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# Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge

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## **Abstract**

The adsorption characteristics of phosphate adsorption on the dewatered alum sludge were identified as a function of pH and ion strengths in solution. In addition, adsorption mechanisms were investigated by conducting batch tests on both the hydrolysis and P-adsorption process of the alum sludge, and making a comparative analysis to gain newer insights into understanding the adsorption process. Results show that the adsorption capacity decreased from 3.5 to 0.7 mg-P/g-sludge when the solution pH was increased from 4.3 to 9.0, indicating that adsorption capacity is largely dependent upon the pH of the system. The results of the competitive adsorption between phosphate and typical anions found in wastewater, such as  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , onto alum sludge reveal that alum sludge can selectively adsorb phosphate ions. The insignificant effect of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on P-adsorption capacity indicates that phosphate adsorption is through a kind of inner-sphere complex reaction. During the adsorption process, the decrease of phosphate concentration in solution accompanied with an increase in pH values and concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and TOC (total organic carbon) suggests that phosphate replaced the functional groups from the surface of alum sludge which infers that ligand exchange is the dominating mechanism for phosphate removal. At the same time, the simultaneous decreases in  $\text{PO}_4^{3-}$  and total aluminium concentration in solution indicate that chemical reaction and precipitation are other mechanisms of phosphate removal.

*Keywords:* Adsorption mechanisms; Alum sludge; Ligand exchange; Phosphate removal; Surface complex

## 1. Introduction

Alum sludge is an inescapable by-product of the processing of drinking water in water treatment works where aluminium salt is used as the coagulant. Aluminium sulphate is arguably the most widely used coagulant in drinking water treatment. When aluminium sulphate is added to raw water, it dissociates into  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$ . The  $\text{Al}^{3+}$  ions are immediately surrounded by water molecules and hexaaquoaluminium ( $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ) is rapidly formed. The hexaaquoaluminium formed then undergoes series of rapid hydrolytic reactions to form charged polymeric or oligomeric hydroxo-complexes of various structures. Such hydrolytic products include  $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ,  $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Al}_6(\text{OH})_{15}]^{3+}$ ,  $[\text{Al}_8(\text{OH})_{20}]^{4+}$  and  $\text{Al}(\text{OH})_3(\text{s})$  etc. [1]. During coagulation in water treatment process, these complexes adsorb and modify the surface charge of the colloidal particles, e.g. natural organic matter (NOM) such as humic and fulvic acid, microorganisms such as bacteria, protozoa and algae, and inorganic substances such as fine soil particles [2]. Thereafter, in the ensuing treatment units including flocculation, sedimentation and filtration, the colloids in the raw water are removed and transferred to the sludge phase together with the hydrolytic aluminium species.

In recent years, the management of alum sludge has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints. In Ireland alone, a double fold increase in alum sludge generation has been forecast by the end of the next decade, from a current estimate of 15,000 to 18,000 t/pa of the dewatered solids. However, as a sustainable approach to mitigate these effects, current trends have indicated a progressive drive towards alum sludge reuse as beneficial material. Such beneficial reuses include the use of alum sludge as an adsorbent for phosphorus removal from wastewaters. In particular, previous works done by the authors showed that the Irish dewatered alum sludge has a latent adsorption capacity, and it can be utilized as a “low-cost” phosphorus sorption medium in wastewater treatment [3,4]. In other instances, conjunctive evidences from literature have also shown that alum sludge can help remove phosphorus in wastewater. This is attributed to the abundant aluminium

ions in the alum sludge, which enhance the processes of adsorption and chemical precipitation that help to remove such pollutants from wastewater [5-7]. However, an in-depth understanding of the mechanisms and characteristics of phosphorus adsorption by the alum sludge is crucial to its effective utilization as an adsorbent material.

Therefore, the aims of this study are (1) to investigate the phosphate adsorption mechanisms of a dewatered alum sludge, (2) to identify the factors that affect the phosphate adsorption capacity of the alum sludge and (3) to examine the structural identity of the phosphate impregnated alum sludge (PIAS).

## **2. Materials and methods**

### *2.1. Preparation of test materials*

Dewatered alum sludge cake (moisture content 72~75%) was collected from an industrial filter press of the sludge dewatering unit of a Water Treatment Works in Southwest Dublin, Ireland where aluminium sulphate is used as coagulant. After collection, the sludge cakes were air-dried and the moisture content decreased to 10.2% at the time of being used. The air-dried sludge was then ground and sieved to provide the test adsorbent with diameter  $< 0.063\text{mm}$ .

Artificial wastewater was synthesized by dissolving pre-weighed potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) in distilled water. The solution was then incubated in the laboratory at  $20 \pm 2$  °C, and adjusted to different pH (using sulphuric acid (0.01M) and sodium hydroxide (0.1M)). Solutions were kept airtight to prevent  $\text{CO}_2$  from affecting solution pH.

Chloride stock solution (6.0M) and sulphate stock solution (3.0M) were prepared by dissolving pre-weighed amount of NaCl and  $\text{Na}_2\text{SO}_4$  respectively, in distilled water.

### *2.2. Characterization of the alum sludge*

Elemental, physical and chemical analyses of the dewatered alum sludge were carried out using Inductively Coupled Plasma-Atomic Emission Spectrometer

(ICP-AES, IRIS Advantage), TOC-V CSH (Shimadzu) and Fourier Transform-infrared (FT-IR, EQUINOX-55). The morphological structure of the dewatered alum sludge was examined by X-ray diffractometer (XRD, D/max-3C) and Scanning Electron Microscope (SEM, JSM-6700F).

