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Coagulation of phosphorus: effects of Al(III) species (Al_a, Al_b, and Al_c)

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ABSTRACT

Phosphorus removal from a secondary sewage effluent using aluminum salt coagulants, such as alum and prehydrolyzed metal salts (PACls with different basicity values), was investigated in this study. It was observed that ortho phosphate was easier to remove by coagulation than other P fractions. The optimum pH for P removal was in the range of 5.0–6.6 using alum and in of 4.5–5.5 using PACl. Applying Ferron assay test, Al species in the coagulants were classified as Al_a (monomeric Al), Al_b (polymeric Al), and Al_c (colloidal and precipitated Al). The results obtained by performing jar tests indicated that phosphorus removal was correlated well with the distribution of Al species in the coagulants. The higher the Al_a content in PACl, the higher the P removal efficiency would be. Positive effects of Al_a for the removal of P might be due to high ability of Al monomer in forming the $Al(OH)_x(PO_4^{3-})_{3-x}$ precipitated complexes and in adsorption of phosphates into $Al(OH)_3$ precipitate that are formed predominantly in hydrolysis process of Al_a coagulants. Although Al_b has been known as the most effective species in coagulation, it did not show any superior performance in P removal. The residual P concentrations obtained were strongly depended on the coagulant type used, such as the basicity of coagulants and also the contents of Al_a, Al_b, and Al_c in the coagulants.

Keywords: Aluminum species; Coagulation; Ferron assay; Polyaluminum chloride (PACl); Phosphorus removal

1. Introduction

Eutrophication causes problems relating to water purification for portable use due to excessive growth of algal and nuisance aquatic plants in surface water. It has been well known that key element causing eutrophication is phosphorus (P). A concentration as very low as 0.05 mg/L ortho-P may cause the growth of algae but fortunately, concentrations of ortho-P below 0.5 mg/L can inhibit algae growth [1]. A significant source of P disposed into surface water comes from municipal wastewater and therefore controlling P discharged from sewage treatment plants into a receiving water body may control the eutrophication process. In 2012, the South Korea imposed a stricter range of 0.2–0.5 mg/L instead of 0.5–1.0 mg/L total P on sewage effluent discharge limit [2]. USEPA published a proposed water quality criteria for nutrients, in which total P in the range of 0.01–0.76 mg/L [3]. The European Union promulgated a guideline that limits value of P in the range of 1.0–2.0 depending on the size of the sewage treatment plants [4]. To meet

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such stringent standards of environmental regulations worldwide, tertiary treatment of secondary sewage effluents has become increasingly necessary.

Many phosphorus removal techniques have been investigated. Physical methods, such as electrodialysis and reverse osmosis, have proved to be either too expensive or inefficient. Biological treatment can be highly variable due to operational difficulties [5–7]. Furthermore, discharge limit concentrations of P are lower than that can be achieved using biological processes alone. Thus, chemical P removal will be required. The chemical removal techniques using metal salts are reliable and well-established processes [6,8,9].

The three main metal salts available for P removal are calcium, aluminum, and iron. Calcium, which is used as lime, is less commonly employed due to handling difficulties and high sludge production. In addition, optimum pH 11 using lime requires an extra chemical to adjust the wastewater before discharge. Iron salts, although have high efficiency in P removal, have a major obstacle in their widespread application due to the yellow color and corrosion caused by residual Fe(III). In addition, no attention has been paid to the recovery of large amount of P transferred into the precipitates, because ferric phosphate is not suitable as fertilizer due to its low solubility. The metal salts, namely alum or polyaluminum chloride (PACl), have also been widely used as coagulants in coagulation–flocculation process to remove P [10–16].

In coagulation/flocculation, the metal salts, when added into water, the metal ion in its structure such as Al^{3+} rapidly undergoes a series of hydrolysis reactions in an uncontrolled manner to form a range of hydrolysic Al species. The hydrolysis Al species help to aggregate various aquatic particles into larger flocs and then these flocs are settled, filtered, and removed from bulk water in subsequent processes. The Al hydrolysic products, but not coagulant itself, are responsible for the coagulation performance [17,18]. Partially hydrolyzed aluminum chloride salts have been developed to afford preformed Al species that are relatively stable after dosing, and thus, their effectiveness can be less influenced by the water quality conditions [19–21]. Ferron assay test has been widely used as a convenient, less time-consuming, and more cost-effective method to classified Al hydrolytic in Al-based coagulants into Al_a (monomer Al), Al_b (polymer Al), and Al_c (high polymer chain and precipitated Al) [22–26]. It has long been known that the Al_b fraction measured by Ferron assay corresponds to Al_{13} measured by Al^{27}NMR [22,27,28]. It is believed that the superior of PACl is due to high positive charge and strong binding ability of preformed Al_{13} (or Al_b), and this Al species was claimed as the most active species responsible for coagulation [29,30]. In coagulation of natural organic matter (NOM) and colloids, PACls with predominant Al_b or Al_{13} have been shown to improve some of the coagulation performance compared with conventional coagulants [31,32]. The role of Al species such as Al_a, Al_b, and Al_c in coagulation of NOM and colloids has also been investigated [33,34]. For the treatment of P in sewage wastewater, results observed by Hatton and Simpson [35] showed that PACl was superior to alum for total phosphorus removal, while dissolved reactive phosphorus removal efficiency was similar. Work conducted by Zouboulis and Traskas [36] resulted in phosphorus removal using PACl was slightly better than using alum as conventional coagulant. On the contrary, many works showed that pre-polymerized salts are less efficient in removing ortho-P [15,16,37,38]. Despite the contradictory, PACl has been widely used to remove P [10–13,39] and most of previous studies aimed to achieve optimum ortho-P concentration in effluents and/or comparison of the performance of metal salts and prepolymerized salts, but a relationship between Al species in coagulants and P removal performance has not been thoroughly considered.

