Effect of phosphate releasing in activated sludge on phosphorus removal from municipal wastewater

Jie Ge¹, Xiaoguang Meng¹,*, Yonghui Song², Amalia Terracciano¹

1. Center of Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, USA
2. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

ARTICLE INFO

Article history:
Received 5 June 2017
Revised 8 September 2017
Accepted 11 September 2017
Available online 20 September 2017

Keywords:
Phosphorus release
Coagulation
Activated sludge (AS)
Wastewater treatment

ABSTRACT

Aluminum and ferric salts are commonly used in municipal wastewater treatment plants (WWPTs) for phosphorus (P) removal. In this study, on-site jar tests were conducted to determine the removal of different P species from the fresh samples in the presence and absence of activated sludge (AS) with different doses of alum, poly-aluminum chloride, and ferric chloride at different pH. The soluble P (SP) concentration in the samples was about 0.63 mg/L. When the mixed liquor containing AS was treated with 8 mg/L of Al, SP could be reduced to 0.13 mg/L, while it was reduced to 0.16 mg/L after sedimentation removal of AS from sample. Chemical analysis determined that AS contained 59.8 mg-P/g-TSS and 43.8 mg-Al/g-TSS and most of the P was associated with the aluminum hydroxide. We discovered that the phosphate in the AS could readily be released from it, which was mainly responsible for ineffective removal of P to low levels in mixed liquor even with very high alum dose. This study provides new insight into the behavior and fate of P in the wastewater treatment plants that use alum to enhance P removal in the final effluent.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

With the rapid economic development and continued growth in human population, phosphorus (P) resources are being consumed with an unprecedented speed, due to both industrial uses and ever-increasing food demands. Eventually, excessive P is released into natural water bodies and causes a significant environmental problem known as eutrophication, which is characterized by uncontrolled growth of plants and algae in water ecosystems. Due to the increasingly serious P pollution, extensive efforts have been made to limit and recover P from wastewater with different techniques. The US EPA (US Environmental Protection Agency) had reported that municipal and industrial wastewater are the significant sources of P to surface waters throughout the country, therefore treating wastewater and regulating P discharge limit in final effluent in municipal and industrial wastewater treatment plants (WWTPs) is one of the well-known solutions to prevent eutrophication.

P in a wastewater treatment system can be classified as soluble phosphorus (SP) and particulate phosphorus (PP). Therein to, SP can be divided into soluble PO₄³⁻, soluble polyphosphate and soluble organic phosphate (SOP) (Li and Brett, 2015; Park et al., 2016). Usually, the discharge criteria are based on the total phosphorus (TP) concentration including both SP and PP. Municipal WWTPs currently are subject to the discharge limit with 1.0 mg/L of TP proposed by the US EPA. In the future, limits will be improved to a much more stringent level, 0.23 mg/L daily maximum TP.

Numerous technologies for P removal have been studied at laboratory, pilot- and full-scale in order to ameliorate current P

* Corresponding author. E-mail: xmeng@stevens.edu (Xiaoguang Meng).
problem and limit P to the satisfied discharge level. According to different removal mechanisms, phosphorus treatments can be briefly categorized as physicochemical and biological treatments (Zhao et al., 2012). Chemical coagulation with aluminum (Alum, AlCl3), iron (FeCl3, FeCl2, Fe2(SO4)3), calcium (CaCl2, CaO) and magnesium (MgCl2, MgCO3·3H2O) is the most common physico-chemical treatment for phosphorus removal from municipal wastewater (Georgantas and Grigoropoulou, 2007; Zelmanov and Semiat, 2015; Martí et al., 2010). The process of phosphorus removal using Al and Fe salts is complex, but well-studied and described as precipitation, coagulation–flocculation, and adsorption on the formed precipitants/metal hydroxide, while adsorption is recognized as the dominant mechanism.

Although massive studies have assessed phosphorus removal by different kinds of coagulants, only limited research has been done in fresh mixed liquor collected from aeration tank and limited work was aimed to study how the compositions of AS affect P removal process, particularly the residual metal precipitates adsorbing phosphate ions.

In this study, the phosphorus profile in a WWTP was monitored from October 2015 to May 2016. P removal in terms of TP, SP, soluble PO4\(^{3-}\), SOP and PP, as well as the pH effect on P removal in fresh samples in the presence and absence of AS, were investigated by using three kinds of inorganic metal coagulants: alum, poly-aluminum chloride (PAC) and FeCl3. P release from AS under various pH conditions and the influence of the presence of AS on P removal were also studied in order to explore the major reason causing the significant difference in P removal in the presence and absence of AS.