### 2.3. Adsorption characteristics tests

#### 2.3.1. Adsorption capacity

Batch tests were conducted by adding pre-determined amount of the sludge to a pH controlled distilled water (pH 4.3 to 9) and measuring the zeta potential. Sulphuric acid (0.01 M) and sodium hydroxide (0.1M) were used to control the pH of the adsorption system to designed values (pH 4.3 to 9) to investigate the effect of pH on adsorption behaviour/capacity and the amount of acid/alkaline required to maintain the pH was calculated from the concentration and volume added, including a correction for the dilution effect. Thereafter, standard aliquots of the phosphate stock solution was introduced, giving a resultant phosphate concentration of 5 mg-P/l, which simulated the P level in typical municipal wastewater [8]. The mixtures were then mechanically agitated for promoting adsorption over a 48 hour pre-determined equilibrium time [3]. After adsorption, equilibrated samples were filtered using 0.45  $\mu\text{m}$  millipore filter paper (Whatman) and analysed for phosphate concentration. Adsorption capacities were evaluated from a linearized form of the Langmuir adsorption isotherm

$$\frac{C_e}{q} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b} \quad (1)$$

where  $q$  is the mass of phosphorus adsorbed per unit mass of sludge;  $C_e$  is the equilibrium concentration of phosphorus (mg-P/l) in suspension after adsorption;  $Q_0$  is the maximum adsorption capacity (mg-P/g-sludge); and  $b$  is a constant related to the energy of the adsorption-desorption process with unit of inverse of concentration  $C_e$ . By plotting  $C_e$  vs.  $C_e/q$ , a straight line with slope  $1/Q_0$  is obtained and the  $Q_0$  can

be calculated.

Phosphate concentrations and pH values were obtained using a Hach spectrophotometer (DR/2400) and a pH meter (WTW, pH 325) respectively. The Zeta potential of the alum sludge was measured at different pH using a Zeta Potential Analyser (ZC-2000). All the adsorption tests were repeated twice and the average value of measurements was reported.

### *2.3.2. Anion selectivity of alum sludge and structural identity of PIAS*

In order to investigate the selective adsorption of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  by the alum sludge, pre-determined amount of the sludge was added to a pH modified distilled water (pH 4.3 to 9) followed by the introduction of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  at concentrations ranging from 300 to 1000 mg/l. The total volume of the mixture was noted. Thereafter, 10 mg-P/l of equal volume as the initial mixture volume was added giving a resultant P concentration of 5 mg-P/l. The final mixture was then mechanically agitated for 48 hours equilibrium time and residual phosphorus concentration determined as in section 2.3.1. The structural identity of the PIAS was studied by investigating the effect of the ionic strength on the equilibrium of the surface complex formed.

## *2.4. Adsorption mechanism*

### *2.4.1. Ligand exchange*

To examine the possibility of ligand exchange in the adsorption mechanism, samples of alum sludge (5g/l) were hydrolyzed in distilled water (initial pH  $7.0 \pm 0.02$ ) in an airtight container and left for 28 days (final pH 5.98). Thereafter, phosphate concentration in the hydrolysed suspended solution was brought up to 5mg-P/l and phosphate adsorption by the hydrolyzed alum sludge was then monitored for 6 hours. Filtered samples from both processes were analyzed for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  concentration with the use of ICP-AES and Ion Chromatography (DX-120) while the pH of the suspended solution was also measured in both cases. Insights into the mechanisms of phosphate adsorption can be gained by measurement of the amount of  $\text{OH}^-$  and other anions/substances released from alum sludge consequent upon the

adsorption of phosphate.

#### *2.4.2. Interaction between dissolved aluminium species and $PO_4^{3-}$*

To investigate interaction between dissolved aluminium species and phosphate ions, the concentration of total aluminium (including  $Al^{3+}$ ,  $Al(OH)^{2+}$ ,  $Al(OH)_2^+$ ,  $Al(OH)_3$  and  $Al(OH)_4^-$  etc.), before and after phosphate addition (as in test 2.4.1) was measured. Particularly, any change in concentration may possibly give an indication of a reaction taking place. The concentration of total aluminum was accurately determined with the use of ICP-AES and Ion Chromatography.

#### *2.4.3. Competition with humic substances*

The concentration of TOC, before and after phosphate addition (as in test 2.4.1) was measured in order to understand likely competition between phosphate ions and humic substances on the surface of alum sludge. Again, a change in the TOC concentration may evidently support the competition hypothesis.

### **3. Results**

#### *3.1. Properties of alum sludge*

##### *3.1.1. Chemical composition*

The principal chemical compositions of the dewatered alum sludge are shown in Table 1. Although the properties of such sludge are highly variable and dependent on both the type of the raw water and the chemical composition of coagulant [9], it can be seen from Table 1 that aluminum is the dominant component in the dewatered alum sludge with ~46% in mass expressed as  $Al_2O_3$ . The other principal chemical components were  $Fe^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $SiO_4^{2-}$ , with mass percentages of 1.7% for cationic ions and 3.6% for anionic ions. In addition, the FT-IR has identified that the alum sludge contains some organic matter and the content expressed in TOC was 9.9% by mass examined by a Shimadzu TOC-V CSH total organic carbon analyzer.



[Table 1. The principal chemical compositions of alum sludge]

### 3.1.2. Morphological structure

XRD was used to identify the morphological structure of the alum sludge although it cannot provide a quantitative description of such structure [10]. The result of XRD pattern shown in Fig. 1 illustrated no sharpening characteristic diffraction peaks over a broad range of  $d$ -spacings ( $15-70^\circ 2\theta$ ), indicating poorly ordered particles within alum sludge. In addition, scanning electron microscope (SEM) observation of powdered alum sludge, shown in Fig. 2, has not found the classical well-crystalline appearance on sludge surface. Although both the XRD and SEM are rather qualitative descriptions on sludge structure, considering Fig. 1 and 2 it is reasonable to believe that the alum sludge is really amorphous.