Therefore, this study characterized Al hydrolysic species presenting in Al-based coagulants as Al_a (monomeric species), Al_b (medium polymer species), and Al_c (colloidal or precipitate species) and evaluated the role of the Al species in the treatment of P in wastewater. Jar tests were carried out using alum and $AlCl_3$ as metal salts and PACls with different basicity as prehydrolyzed metal salts, in a coagulation process of secondary sewage effluent. Because formation of Al species after adding Al salts into water should be closely related to basicity of PACl, coagulation pH, and coagulant dose, influences of these factors must also be investigated.

2. Materials and methods

All chemical reagents used were analytically pure chemicals. Deionized water with conductivity lower than $0.5\,\mu S/cm$ was used in preparing all the solutions.

2.1. Raw water

Secondary sewage effluent was used as raw water in the coagulation process. The water was collected from Nambu Sewage Treatment Plant in Busan city, South Korea. The characteristics of wastewater are listed in Table 1.

Table 1
The physicochemical characteristics of secondary sewage effluent

Parameters	Unit	Range
Turbidity	NTU	1.5–2.1
TN	mg/L	16.50–17.3
TP	mg/L	2.10–3.40
pH	–	6.10–7.30
Alkalinity	mg/L as $CaCO_3$	103.90–125.40

2.2. Coagulants

Alum ($(Al_2(SO_4)_3{\cdot}16H_2O$, CAS No. 16828-11-8, Sigma, USA) and aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, CAS No. 7784-13-6, Sigma, USA) were used as "zero basicity" coagulants. Prehydrolyzed PACl solutions with different basicity were synthesized at laboratory according to a procedure described by Kang and co-workers [40]. A predetermined amount of 0.5 M NaOH was slowly added into the solution of 0.2 M $AlCl_3$ in a reactor. A 2-L double-walled acrylic vessel was fitted with an acrylic lid on which five inlets were made, and four baffles were used to the reactor wall. A pH electrode was inserted through one inlet and another one was for an acrylic capillary, through which hydrated high purity N_2 gas was bubbled through the solution to strip off CO_2. Through another port, an acrylic capillary was lowered into the reactor to slowly inject the NaOH solution. The aperture at the tip of the capillary was less than 0.15 mm in diameter to minimize diffusion of the metal solution into the capillary during mixing. A stainless shaft with propeller stirrer was inserted in another port for mixing of solutions. The solution temperature in the reactor was maintained at 20˚C by circulating a temperature-controlled water through the jacket of the reaction vessel. The PACl solutions were aged for 24 h before analyzing of Al species.

2.3. Analytical methods

2.3.1. Ferron assay

Using Ferron method to differentiate Al species in Al-based coagulants was first conducted for more than 20 years, and the work of Parker and Bertsch [22] are most cited. Since then, the method has been developed and modified [24–26]. It has been used as a convenient, less time-consuming, and more cost-effective method compared with NMR analysis method. Based on the kinetic difference of the reactions between the aluminum species and ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid), the hydrolyzed Al species can be divided into Al_a (monomeric species, instantaneous reacted species), Al_b (medium polymer species, reacted less than 120 min), and Al_c (colloidal or solid species, need much more time to react, or does not react at all). A mixed ferron reagent containing 3 mM Ferron ($C_9H_6INO_4S$, CAS no. 547-91-1, Sigma, USA), 0.26 mM 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$, CAS no. 5144-89-8, Sigma, USA), 853 mM Sodium acetate ($C_2H_3O_2Na$, CAS no. 127-09-3, Sigma, USA), 288 mM Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, CAS no. 5470-11-1, Sigma, USA), and 106 mM HCl was first prepared. The mix ferron reagent was prepared frequently such that a 5–7 day aged solution was always available for use. The PACl was diluted to 0.1 M Al just before reacting with the ferron reagent. A volume of 15 μL of 0.1 M Al coagulant was injected to a colorimetric solution containing (25 mL minus 15 μL) mixed ferron reagent. The selected volume of the PACl sample and the working solution assured the ferron/Al molar ratio kept at value $\geqslant 50$. Reaction time was recorded immediately after adding the Al solution by a stopwatch. After homogeneous mixing, the reacting sample was quickly added to a 1-cm glass cell of a Shimadzu UV-1650 PC spectrophotometer, and time absorbance measurements at 370 nm were automatically recorded for every 10 s during 2 h. A standard Al concentration/absorbance equation was obtained by conducting experiments with a series of different Al concentrations diluted from Al monomer standard solution (1,000 mg/L in 0.2 M HNO_3, Kanto Chemical Co., Inc. (Tokyo, Japan)). It is noted that the blank for the spectrophotometric measure was solution of mixed ferron reagent. Absorbance/time data were fitted to a binary pseudo-first-order rate equation, and the quantitative calculation of Al species was made using model fitted parameters.