1. Materials and methods

1.1. Biological and chemical materials

AS was obtained from an aeration tank operated with a volume of 928 m\(^3\) and retention time of 8 hr in the WWTP. The mixed liquor samples collected near the aeration tank effluent spot at different time were used to characterize the parameters of TSS, VSS, soluble TOC, Zeta potential and the chemical composition of AS. The characteristics of the mixed liquor sample are as follow: TSS 5000 mg/L, VSS 3800 mg/L, soluble TOC 10.0 mg/L, zeta potential – 6.7 mV, Al 43.8 mg/g TSS, Fe 1.5 mg/g TSS, Ca 10.4 mg/g TSS, Mg 2.8 mg/g TSS, P 59.8 mg/g TSS. The relatively high Al content was caused by the return of activated sludge undergoing alum treatment in secondary clarifier.

The working solution for alum, PAC and FeCl3 were prepared by commercial alum products provided by Chemtrade Logistics Inc., commercial PAC product purchased from USALCO LLC., and laboratory-grade FeCl3 chemical purchased from Fisher Scientific. In this work, all the coagulant dosages were in the unit of mg/L as Al or Fe.

1.2. Experimental procedure

Uniform mixed liquor containing AS and supernatant samples after removal of sludge by settling were used in different tests. All experiments were conducted on site by a conventional jar test with a sixe paddle stirrer at room temperature. The operating conditions, after a pre-determined amount of coagulant was added into a 1-L beaker, were referred the standard method ASTM D2035 as follows: rapid mixing at the speed of 120 r/min for 1 min, slow mixing at the speed of 40 r/min for 4 min, then settling for 1 hr. The supernatant was collected from the treated samples for TP analysis and a portion of it was passed through a 0.45 μm membrane filter (A Chemtek Inc.) for analysis of soluble PO4\(^{3-}\) and SP. pH values were governed in the same range of 6.0–6.6 to examine the effect of coagulant dose on P removal.

The study of P removal at different initial pH values was carried out by adding 4 mg/L of coagulant as Al or Fe into a series of samples at pH 5.0, 6.0, 7.0, 8.0, and 9.0. A blank control test without any coagulant addition was performed in order to check the impact of pH on AS itself. 0.1 mol/L hydrochloric (HCl) and sodium hydroxide (NaOH) were used to adjust pH. The pH of the samples was not further regulated during the reaction, therefore the final pH values of supernatants were recorded and plotted against residual P concentrations of different P species. 

P released from AS in the original sample at various pH values and in deionized water at neutral pH was also evaluated. When the experiment was conducted in deionized water, in order to maintain the same activity of the sludge as in the original sample, AS was collected by settling so that there was still some wastewater content in the sludge. Therefore, P concentration at time zero did not start from 0 mg/L. The supernatant samples passed through 0.45 μm membrane filters were collected for analysis of soluble PO4\(^{3-}\) and SP.

1.3. Analytical methods

TSS and VSS analyses of the original samples were performed following Standard Method 2540D (Rice et al., 2012). Zeta potential analysis for the original samples was carried out using a Zeta Nano Sizer Malvern Instrument.

AS dried at 103°C was digested according to EPA Method 3051 (Microwave Assisted Acid Digestion). The digested solution was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent Technologies) and total organic carbon analyzer (PHOENIX 8000).

The soluble PO4\(^{3-}\) concentration was quantified by a spectrophotometer (HACH, DR6000) using the USEPA PhosVer 3 Method (Method 8048, HACH), which is accepted for reporting wastewater analysis and is equivalent to Standard Method 4500-P. TP and SP were both determined following USEPA PhosVer 3 with the acid persulfate digestion method (Method 8190, HACH). Heating the samples for half an hour at 150°C was included in the digestion procedure. The PP concentration was obtained from the subtraction between the TP and SP concentrations, while SOP was the difference between SP and soluble PO4\(^{3-}\). In this study, all the P concentrations in different species were in the unit of mg/L as P.
2. Results and discussion

2.1. P concentration profile in WWTP

Four locations distributed in different treatment units were selected to collect uniform samples for monitoring spatial changes in P concentration. Fig. 1 briefly shows the schematic diagram of the sampling positions. Approximately 5 mg/L of Al in alum form was added into wastewater for P removal after the aeration tank but before the secondary clarifier.