[Fig. 1. X-ray diffraction pattern of dewatered alum sludge]

[Fig. 2. SEM observation of dewatered alum sludge]

## 3.2. Adsorption characteristics

### 3.2.1. Adsorption capacity

The experimental data from the adsorption tests fit well the Langmuir behaviour, as illustrated in Fig. 3. Computed results of adsorption capacities at different pH together with the results of Zeta potential measurement are shown in Fig. 4. It can be seen that pH has a significant effect on the adsorption capacity. A pH increase from 4.3 to 9.0 remarkably decreased the P-adsorption capacity from 3.5 to 0.7mg-P/g-sludge. The measured zeta potential shows the variation of surface charge from +75.8 mV to -33.7 mV, corresponding to a pH change from 4.3 to 9.0.

[Fig. 3. Langmuir isotherm plots to determine the maximum adsorption capacities]

[Fig. 4. Effect of pH on adsorption capacity and surface charge of alum sludge]

### 3.2.2. Selective adsorptivity of alum sludge and structural identity of PIAS

The effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on the phosphate adsorption capacity of the alum sludge are shown in Fig. 5. At pH 4.3, despite the wide variation in the concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  from 300 to 1000 mg/l, there was no significant difference in the adsorption capacity of the alum sludge which ranged from 3.5 to 3.4 mg-P/g-sludge. The same insignificant difference was observed at all the other pH values. This result is a good agreement with the findings reported by Tanada et al. [11] in which the selectivity of phosphate adsorption onto pure aluminium oxide hydroxide was evaluated to be about 7000 and 260 times compared with that of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , respectively. Fig. 6 illustrates the FT-IR spectra of the sludge samples before and after adsorption for the purpose to explore the identity of PIAS. Unfortunately, by examining the spectral region from  $1200\text{-}800\text{cm}^{-1}$ , which was proposed to be the region for structural diagnosis of metal orthophosphate complexes in aqueous solutions [12], a nearly identical spectrum can be observed from Fig. 6. The reason of not identifying phosphate on the PIAS by FT-IR is unclear, but having something linked with the complication of phosphate-alum adsorption behaviour in alum sludge. Unlike the phosphate-alum adsorption on pure aluminium oxide hydroxide, alum sludge contains some other ions and organic matter, which may interfere the FT-IP results.

[Fig. 5. Effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on phosphate adsorption capacity at different pH]

[Fig. 6. The FT-IR spectra of the sludge samples before and after adsorption]

### 3.3. Adsorption mechanisms

Results of the pre-hydrolysis process of the alum sludge followed by the

P-adsorption process are shown in Fig. 7. Emphasis was on the changes in the pH and concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , TOC, and total aluminium during the hydrolysis process of the alum sludge and the immediate P-adsorption process. The results show that alum sludge exhibited a strong hydrolysis potential characterized by an initial rapid release of  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , TOC and total aluminium in the first 24 hours followed by a slow release, which was monitored until an equilibrium concentration of each ion/substance was reached. Thereafter phosphate was added on 28<sup>th</sup> day to initialize the adsorption process.

During the hydrolysis stage, a decrease in pH from 7.0 to 5.98 was observed indicating complex reactions between the alum sludge and  $\text{OH}^-$  ion, resulting in a release of  $\text{H}^+$  ions, which leads to the decrease in pH. Concurrently, the concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , TOC and total aluminum increased from 0 to 3.13 mg/l, 2.45 mg/l, 5.38 mg/l and 33  $\mu\text{g/l}$ , respectively, as the hydrolysis progressed (Fig. 7, hydrolysis stage). However, during the adsorption stage, the reduction in phosphate concentration occurred simultaneously with increases in pH (5.98 to 7.21), and concentrations of  $\text{Cl}^-$  (3.13 to 7.89mg/l),  $\text{SO}_4^{2-}$  (2.45 to 3.67 mg/l) and TOC (5.38 to 9.16 mg/l) coupled with a decrease in the concentration of total aluminium from 33 to 23  $\mu\text{g/l}$  (Fig. 7, adsorption stage). These results give valuable insights that are vital to the understanding of the adsorption mechanism and which are further discussed in this paper.

[Fig. 7. Variation of pH,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , TOC and total aluminium during the hydrolysis and P-adsorption process]

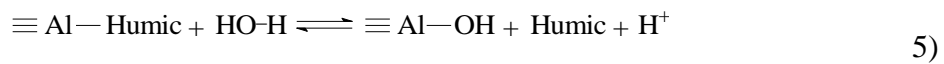
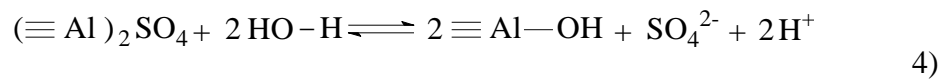
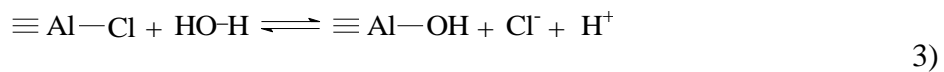
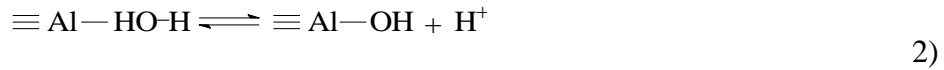
## 4. Discussion

### 4.1. Functional groups on the surface of alum sludge

The decrease of pH from 7.0 to 5.98 during the hydrolysis stage of the alum sludge (Fig. 7, b) shows that alum sludge has a particularly strong tendency to hydrolyze in water. Result of the Zeta potential measurement of the alum sludge at pH 7.0 gave a value of +28 mV, which indicates the presence of unsatisfied positive

charges on the surface of the alum sludge. Drawing on similar findings by Hem and Roberson [13], when alum sludge is added to water, it can be expected that the alum sludge is surrounded by a tightly bound shell of oriented water molecules (HO–H) on its surface and the positive charge on the alum sludge tends to weaken the forces holding the protons (–H) to the oxygen, and thus the protons are relatively easy to release. The release of H<sup>+</sup> causes the decrease of pH which suggests a change in the number of OH bonded on the surface of the alum sludge, leading to a hydroxylated surface [13]. These surface hydroxyl groups can take part in complexation reactions with metal ions and ligands [14].