2.3.2. Phosphorus analyses

All phosphorus (P) analysis was completed immediately after sample collection. All glass containers were acid-washed before use, and the membrane filters were soaked in distilled water for 24 h prior to use. Total P (TP) was oxidized using the Persulfate Digestion Method adopted from Standard Methods [41], and the released orthophosphate ion (PO_4^{3-}) from the oxidation was measured according to the ascorbic acid method [41]. Ascorbic acid (CAS No. 50-81-7, Sigma, USA), ammonium molybdate (CAS No. 13106-76-8, Sigma, USA), and antimony potassium tartrate ($K(SbO)C_4H_4O_6{\cdot}0.5H_2O$, CAS No. 28300-74-5, Sigma, USA) were used for color development. The ortho-P concentration was determined by a Shimadzu UV-1650 PC spectrophotometer based on a calibration curve between absorbance measured at 880 nm and a series of standard P concentration. Dissolved phosphorus (DP) as TP was filtered through 0.45-μm membrane (Millipore) and dissolved reactive phosphorus (DRP, dissolved ortho-P) as DP was measured directly without digestion as determined by the ascorbic acid method.

2.4. Jar tests

Jar tests was carried out using 2-L square jars with six paddle stirrers (Phipps and Bird) to perform the coagulation/flocculation process. The time and speed for rapid and slow mixing were set with an automatic controller. Samples were mixed at 250 rpm ($G = 550\,s^{-1}$) for 1 min after coagulant addition to provide rapid mixing, and then, the speed was reduced to 30 rpm ($G = 22\,s^{-1}$) for 30 min to provide flocculation. Coagulation pH was adjusted (if needed) by adding 0.1 M HCl or 0.1 M NaOH, just before dosing of the coagulants. After 30 min of settling, the supernatant from each jar was withdrawn from a sampling port and analyzed for pH and residual phosphorus.

3. Results and discussion

3.1. Aluminum species analysis

The Ferron assay test was used to analyze the distribution of Al species, and the results are listed in Table 2. As shown in the table, the basicity of PACl is expressed as r value ($r = [OH]/[Al]$) which is the molar ratio of hydroxide bound to metal ion. The higher the basicity of PACl, the lower the Al_a, higher the Al_b and higher the Al_c. Alum and $AlCl_3$ (as PACl with $r = 0$) have highest amount of Al_a. At r values > 2.5, precipitates appeared in PACl solution resulted in a quickly increase in Al_c and decrease in Al_b (data not shown).

3.2. Phosphorus removal by coagulation

3.2.1. Effects of coagulation pH

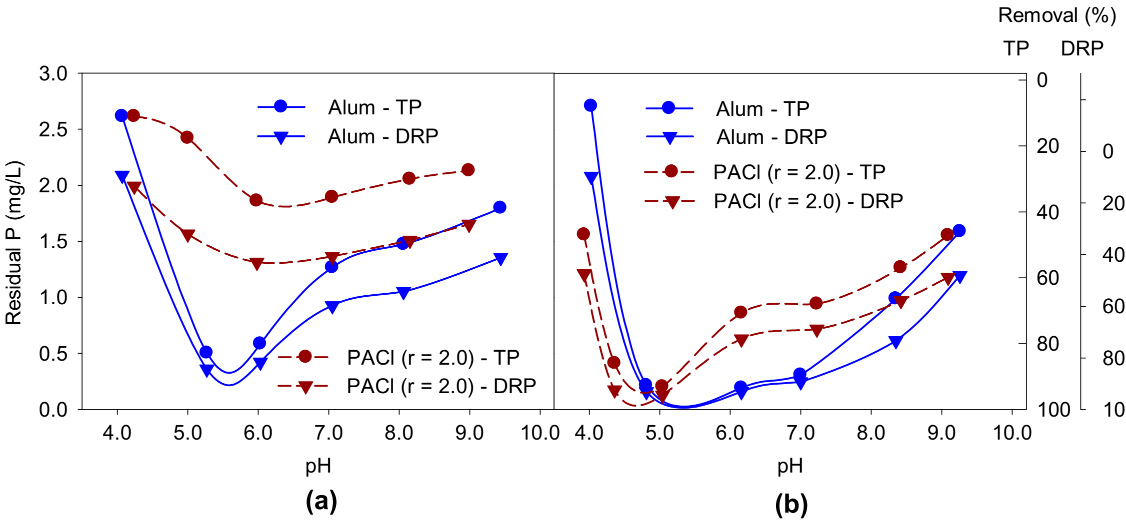
Jar tests were performed using alum and PACl ($r = 2.0$) to investigate effect of coagulation pH on P removal. The experiments were carried out at the two coagulant dosages which is predetermined from preliminary experiments: [Al]:[P] (the mol ratio of Al to TP in raw water) = 1.0:1.0 and 1.8:1.0. As shown in Fig. 1, patterns of TP and DRP removal were similar. In other words, pH affected the removal of TP and DRP in a similar way. However, coagulation removed DRP better than other P fractions. This can be seen by higher % removal of DRP compared with % removal of TP at same pH values.