The average P concentrations in different species and different samples are summarized in Fig. 2. The results show that the TP concentration in raw sewage (S0) was in the range of 5.60 to 9.00 mg/L while PP, soluble PO$_4^{3-}$ and SP accounted for about 25%, 68%, and 79% of TP, respectively, which indicates that soluble P was the major species in raw WW.

According to Fig. 2, P concentration decreased significantly, from raw WW to the secondary clarifier. The first significant drop occurred in the primary clarifier, where TP and PP were reduced by 34% and 45%, respectively. The second drop was in the aeration tank operated at an 8 hr residence time; TP, SP and soluble PO$_4^{3-}$ in this process could be removed by up to 65%, 82% and 91%, respectively. By contrast, the PP concentration increased from 0.98 mg/L to 1.27 mg/L due to the aeration. The last dramatic drop occurred in the secondary clarifier operated at a 3 hr residence time. Because alum was added in the influent to the secondary clarifier, soluble P could be removed by more than 80%. However, there was still about 0.3 mg/L of TP remaining in effluent.

Recalling that a portion of AS in the secondary clarifier was returned to the aeration tank, it means the aluminum precipitates formed after alum treatment in the secondary clarifier will be transferred to the aeration tank together with AS; therefore, sludge in the aeration tank and secondary clarifier had similar characteristics. Considering the different residence times and soluble P removal efficacy in these two unit processes, the removal rate of soluble PO$_4^{3-}$ in the aeration tank was 0.4 mg/(L·hr), while the rate in the secondary clarifier was 1.5 mg/(L·hr). This indicates that alum addition was the leading cause of soluble P removal in the secondary clarifier, while the dominant contribution to soluble P removal in the aeration tank would be biomass growth.

2.2. Effect of coagulant dose on P removal in mixed liquor

P removal as a function of the various coagulant dosages in the pH range of 6.0–6.6 is presented in Fig. 3. It was found that the residual phosphorus was dependent on coagulant addition, and a higher dosage favored TP removal. By comparing the performance of all three coagulants, alum was more efficient for the removal of TP, SP, and soluble PO$_4^{3-}$ than the other two inorganic coagulants. From Fig. 3, it can also be found that SP and soluble PO$_4^{3-}$ concentrations decreased rapidly with alum dose up to 4 mg/L, and gradually reduced by only 0.06 mg/L of SP and 0.07 mg/L of soluble PO$_4^{3-}$ when the alum dose increased to 8 mg/L. The removal curves of PAC and FeCl$_3$ in Fig. 3 were more linear in terms of TP, SP and soluble PO$_4^{3-}$. Moreover, SOP did not show significant removal with increasing dosage, which is consistent with other studies; in fact it has been reported that coagulation is more effective in removing inorganic P than organic P due to the strong reactive affinity for inorganic P (Winkler, 1999; Park et al., 2016; Zhao et al., 2012).

The mechanisms of P removal by these three common coagulants containing aluminum and iron have been well established (Georgantas and Grigoropoulou, 2007; Jiang and Graham, 1998; Thistleton et al., 2002; Aguilar et al., 2002; Banu et al., 2008; Gao et al., 2013). Within the pH range of 6.0–6.6, the predominant P species is H$_2$PO$_4^-$ (Dihydrogen phosphate), with a negative charge. On the other hand, once the coagulant contacted with water, the trivalent ions (Al$_3^+$ and Fe$_3^+$) were rapidly hydrolyzed to form amorphous species. In the case of alum treatment, the dominant Al species formed in the studied pH range was proved to be amorphous Al(OH)$_3$ (Georgantas and Grigoropoulou, 2007). H$_2$PO$_4^-$ can be adsorbed on aluminum hydroxide precipitates through ligand exchange between phosphate ions and hydroxyl groups (Lijklema, 1980; Anderson and Berkowitz, 2010; Yang et al., 2006). Hence, the higher the dose applied, the more hydroxide precipitates will be formed, and better P removal can be achieved. However, the increasing dose of alum from 6 to 8 mg/L did not improve the soluble PO$_4^{3-}$ removal.