At the same time, the decrease in pH was accompanied by an increase in the concentration of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and humic substances (as TOC) in solution (Fig. 7 c & d, hydrolysis stage). The change in the concentration of these ion/substances is attributable to an ion exchange process between –OH (in solution) and Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and humic substances (on the surface of the alum sludge) to form a new counter-ion layer on the surface of the alum sludge. The reactions occurring during the hydrolysis stage can be possibly explained by equations (2, 3, 4 & 5).



It is evident from the hydrolysis stage that there are some functional groups on the alum sludge surface, such as –OH, –Cl, –SO<sub>4</sub> and humic substances, which are a kind of an activated group, and have the potential to be selectively exchanged with the alum sludge affinity anion. In addition, if all the increases of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations were due to equations (2, 3 and 4), then the calculated pH of the

solution should decrease from 7.0 to 3.85. However, the change of pH during the hydrolysis stage was found to be 7.0 to 5.98 (Fig 7 b, hydrolysis stage). This means that there are still some other mechanisms involved in the increase of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations, which could be the dissolution of chlorine or sulphate salts during the hydrolysis stage, such as  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$  etc since the alum sludge contains such cations (see Table 1).

#### 4.2. The pH dependence of adsorption capacity

The results of the effect of pH on adsorption capacity show that the adsorption capacity of alum sludge is strongly dependent on solution pH and several reasons may be adduced to this. First, the change of surface characteristics can affect adsorption capacity to some extent. The surface characteristics of alum sludge, such as the surface charge (as related to the zeta potential measurements) as shown in Fig. 4 resulted from proton transfers at the surface [15]. It can be seen from Fig. 4 that as pH increases, the surface charge of the alum sludge, which is pH dependent [16], changes from positive to negative. This gives valuable information regarding the changing nature of the surface of the alum sludge. The increase of  $\text{OH}^-$  in solution could affect the electrostatic properties of the alum sludge. For example, the adsorption of  $-\text{OH}$  on the surface of alum sludge leads to the formation of a new charged counter-ion layer, making the alum sludge surface being a comparable lower affinity to phosphate. Again, with an increase in pH,  $\text{OH}^-$  competes strongly with phosphate for active sites, which, in turn affects the adsorption capacity of the alum sludge. Second, the pH dependence of phosphate adsorption capacity may be associated with ligand exchange between phosphate ions (in solution) and  $-\text{OH}$  (on the surface of alum sludge). One characteristic feature of phosphate adsorption on hydrous aluminium oxide is the release of hydroxyl ions into the solution [17]. This therefore implies that adsorption is favored by low pH values and that adsorption capacity would be higher at low pH values than at high pH values. This agrees with the report of Kim *et al.* [7] on the effect of pH on phosphate adsorption, which shows a lower pH being favourable to

phosphorus adsorption.

#### 4.3. Structural identity of PIAS

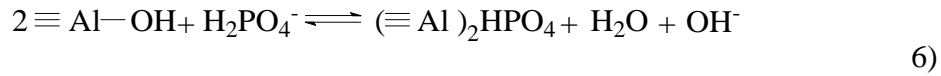
With regards to further adsorption characteristics of phosphate on the surface of alum sludge, the result of the effect of anions on adsorption capacity is particularly useful in determining whether the phosphate is associated with the surface of the alum sludge as an inner-sphere or outer-sphere complex. It is important to distinguish between outer-sphere and inner-sphere complex in order to understand the different stability of adsorbed ion, and the various chemical and physicochemical properties of alum sludge. Generally, direct evidence for inner-sphere complex can be obtained from spectroscopic methods, such as Fourier transform infrared spectroscopy [18,19]. However, the FT-IR results of PIAS obtained in this study did not show any distinctive characteristic peaks (see Fig. 6). Therefore, the structural identity of PIAS cannot be determined by the FT-IR method. However, a simple method of distinguishing between inner-sphere and outer-sphere complex is to assess the effect of ionic strength on the surface complex formation equilibrium. A strong dependence of the surface complex formation equilibrium on ionic strength is typical for an outer-sphere complex while the inverse is also implied [2, 20]. In this study, the insignificant effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  at different concentrations on the adsorption capacity (see Fig. 5) reflect that the ionic strength does not affect the adsorption behaviour, indicating an inner-sphere complex. Therefore, it is reasonable to speculate that the phosphate is adsorbed on the surface of alum sludge by chemical bond.

#### 4.4. Adsorption mechanisms

##### 4.4.1. Ligand exchange

Unlike the hydrolysis process, the rapid increase of pH from 5.98 to 7.12 coupled with the rapid decrease of phosphate concentration in 1 hour (Fig. 7 a & b) in P-adsorption process. The increase of pH is a sign of the release of hydroxyl ion from alum sludge into the solution; this indicating that phosphate is adsorbed by surface complex, *i.e.* the ligand exchange between phosphate (in solution) and  $-\text{OH}$  (on alum

sludge surface). The OH involved in the ligand exchange process is a kind of nonstructural OH, formed during both the formation process of alum sludge in drinking water treatment and the hydrolysis process. According to the calculation on the basis of chemical equilibrium reaction and constant of the phosphate speciation [21] in solution at pH 5.98 when the P-adsorption process took place, the approximately 96.5% of phosphate in solution existed as  $\text{H}_2\text{PO}_4^-$ . Therefore the adsorption process could be described by equation (6).