As previous shown in Fig. 1, under the investigated pH range, the alum showed a narrower pH range from 5.0 to 6.0 for optimal P removal at [Al]:[P] = 1.0:1.0. As the alum dosage increased, that is, at [Al]:[P] = 1.8:1.0, the optimum pH range widened to the direction of higher pH. The PACl, however, behaved in a different manner to alum. The optimum pH range using PACl at [Al]:[P] = 1.0:1.0 was rather wide, while the range for a [Al]:[P] = 1.8:1.0 was narrower. A maximum of 40% DRP removal with PACl was obtained in comparison with higher than 90% DRP removal in case of using alum. With increasing the Al:P mole ratio to 1.0:1.8, the P removal efficiency also increased and at optimum pH of 4.7, P removal efficiency for PACl was comparable to alum.

Coagulation removes P by transformation dissolved and fine colloidal phosphorus into particulate form followed by solids separation process of P-containing particles, such as sedimentation and filtration. The mechanisms involved can be summarized: (a) Chemical precipitation: depends on the solubility of the various complexes formed in water. As can be

Table 2
Characteristics and distribution of Al species in coagulants

Coagulant	Al_2O_3 (%)	r [OH]/[Al]	Basicity (%)	pH	Density (g/L)	Al_a (%)	Al_b (%)	Al_c (%)
Alum	0.15	0.0	0.0	3.07	1085.5	88.1	11.9	0.0
PACl ($r = 0.0$)	1.02	0.0	0.0	3.05	1023.8	97.0	0.0	3.0
PACl ($r = 0.5$)	0.85	0.5	16.7	3.52	1017.0	78.9	18.8	2.3
PACl ($r = 1.0$)	0.73	1.0	33.3	3.64	1020.2	69.4	26.9	3.7
PACl ($r = 1.5$)	0.64	1.5	50.0	3.83	1024.1	56.3	38.3	5.5
PACl ($r = 2.0$)	0.57	2.0	66.7	4.04	1020.5	34.6	53.4	11.9
PACl ($r = 2.5$)	0.51	2.5	83.3	4.55	1025.5	12.5	72.9	14.7



(a)

(b)

Fig. 1. Effects of coagulation pH on P removal at [Al]/[P] of (a) 1.0:1.0 and (b) 1.8:1.0.

seen in Fig. 2, phosphates can be removed by the formation of the $AlPO_4$ precipitate in a wide pH range of 4–7; (b) Formation of Al–hydroxo–phosphate complexes: $Al(OH)_{3-x}(PO_4)_x$. These complexes either adsorb onto positively charged Al hydrolysis species or act as centers of precipitation for Al hydrolysis products; (c) Selective adsorption of phosphates onto freshly precipitated metal–hydroxo complex surfaces. In the case of using conventional coagulants such as alum, amorphous $Al(OH)_3$ is the predominant hydrolysis species in water treatment practice. If prepolymerized inorganic coagulant such as PACl is used, polymeric species are predominant, and PO_4 ions may also complex with the positive sites of such species; and (d) Destabilization of negatively charged P containing colloids by positively charged polynuclear metal–hydroxo complexes and agglomeration to separable flocs by flocculation. These mechanisms are not independent of each other and take place simultaneously when Al coagulants are added into wastewater. Predominant mechanism is determined by amount and type of Al species and P species presenting in solution after adding coagulants and these species are strongly dependent on coagulation pH.