2.3. Effect of coagulant dose on P removal in samples without AS

Supernatant from the mixed liquor was used to investigate P removal by the three different coagulants. The pH value was
controlled in the same range as in previous tests. The residual P concentrations in the form of SP, soluble PO$_4^{3-}$ and SOP against coagulant dosages are shown in Fig. 4. The results indicate that alum still performed more efficiently on P removal than FeCl$_3$ and PAC (as shown in Fig. 3). Moreover, another similar phenomenon observed was that SP and soluble PO$_4^{3-}$ declined rapidly within the first 1 mg/L of alum addition, and no more improvement could be achieved when alum addition increased to 2 mg/L. The remaining SP can be attributed to SOP of the difficult removal, with lower adsorption affinity compared with soluble PO$_4^{3-}$ (Park et al., 2016; Georgantas and Grigoropoulou, 2007; Winkler, 1999).

The flocs produced by aluminum and ferric coagulants are poorly crystalline but more amorphous, high surface areas could be detected which is contributed to the rapid P removal from wastewater (Zhao et al., 2012; Hsu, 1976; Adler and Sibrell, 2003; Dayton and Basta, 2005; Babatunde et al., 2009). However, different coagulants show different capabilities to remove P. Elliott et al. (2002) stated that aluminum hydroxide had better adsorption ability than ferric hydroxide, which is

---

**Fig. 2** – Spatial changes of P concentration in WWTP.

**Fig. 3** – Comparison of treatment of P by alum, Polyaluminum chloride, and ferric chloride in the pH range of 6.0–6.6 in mixed liquor collected from aeration tank.
consistent with our results. This observation can be explained by the fact that the formed aluminum precipitates have higher adsorption affinity to phosphorus ions than ferric precipitates (Dayton and Basta, 2005).

In comparison to P removal under Al addition of 2 mg/L in alum form shown in Figs. 3 and 4, it can be seen that the residual SP and soluble PO$\text{4}^{3-}$ concentrations in the presence of AS were two times and eight times the residual SP and soluble PO$\text{4}^{3-}$ concentrations in the absence of AS. This demonstrates that the existence of AS had a significant inhibitory effect on P removal. Thus, in Fig. 4, less coagulant was required to remove SP and soluble PO$\text{4}^{3-}$.

2.4. pH effect on P removal in presence and absence of AS

In this section, the coagulant dosage of 4 mg/L in Al or Fe was employed to study the pH effect on P removal in the presence and absence of AS. The results in Fig. 5 show that alum performed much better than the other two coagulants in the pH range from 4.0 to 9.0 regardless of the presence of AS.

It was reported in literatures that the efficiency of P removal using these three coagulants was highly dependent on pH, with an optimal range of 5.5–5.9 for alum (Banu et al., 2008; Malhotra et al., 1964), 6.0–7.0 for PAC (Aguilar et al., 2002; Wang et al., 2005), and 5.0–7.0 for FeCl$_3$ (El Samrani et al., 2004; Pham et al., 2006; Zhang et al., 2010). The general removal trend reported in other works (Altundo$\breve{g}$an and Fikret, 2002; Yan et al., 2010) was similar to that observed in supernatant sample in present study. The P removal appears to peak around pH = 6.0. However, the P removal efficiency in mixed liquor sample remained similar in the pH range of 4.5 to 6.0, and then decreased with pH increased.

pH is the most important factor of P removal process in this study that it determines the concentration and nature of P species as well as the aluminum or ferric hydrolysis products (Karageorgiou et al., 2007). Within the studied pH range from 4.0 to 9.0, the majority of Al$^{3+}$ and Fe$^{3+}$ ions formed Al(OH)$_3$ and Fe(OH)$_3$ precipitates (Georgantas and Grigoropoulou, 2007; Jiang and Graham, 1998; Pham et al., 2006), and the dominant P species was either H$_2$PO$\text{4}^-$(4.0 < pH < pH$_\text{pK}_{2}$ for H$_2$PO$\text{4}^- = 7.2$) or HPO$\text{4}^{2-}$(7.2 < pH < 9.0). In acidic condition, the P ions were more protonated and possibly favored to form H$_3$PO$_4$, which cause the decrease of P removal with decreasing pH. In alkaline condition, the surface of metal hydroxide precipitants will become more negatively-charged (S−OH + OH$^-$ → S−O$^-$ + H$_2$O) and then strengthen the electrostatic repulsion between the P ions and metal hydroxide which lead to a decrease for P removal. On the other hand, the high pH will affect the ligand exchange between P ions and surface hydroxyl group (S−OH + Al$^{3+}$ → S−O$_\text{al}$ + Al$^{3+}$OH$^-$) which also inhibit the P removal. Therefore, P removal firstly increased and then decreased in the pH range from 4.0 to 9.0. In this study, P removal in the presence of AS was not shown the same trend as that in the absence of AS. The only difference between the two treated samples was the sludge. The aluminum contents, whether from the fresh formation through alum addition or the already formed precipitates embedded in sludge, had the same performance for P removal, which means that the biomass matter in the sludge can remove P in the low pH range.