Quantitative relationship between adsorbed phosphate and hydroxyl ions released from alum sludge (Eq. (6)), would suppose that if the OH ligand exchange were the sole adsorption mechanism, the release of hydroxyl ion into the solution would increase the solution pH from 5.98 to at least 10.2. However, the pH only increased from 5.98 to a maximum of 7.21 (Fig. 7 b, adsorption stage). This limited increase of pH implies that there are some other mechanisms contributing to the phosphate adsorption. The fact that the decrease of phosphate accompanied with the increase of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in solution, as shown in Fig. 7 c, indicates that the alternative mechanism of P-adsorption by alum sludge could be the ligand exchange between phosphate (in solution) and  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (on alum sludge shown in Table 1). P-adsorption based on this mechanism accompanied with the release of  $\text{H}^+$  to the solution could cause a limitation on pH increase. This proposed ligand exchange process can be shown as equations (7 & 8).



Although the ligand exchange may be one of the major mechanisms of

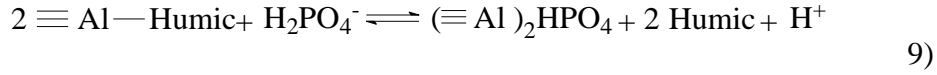
phosphate-alum adsorption, it should be pointed out that the P-adsorption is a complicated process due to the differences in the formation of phosphate-alum complexes. Rajan [17] and Guan et al. [22] concluded that phosphate adsorbs onto metal hydroxide by forming not only monodentate complexes, but also bidentate or binuclear complexes. Different P species may have different adsorption behaviours on the same adsorbent. For ortho-P source used in this study, Guan et al. [23] claimed that the ortho-P tended to form monodentate complex with aluminium hydroxide surface in adsorption process. Thus, the P-adsorption with Al in a real adsorption system could be far more complicated. In addition, it is noted in Fig. 7 b that a slow increase of pH after 1 hour adsorption was observed. This is a sign of the slow release of hydroxyl ion, leading to a slow decrease of P in solution (see Fig. 7 a), implying the slow P-adsorption process. Makris *et al.* [24] opined that the slow P-adsorption process of drinking water treatment plant sludge might be explained by intraparticle phosphate diffusion in micropores.

#### 4.4.2. Competitive effect with humic substances

Based on the fact that the increase of humic substances (TOC) was positively correlated with the removal of phosphate in solution (Fig. 7 d, adsorption stage), the release of humic substances to the solution would be due to the competitive effect of phosphate for surface sites with the humic substances. Therefore, as a result, part of the functional humic substances on the alum sludge surface is replaced by the phosphate, as shown in equation (9). Similar findings were reported in studies on competition between phosphate ion and humic substances for active sites during adsorption process [25]. In spite of the release of TOC in both the hydrolysis and the adsorption processes, it is noted that the increase of TOC in the solution was from 5.38 to 9.16 mg/l during the P-adsorption stage. The released TOC in the tested pH range (5.98-7.21) compared with the TOC in alum sludge (see Table 1), represents just 3.9% of the TOC contained in the sludge. In other words, the release of TOC from alum sludge is not a significant issue as far as effluent quality is concerned,



particularly when alum sludge is used as an adsorbent for phosphate removal in practice.



#### 4.4.3. Chemical reaction and coprecipitation

The variation of soluble aluminium hydrolysis products (as total aluminium) during sludge hydrolysis and adsorption processes shown in Fig. 7 e, reveals that: (1) the magnitude of aluminium release from hydrolysis is insignificant although aluminium is the major component in the alum sludge (Table 1). This implies that the aluminium in the alum sludge is in a stable and immobilized form, at the test pH value (5.98-7.21). It should be pointed out that the calculated solubility limit of the “total aluminium” by considering aluminium phosphate and aluminium hydroxide species is 56.4 µg/l. However, monitored "total aluminium" is 23 µg/l as shown in Fig. 7 e. The difference could be attributed to the multi-ions interactions in the system; (2) chemical reactions and coprecipitation occur between phosphate and aqueous aluminium since a decrease in total aluminium concentration from 33 to 23 µg/l is accompanied by a decrease of phosphate concentration. The precipitation formed in this process is thermodynamically and kinetically favored over aluminium hydroxide precipitation [26]. As pointed out by Hsu [27] and Omoike and Vanloon [8], the precipitation is governed by the integration of Al–OH–Al and Al–PO<sub>4</sub>–Al types of linkages into an aluminium hydroxyphosphate complex, rather than by precipitation of discrete phases such as Al(OH)<sub>3</sub> or AlPO<sub>4</sub>; (3) the dissolution of the alum sludge result in the increase of total aluminium which could provide a continuous supply of aluminium for the chemical reaction and the coprecipitation process. The intricacies of the phosphate-alum sludge adsorption system make a distinctive quantitative analysis of the amount of adsorption and chemical coprecipitation rather difficult.

## 5. Conclusions

Results obtained from this study have provided valuable information regarding the characteristics and mechanism of phosphate adsorption by alum sludge. In particular,

(1) The maximum adsorption capacities ranged from 0.7 to 3.5 mg-P/g when the pH of the synthetic phosphate solution was varied from 9.0 to 4.3. Solution pH has been shown and established as a vital factor influencing the adsorption behaviour. It is believed that phosphate adsorption by alum sludge is highly dependent on solution pH and the surface characteristics of the alum sludge.

(2) The results from the hydrolysis process of alum sludge provides evidence that the surface of alum sludge contain a significant amount of reactive functional groups, such as  $-OH$ ,  $-Cl$ ,  $-SO_4$  and humic substances. These functional groups are responsible for the ligand exchange mechanism of the adsorption of phosphate onto the surface of alum sludge.

(3) Alum sludge has a higher selective affinity to adsorb phosphate than typical anions found in wastewater, such as  $Cl^-$  and  $SO_4^{2-}$  and the adsorption of phosphate on the surface of alum sludge is shown to be a kind of inner-sphere complex (“chemical bond”).