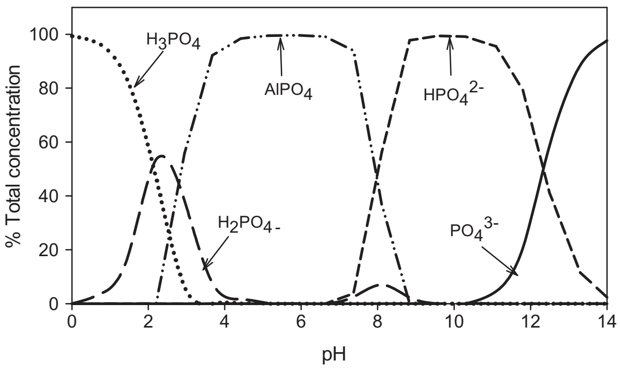


Fig. 2. Phosphate speciation diagram using MineQL$^+$ program (thermochemical data at 25˚C, 1 atm; without crystalline solids and ionic strength corrections; 2.9 mgP/L) in the presence of Al species at [Al]/[P] ratio of 10:1.0.

The PACl showed lower P removal than alum and it can be explained by the difference in formed Al species in bulk solution between alum and PACl: predominant monomeric Al_a in alum versus predominant polymeric Al_b in PACl. As can be seen in Fig. 3, at low pHs (<6), both mono- and polynuclear Al species exist but monomeric Al species with less OH^- in their formula are more effective than polynuclear Al species in forming complexes $Al(PO_4)_x(OH)_{3-3x}$. At high pHs, $Al(OH)_3$ precipitate is formed and adsorption of P onto the precipitate was predominant mechanism. However, Al_b species in PACl was stable with hydrolysis, and $Al(OH)_3$ was hardly formed. Therefore, adsorption mechanism was probably not effective.

The P removal by complexing of Al–hydroxo–phosphate can occur as a result of the competitive action of phosphates, hydroxyls and other ions to react with aluminum ion. The optimum pH is the one where the phosphorus fraction in the complexes is largest. The increase of aluminum dosage may give

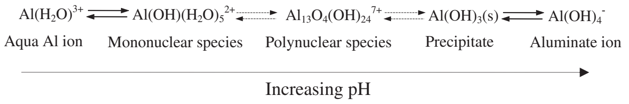


Fig. 3. Aluminum hydrolysis products (the dash lines are used to denote an unknown sequence of reactions).

more opportunities for PO_4^{3-} to complex with Al ion, thus increased formation of metal–hydroxide–phosphate complexes. In addition, the acceptability of higher pH values at high Al dosages for optimal P removal suggests a shift in the predominant removal mechanisms, with an increasing influence of P adsorption to the hydroxide complexes, in addition to the complexation.

Using PACl, as the dosage increased to [Al]:[P] = 1.8:1.0, the highest P removal occurred within a tight pH range of 4.3−5.0 and in this range, the P removal efficiency was comparable to alum as previous shown in Fig. 1. However, obtaining the optimal P removal efficiency at this pH range should be infeasible in real application. Lower or higher pH values beyond this range quickly worsened the P removal.

The findings in this study demonstrated an optimum pH range from 4.5 to 6.5, depends on the coagulant dosages and the coagulant type used. The optimum pH for P removal using aluminum coagulants is normally within the range 5.5–6.5, although some removal occurs above pH 6 [42,43]. The differences are probably due to difference in wastewater quality.

3.2.2. *Effects of coagulant basicity*

Fig. 4(a) and (b) shows the results of using various PACls with different *r* values in coagulation of TP and DRP, respectively. Again, coagulation pattern of the two forms of P was similar. Measuring TP requires time to oxidize other P forms to release ortho-P as reactive P and the reactive P is subsequently detected by a colorimetric method. For convenience, DRP can be used as a simple index to evaluate P removal performance of a coagulant.

As previous shown in Fig. 4, the higher the *r* value, the lower the P removal efficiency. Considering the distribution of Al species as previous shown in Table 2, Al_a species decrease, whereas Al_b and Al_c increase along with increase in *r* values. Decrease in Al_a was probably not favorable for P removal. Although increasing of Al_b and Al_c by increasing *r* value reduced P removal efficiency, it is unlikely that P removal efficiency was strongly affected by Al_b and Al_c. The most effective species in P removal should be Al_a, and the higher the Al_a in coagulants, the higher the P removal they showed.

Theoretically, phosphates can be removed completely by formation of the $AlPO_4$ precipitate at [Al]/[P] ratio of 10:1.0 as previous mentioned in the phosphate speciation diagram (Fig. 2). However, in practical treatment, to obtain an efficient P removal, the required Al dosage significantly exceeded the theoretical demand. 93.5% DRP was removed at [Al]:[P] ratio of 1.8:1.0 as shown in Fig. 4(b). P removal may be related more to other mechanisms rather than precipitating with Al as $AlPO_4$. Quickly hydrolysis of Al^{3+} formed a range of hydrolysis species, and ultimately, metal hydroxide. Therefore, Al^{3+} ion hardly existed in solution and the $AlPO_4$ (s) might not form or only form to a limited extent. In addition, the formed coagulating species destabilize the other contaminants present in the wastewater, and these competing reactions also increase the amount of Al coagulants required to remove P.