2.5. P release from AS at various pH values

Considering the two observations that the different P removal efficiencies were obtained in mixed liquor and supernatant samples (Figs. 3 and 4) and the residual SP concentration at higher pH was higher than initial concentration (Fig. 5), P released from AS was discovered. The release test in the original sample at various pH values and in deionized water at neutral pH was examined in order to study how AS affects P removal. According to the results in Fig. 6a, SP, soluble PO$\text{4}^{3-}$ and SOP concentrations stayed constant when pH was less than 7.0, then they rapidly increased over the initial concentrations with increasing pH from 7.0 to 9.5. The P release under neutral pH in the deionized water, where the initial concentration was quite low, is shown in Fig. 6b. Based on the observation in Fig. 6a, no P release should occur. However, it was found that the release process only took about 2 min and 15 min to exceed the initial soluble PO$\text{4}^{3-}$ and SP concentrations, respectively, following a linear relationship, whereas for SOP not much release was observed. Even though the experiment was stopped at 1 hr, it clearly shows that P released from AS has great potential to affect P removal.

Recalling the composition of AS in Section 1.1, there were about 59.8 and 43.8 mg/g TSS of P and Al in sludge, respectively. As other studies reported, the biomass concentration can be
represented by VSS (Maree et al., 1991; Chen et al., 2001; Chang et al., 2002). Based on this assumption, the AS composition can be simply separated divided into 77% biomass and 23% aluminum precipitates. According to the molar ratio of C:N:P (=45:9:1) in bacteria (Goldman et al., 1987), the P content in biomass can be estimated about 44 mg/g TSS, which accounted for 57% (W/W) of the total P content in AS. The remaining 43% of P was adsorbed on the 23% fraction of aluminum precipitates. The over amount of phosphate ions were stayed on the aluminum precipitates surface and they were readily peeled off from the surface due to the competitive exchange between OH$^-$ groups and PO$_4^{3-}$ ion. In Xu’s study (2015), the activated sludge he worked with did not contain any aluminum precipitates and he found that the P concentration decreased a little rapidly under the basic condition which is not consistent with our results. The difference between the AS studied by Xu and the sludge studied in this work is the aluminum precipitates adsorbing phosphate ions. Thereby, the main P release source in the higher pH range in this work was attributed to the P desorption from aluminum precipitates. This significant P release occurred at higher pH was also observed during the coagulant treatment and the release far exceeded the removal as Fig. 5 illustrated. Therefore, the P desorption can be described by $S$–PO$_4^{3-}$ + H$_2$O $\leftrightarrow$ $S$–O$^-$ + H$_2$PO$_4^-$, and it can be triggered when the H$_2$PO$_4^-$ concentration in aqueous solution phase is low, according to the results in of the deionized water test (Fig. 6b).

Considering all the P removal and release results, the P removal by coagulants in this study can be understood by two simultaneous processes: the adsorption due to coagulant addition and the desorption from metal hydroxide previously existed in AS. In other words, the added coagulant removed not only the original P but also the desorbed portion. This is the reason why less P removal was observed in mixed liquor than in
supernatant sample without AS when the same amount of alum was applied to the system.

3. Conclusions

The P removal using three inorganic metal coagulants was investigated in terms of TP, PP, SP, SOP and soluble PO\textsubscript{4}\textsuperscript{3−}. Jar tests showed that alum always achieved higher P removal than PAC and FeCl\textsubscript{3}. Comparing the P removal in mixed liquor with that in the supernatant sample without AS, the inhibitory effect of AS was discovered and explained by P desorption from aluminum precipitates in sludge. Therefore, the P desorption from AS significantly hampered the P removal performance of coagulant. This study provides a new perspective of how P is removed through coagulants in secondary clarifier where the AS already contained aluminum precipitates adsorbing phosphate ions. The results show that the adsorbed phosphate can be released from aluminum precipitates and the added coagulant removed both the original P and the desorbed portion. This study will provide valuable information for upgrading and designing wastewater treatment systems to remove phosphate to low levels.

Acknowledgment

The authors would like to thank SUEZ Water Princeton Meadows for sponsoring the project and thank the CSC (China Scholarship Council) for providing a scholarship to Jie Ge.

REFERENCES