(4) Ligand-exchange is shown to be the dominating mechanism based on exploratory evidence from the adsorption mechanism of phosphate onto the alum sludge. Although chemical reaction between phosphate and dissolved aluminium was demonstrated, it is believed that the chemical reaction played only a marginal role in the phosphate removal process.

(5) Increased phosphate adsorption coupled with a release of humic substances indicates the desorption of organic matter as a result of the competition between phosphate and humic substances for surface site. Experiments also revealed that the release of humic substances from the alum sludge is not significant at the tested pH condition (5.98-7.21), thus eliminating concerns over the practicality of reusing dewatered alum sludge as an adsorbent.

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Table 1. The principal chemical compositions of alum sludge

Chemical composition	Amount (mg/g-sludge)
Aluminum (as Al <sub>2</sub> O <sub>3</sub> )	458-463
Iron (as Fe <sub>2</sub> O <sub>3</sub> )	11.9-12.3
Calcium (as CaO )	11.6-11.7
Magnesium (as MgO)	7.4-7.6
Humic acid (as TOC)	96.4-98.5
Cl <sup>-</sup>	16.0-16.2
SO <sub>4</sub> <sup>2-</sup>	8.2-8.4
SiO <sub>4</sub> <sup>2-</sup>	10.6-11.8
H <sub>2</sub> O at 105 °C (moisture content)	102
H <sub>2</sub> O at 1000 °C	260-270

Note: The range of value indicates the lowest to highest values of the 3 parallel measurements. Other trace elements analyzed were not reported due to the very small amount.

