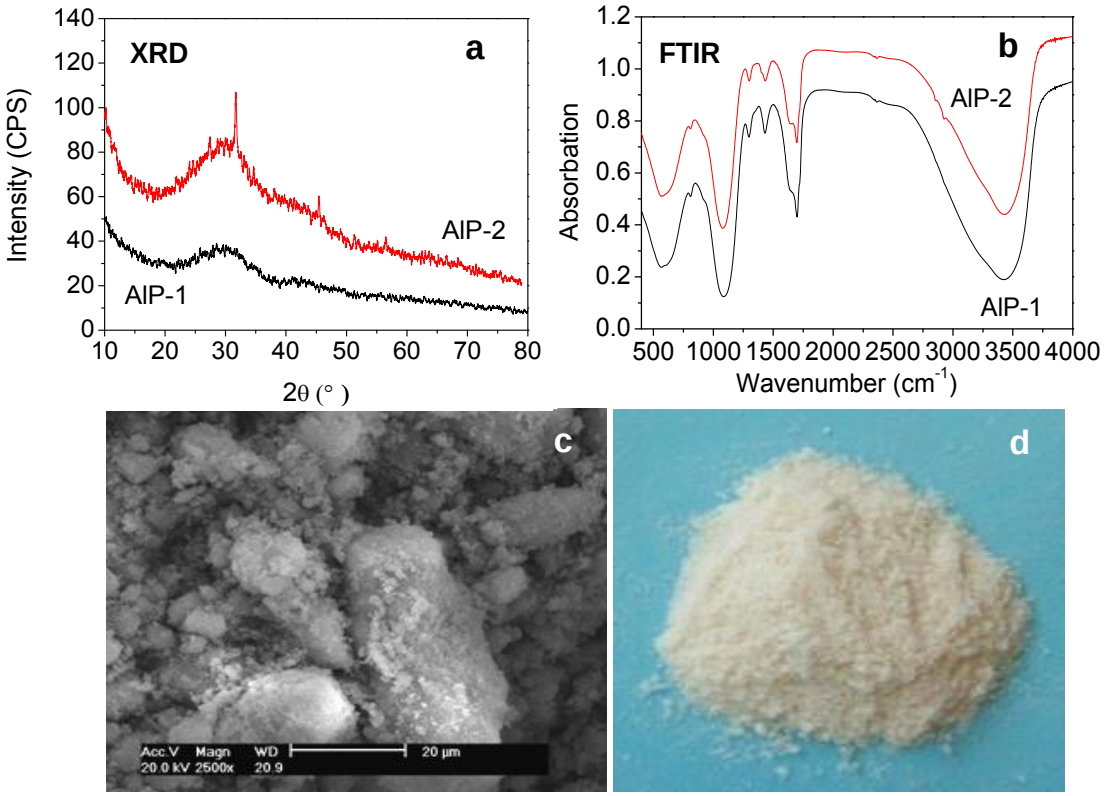

a
DSAL
After adjusting pH to 6, stirred 15 min
AlP-1
Concentration (mg/L)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
SO4 2-
Al3+
PO4 3-
b
DSAL
After adding 3.13g BaCl2, stirred 30 min
After adjusting pH to 6, stirred 15 min
AlP-2

Fig. 3.



372

373 **Fig. 4.**

374

375

376

377

378

379

380

381

382

383