With respect to formation of aluminum–phosphate–hydroxo complexes $Al(PO_4)_x(OH)_{3-3x}$, hydroxyl

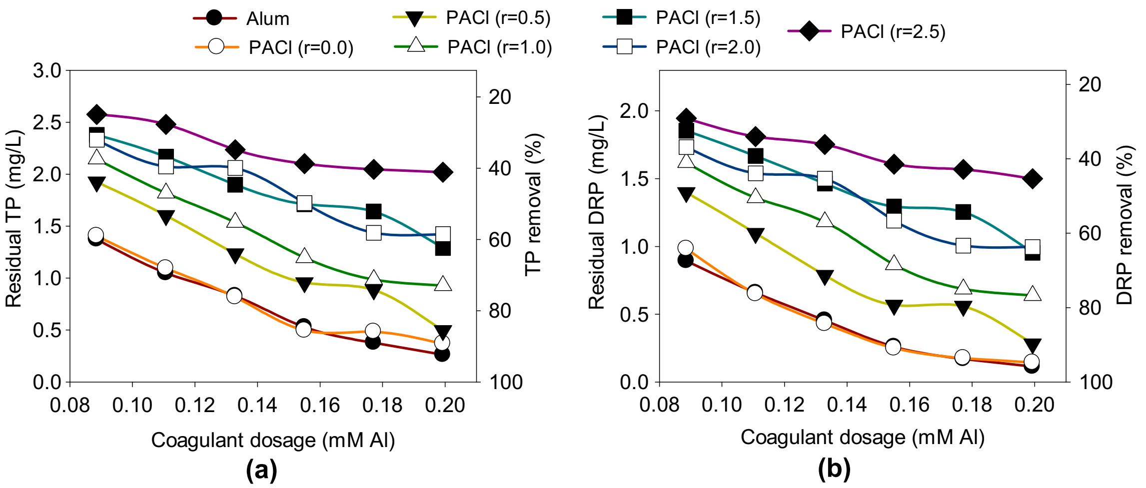


Fig. 4. (a) TP and (b) DRP removal using different PACls (the dosages as Al/P at 6 experimental points are 0.8:1.0, 1.0:1.0, 1.2:1.0, 1.4:1.0, 1.6:1.0, and 1.8:1.0, respectively).

ion (OH^-) is the strongest competitor in the complexes precipitation. Adding OH^- to coagulants reduces the P removal efficiency [8]. Therefore, high OH/Al ratio coagulants are less effective than lower OH/Al ratio coagulants. In other words, since Al_b and Al_c species in the prehydrolyzed Al coagulant possess more OH^- in their formulae, for example $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and $AlO_4Al_{28}(OH)_{56}(H_2O)_{26}^{18+}$, they were not effective in precipitating P.

Dissolved polynuclear Al_b is well known as the most efficient Al species for destabilizing colloids due to their high stable and positively charged species [36,44]. Although a low turbidity and low suspended P content of the raw wastewater in the study made it unclear to conclude, it is possible that Al_b could be responsible for the removal of suspended P in a high turbidity wastewater.

Adsorption mechanism that involves in the PO_4 sorption onto $Al(OH)_3(s)$, has also been strongly suggested as primary mechanism for P removal [45] and a range of studies showed that at low phosphate concentrations (1–5 mg/L), phosphate is removed largely by the adsorption onto formed $Al(OH)_3$ flocs [8,46]. The phosphate concentration in the secondary effluent used in this study was relatively low (average 3.43 mg/L) and the coagulation pH range of 6.0–6.7 was considered to be favorable for the formation of $Al(OH)_3(s)$. Therefore, adsorption of phosphates onto $Al(OH)_3(s)$ played an important role in the study, especially at high dosages of coagulants used. Since monomeric Al_a is the most unstable species after dosing, it would quickly hydrolyzed to form hydrolyzed species (in competition between PO_4 and OH^-) and finally $Al(OH)_3(s)$ (if a large enough amount of Al dosage is applied). With respect to the adsorption of phosphates onto $Al(OH)_3(s)$, Al_b in PACl is also not superior to Al_a because polymeric Al_b species are relatively stable and resistant to hydrolysis. They remain for a greater duration in solution and hydroxide precipitates is formed slowly.

4. Conclusions

The optimum pH for P removal was in the range of 5.0–6.6 for alum and a narrow optimum range of 4.5–5.5 was observed for PACl. At high metal dose, the optimum pH range tended to widen toward higher pH values.