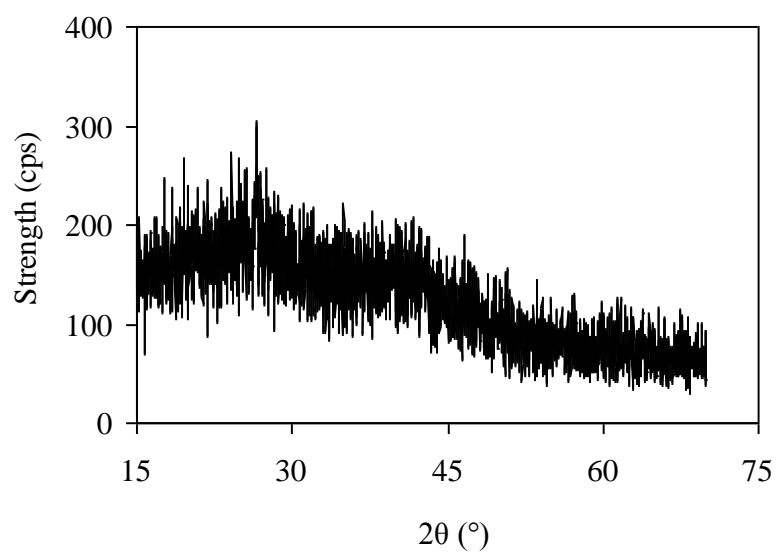


Fig. 1. X-ray diffraction pattern of dewatered alum sludge

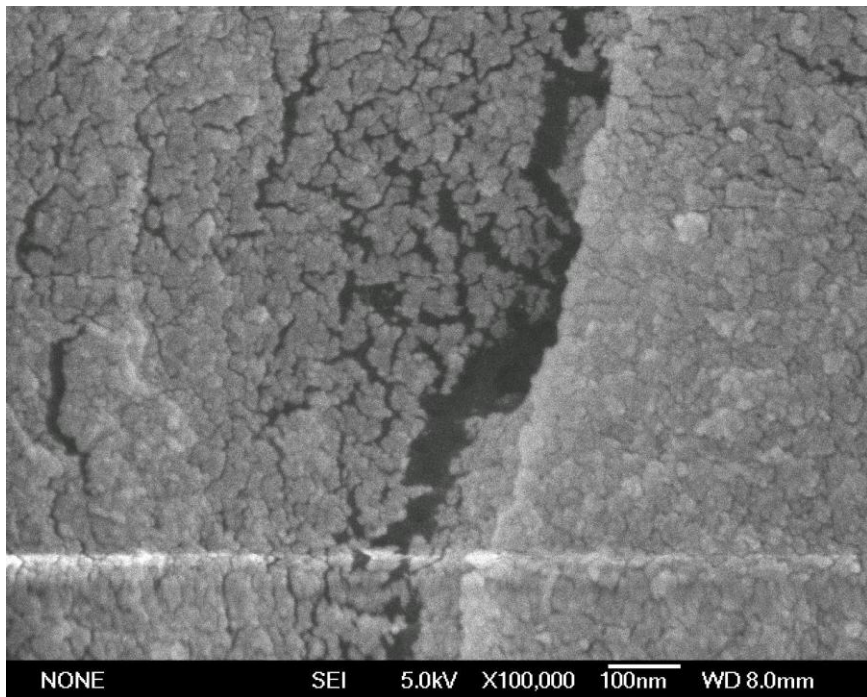


Fig. 2. SEM observation of dewatered alum sludge

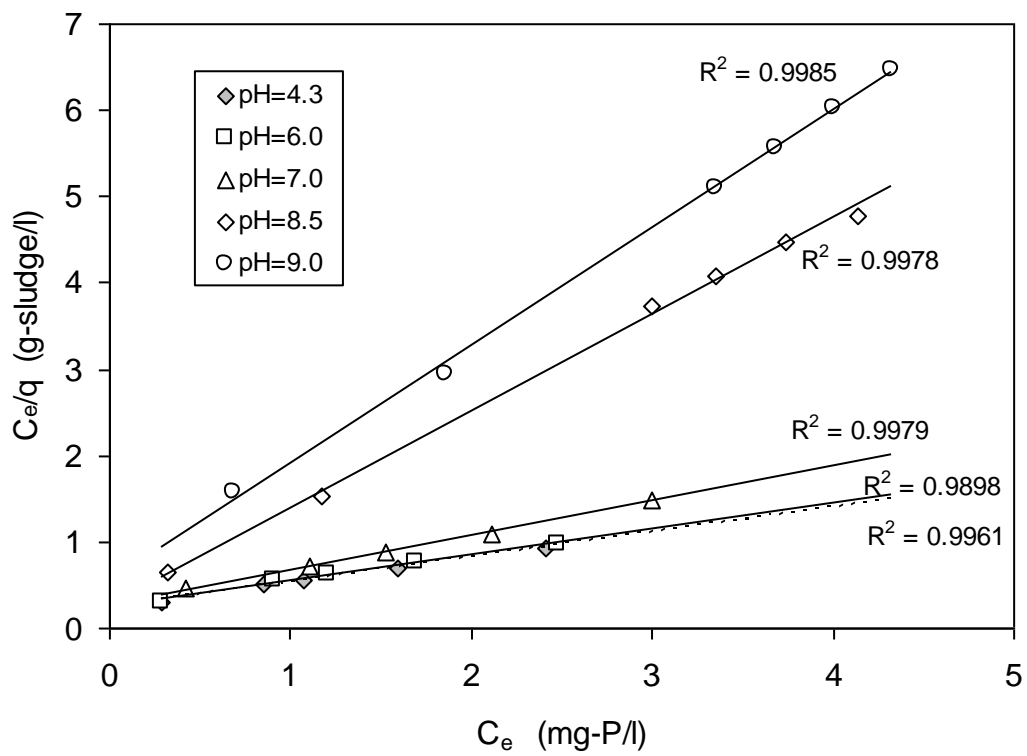


Fig. 3. Langmuir isotherm plots to determine the maximum adsorption capacities



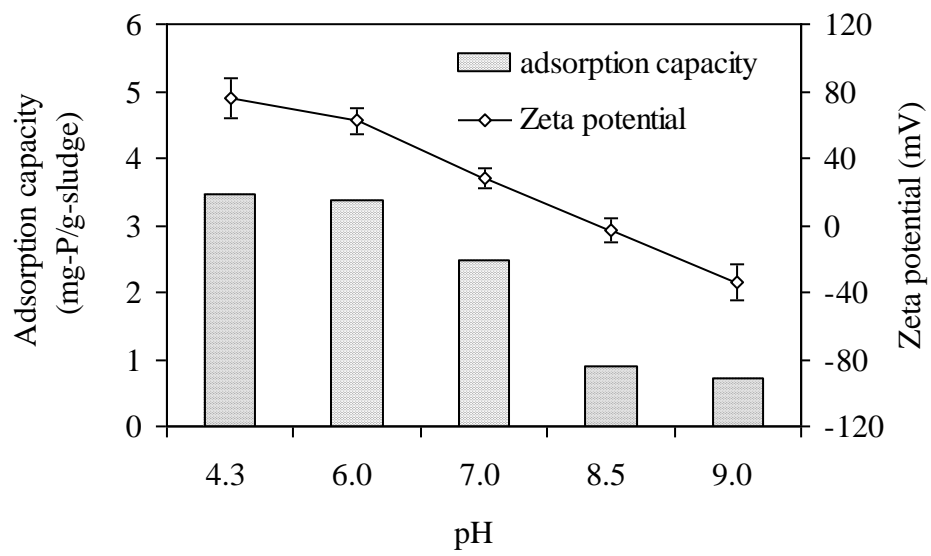


Fig. 4. Effect of pH on adsorption capacity and surface charge of alum sludge

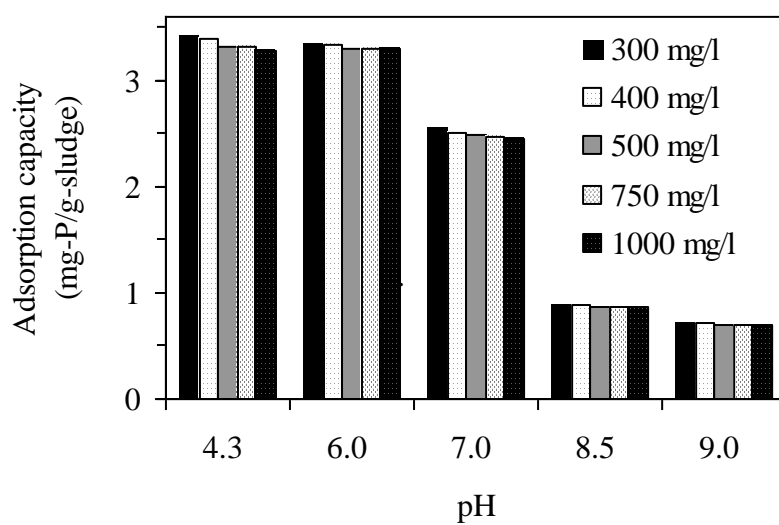


Fig. 5. Effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on phosphate adsorption capacity at different pH

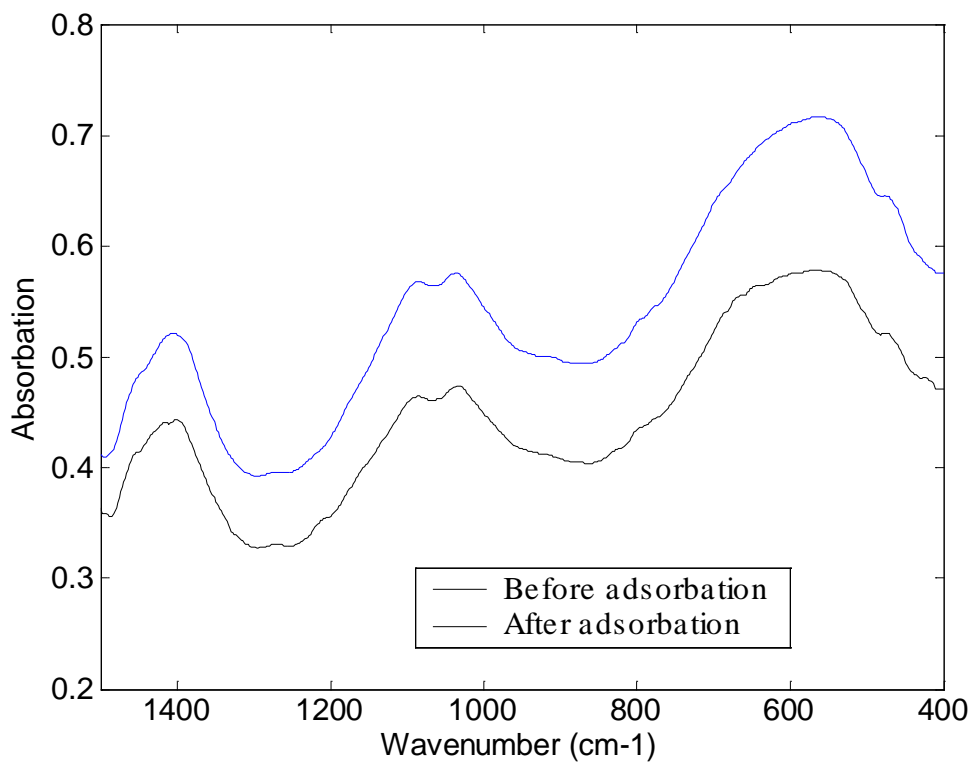


Fig. 6. The FT-IR spectra of the sludge samples before and after adsorption

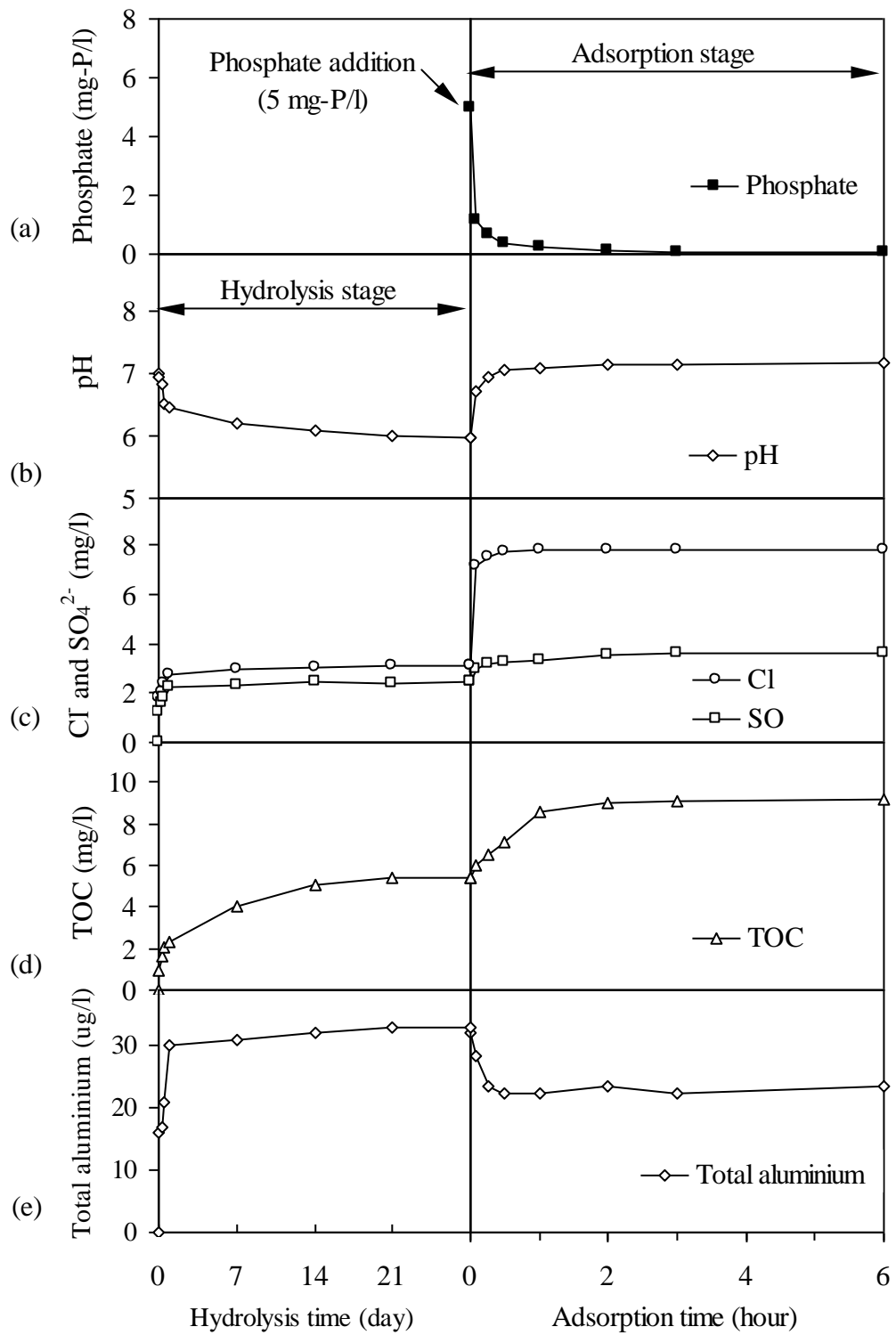


Fig. 7. Variation of pH, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, TOC and total aluminium during the hydrolysis and P-adsorption process