Phosphorus removal efficiencies correlate well with the distribution of Al species in PACl. The removal of phosphorus was mainly attributed to Al_a due to high ability of forming the precipitated complexes $Al(OH)_x(PO_4^{3-})_{3-x}$ as well as adsorption of P onto $Al(OH)_3$ precipitate that predominantly formed in hydrolysis of Al_a. Although Al_b or Al_{13} has been known as the most effective species in coagulation, it did not show any superior performance in P removal. More hydroxyl ions in structure of Al_b make it less competitive in forming $Al(OH)_x(PO_4^{3-})_{3-x}$ complexes. In addition, because Al_b is relative stable to hydrolysis, forming $Al(OH)_3$ precipitate (Al_c) is limit, and therefore, adsorption was less effective. Al_c may promote adsorption mechanisms, but with small amount of them in the PACls in the study, their influence on P removal was not a consideration.

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References

[1] S.E. Manahan, Fundamentals of Environmental Chemistry, Lewis, Boca Raton, FL, 2001.

[2] NIER, A Manual for Phosphorus Control, Korea National Institue of Environmental Research, Seoul, 2010.

[3] USEPA, Integrated Water Quality Monitoring and Assessment Report Guidance Memorandum November 19, 2001, in, 2001.

[4] Council of the European Communities Directive concerning the collection, treatment and discharge of urban wastewater and the discharge of wastewater from certain industrial sectors (91/271/EEC), Official J. L 135 (1991) 40–52.

[5] Y. Yao, B. Gao, M. Inyang, A.R. Zimmerman, X. Cao, P. Pullammanappallil, L. Yang, Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings, J. Hazard. Mater. 190 (2011) 501–507.

[6] T. Clark, T. Stephenson, P.A. Pearce, Phosphorus removal by chemical precipitation in a biological aerated filter, Water Res. 31 (1997) 2557–2563.

[7] S. Vasudevan, J. Lakshmi, G. Sozhan, Optimization of the process parameters for the removal of phosphate from drinking water by electrocoagulation, Desalin. Water Treat. 12 (2009) 407–414.

[8] M. Özacar, İ.A. Şengil, Effect of tannins on phosphate removal using alum, Turk. J. Eng. Environ. Sci. 27 (2003) 227–236.

[9] K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, J. Hazard. Mater. 139 (2007) 447–452.

[10] J.Q. Jiang, N.J.D. Graham, Pre-polymerised inorganic coagulants and phosphorus removal by coagulation—a review, Water SA 24 (1998) 237–244.

[11] A.I. Omoike, G.W. Van Loon, Removal of phosphorus and organic matter by alum during wastewater treatment, Water Res. 33 (1999) 3617–3627.

[12] J.M. Ebeling, P.L. Sibrell, S. Ogden, S.T. Summerfelt, Evaluation of chemical coagulation-flocculation aids for the removal of phosphorus from recirculating aquaculture effluent, Aquacult. Eng. 29 (2003) 23–42.

[13] F. Auvray, E.D. van Hullebusch, V. Deluchat, M. Baudu, Laboratory investigation of the phosphorus removal (SRP and TP) from eutrophic lake water treated with aluminium, Water Res. 40 (2006) 2713–2719.

[14] J. Kim, Q. Deng, M.M. Benjamin, Simultaneous removal of phosphorus and foulants in a hybrid coagulation/membrane filtration system, Water Res. 42 (2008) 2017–2024.

[15] L. Gillberg, D. Nilsson, M. Akesson, The influence of pH when precipitating orthophosphate with aluminum and iron salts, In: H.H. Hahn, E. Hoffmann, H. Ødegaard (Eds), Chemical Water and Wastewater Treatment IV – Proceedings of the 7th Gothenburg Symposium Edinburgh, Springer, New York, NY, 1996, pp. 95–105.

[16] H.C. Ratnaweera, H. Ødegaard, J. Fettig, Coagulation with prepolymerised aluminium salts and their influence on particle and phosphate removal, Water Sci. Technol. 26 (1992) 1229–1237.

[17] J.Q. Jiang, Development of coagulation theory and pre-polymerized coagulants for water treatment, Sep. Purif. Methods 30 (2001) 127–141.

[18] B. Shi, Q. Wei, D. Wang, Z. Zhu, H. Tang, Coagulation of humic acid: The performance of preformed and non-preformed Al species, Colloid Surf. A 296 (2007) 141–148.

[19] K. McCurdy, K. Carlson, D. Gregory, Floc morphology and cyclic shearing recovery: Comparison of alum and polyaluminum chloride coagulants, Water Res. 38 (2004) 486–494.

[20] C.Z. Hu, H.J. Liu, J.H. Qu, D.S. Wang, J. Ru, Coagulation behavior of aluminum salts in eutrophic water: Significance of Al-13 species and pH control, Env. Sci. Technol. 40 (2006) 325–331.

[21] P.M. Bertsch, D.R. Parker, Aqueous polynuclear aluminum species, In: G. Sposito (Ed), The Environmental Chemistry of Aluminum, CRC Press, Boca Raton, FL, pp. 117–168, 1996.

[22] D.R. Parker, P.M. Bertsch, Identification and quantification of the “Al13” tridecameric aluminum polycation using ferron, Env. Sci. Technol. 26 (1992) 908–914.

[23] P.M. Jardine, L.W. Zelazny, Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with ferron, Soil Sci. Soc. Am. J. 50 (1986) 895–900.

[24] D. Wang, W. Sun, Y. Xu, H. Tang, J. Gregory, Speciation stability of inorganic polymer flocculant–PACl, Colloid Surf. A 243 (2004) 1–10.

[25] J.-L. Lin, C. Huang, C.-J.M. Chin, J.R. Pan, The origin of Al (OH)3-rich and Al13-aggregate flocs composition in PACl coagulation, Water Res. 43 (2009) 4285–4295.

[26] Z. Bi, C. Feng, D. Wang, X. Ge, H. Tang, Transformation of planar Mögel Al13 to epsilon Keggin Al13 in dissolution process, Colloid Surf. A 407 (2012) 91–98.

[27] C. Feng, B. Shi, D. Wang, G. Li, H. Tang, Characteristics of simplified ferron colorimetric solution and its application in hydroxy-aluminum speciation, Colloid Surf. A 287 (2006) 203–211.

[28] C. Ye, D. Wang, X. Wu, J. Qu, K-Value-based ferron assay and its application, J. Colloid Interface Sci. 335 (2009) 44–49.

[29] J.M. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[30] J.E. Van Benschoten, J.K. Edzwald, Chemical aspect of coagulation using aluminum salts-I: Hydrolytic reactions of alum and polyaluminum chloride, Water Res. 24 (1990) 1519–1526.

[31] J.K. Edzwald, Coagulation in drinkingwater treatment—particles, organics and coagulants, Water Sci. Technol. 27 (1993) 21–35.

[32] Y. Matsui, A. Yuasa, Y. Furaya, T. Kamei, Dynamic analysis of coagulation with alum and PACl, J. Am. Water Works Assn. 90 (1998) 96–106.

[33] H. Zhao, C.Z. Hu, H.J. Liu, X. Zhao, J.H. Qu, Role of aluminum speciation in the removal of disinfection byproduct precursors by a coagulation process, Env. Sci. Technol. 42 (2008) 5752–5758.

[34] H. Liu, C. Hu, H. Zhao, J. Qu, Coagulation of humic acid by PACl with high content of Al13: The role of aluminum speciation, Sep. Purif. Technol. 70 (2009) 225–230.

[35] W. Hatton, A.M. Simpson, Use of alternative aluminium based chemicals in coagulation with particular reference to phosphorus removal, Environ. Technol. Lett. 6 (1985) 225–230.

[36] A.I. Zouboulis, G. Traskas, Comparable evaluation of various commercially available aluminium-based coagulants for the treatment of surface water and for the post-treatment of urban wastewater, J. Chem. Technol. Biotechnol. 80 (2005) 1136–1147.

[37] X. Zheng, S. Plume, M. Ernst, J.-P. Croué, M. Jekel, In-line coagulation prior to UF of treated domestic wastewater—foulants removal, fouling control and phosphorus removal, J. Membr. Sci. 403–404 (2012) 129–139.

[38] J. Fettig, H.C. Ratnaweera, H. Ødegaard, Simultaneous Phosphate Precipitation and Particle Destabilization using Aluminium Coagulants of Different Basicity, Springer, Berlin, 1990.

[39] F. Ni, X. Peng, Y. Zhao, J. He, Y. Li, Z. Luan, Preparation of coagulant from red mud and semi-product of polyaluminum chloride for removal of phosphate from water, Desalin. Water Treat. 40 (2012) 153–158.

[40] L.-S. Kang, S.-W. Han, C.-W. Jung, Synthesis and characterization of polymeric inorganic coagulants for water treatment, Korean J. Chem. Eng. 18 (2001) 965–970.

[41] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 2005.

[42] USEPA, Design Manual: Phosphorus Removal, Center for Environmental Res. Information, Cincinnati, OH, 1987.

[43] K. Fytianos, E. Voudrias, N. Raikos, Removal of phosphate from aqueous and wastewater samples using aluminum salts, J. Environ. Sci. Health A 31 (1996) 2621–2634.

[44] J. Gregory, J. Duan, Hydrolyzing metal salts as coagulants, Pure Appl. Chem. 73 (2001) 2017–2026.

[45] E. Galarneau, R. Gehr, Phosphorus removal from wastewaters: Experimental and theoretical support for alternative mechanisms, Water Res. 31 (1997) 328–338.

[46] J.P. Boisvert, T.C. To, A. Berrak, C. Jolicoeur, Phosphate adsorption in flocculation processes of aluminium sulphate and poly-aluminium-silicate-sulphate, Water Res. 31 (1997) 1939–1946.