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Preparation of coagulant from red mud and semi-product of polyaluminum chloride for removal of phosphate from water

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ABSTRACT

Traditionally, calcium aluminate, caustic soda, lime or aluminum slag was employed as alkali for basicity adjustment in the production of polyaluminum chloride (PACl). In this work, red mud (RM), a highly alkaline waste from alumina industry, was utilized instead of the traditional alkali. A composite coagulant (RMPACl) was prepared from RM and the semi-product of polyaluminum chloride (ACl). Important factors for preparation, such as RM/ACl ratio, reaction temperature and reaction time, were investigated and optimized to be as follows: RM/ACl ratio of 0.25 (w v^{-1}), reaction temperature of 80°C and reaction time of 4 h. The results of coagulation tests showed that RMPACl exhibited better performance than PACl for removal of phosphate. The optimum coagulation pH range of RMPACl was found to be 6.0–8.5. High phosphate removal efficiency (>94.9%) was achieved by dosing RMPACl at the dosage of 147.5 mg l^{-1}. Therefore, RMPACl was considered as a low-cost coagulant, which possessed a good coagulation performance for removal of phosphate.

Keywords: Alkalinity; Composite coagulant; Red mud; Semi-product of polyaluminum chloride; Basicity; Phosphate removal

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1. Introduction

Red mud (RM), composed of aluminum oxide, iron oxide, silicon dioxide, and calcium oxide is a highly alkaline waste generated in the production of aluminum [1]. The manufacture of 1 ton of alumina generally results in the production of 1.0–1.5 tons of RM. As digested in the caustic solution of soda, RM carries with high alkali. It is reported that up to 2 tons of liquor at 5–20 g l^{-1} caustic (as Na_2CO_3) accompanied with every ton of dry mud solids [2]. Each year, about 90 million tons of RM is produced worldwide and 10–20 million tons of caustic RM must be disposed of annually in China [3,4]. RM is usually discharged into storage impoundments. Environmental pollution has occurred near the impoundments include the leakage of alkaline leachate into the ground water, erosion of RM and discharge into nearby surface waters. As a result, final disposal of RM faces a huge challenge due to its high alkalinity and large amount. In previous studies, RM has been used for preparation of adsorbents [5–11], coagulants [12–15], catalysts [16]. However, there has been little report on the utilization of the alkali in RM for the preparation of coagulants.

Traditionally, a two-step process is employed in the production of polyaluminum chloride (PACl). In the first step, aluminum hydroxide is digested with hydrochloric acid and the semi-product of polyaluminum chloride (ACl) is obtained. In the second step, calcium aluminate,

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caustic soda, lime or aluminum slag is dosed into ACl in order to adjust the basicity and final product of PACl with basicity of 30%–95% is produced. The increase of basicity not only reduces the corrosivity of the coagulant, prevents the water from decreasing of pH, but also enhances the polymerization extent of the coagulant, and thus the coagulation performance. Reactions of the production are as follows:

$$Al(OH)_3 + HCl = Al(OH)_2Cl + H_2O \tag{1}$$

$$2Al(OH)_2Cl + HCl = Al_2(OH)_3Cl_3 + H_2O \tag{2}$$

$$Al_2(OH)_3Cl_3{}^{®}[Al_2(OH)_nCl_{6-n}]_m \; m < 10 \tag{3}$$

Since RM is an industrial waste with high alkali, it would be cost-effective to employ RM in the preparation of coagulant. Three benefits are achieved by employing RM: (1) The alkali in RM can be utilized for basicity adjustment; (2) Dissolved metals from RM can increase the content of the coagulant; (3) Residual RM particles can serve as nucleus for coagulation. In this investigation, RM composite coagulant (RMPACl) was prepared from RM and the ACl. The purpose of this work is to examine the feasibility of employing RM as alkali for basicity adjustment in the preparation of RMPACl. The effect of important factors for preparation, such as RM/ACl ratio, reaction temperatures and reaction time, on phosphate removal efficiency and basicity of the coagulant was investigated in order to determine the optimal preparation conditions. Coagulation performance of RMPACl in terms of phosphate removal efficiency was also investigated and compared with that of PACl.

2. Materials and methods

2.1. Materials

Industrial ACl (Al_2O_3% = 13.6, basicity = 2.0%) and PACl (Al_2O_3% = 10.0, basicity = 76.3%) were obtained from Tianjin Dagang Flocculants Corporation, China. RM (Al_2O_3% = 37.6, Fe_2O_3% = 29.2, SiO_2% = 21.3, CaO + MgO% = 6.3%) was obtained from Shandong Aluminum Corporation, China.

2.2. Preparation of RMPACl

The preparation of RMPACl was carried out in a bench scale using a flask, which was placed in an electric heat constant water bath. Prescribed amount of RM was added to an aliquot of 100 ml of ACl under stirring (250 rpm). Preparation conditions, such as RM/ACl ratio (w/v), reaction temperature and reaction time were varied from 0.1 to 0.5, 25°C to 100°C and 0.5 to 4.0 h, respectively. Finally, RM and ACl mixture was cooled down to room temperature naturally and the composite coagulant RMPACl was prepared. The optimum preparation conditions were determined according to phosphate removal efficiency of the prepared coagulants.

2.3. Analytical methods

Basicity value, defined as Eq. (4), was determined by titrimetric method (standard method of the chemical industry of China).

$$B = \frac{[OH]}{3[Al]} \times 100(\%) \tag{4}$$

Residual RM remained in RMPACl was separated by centrifugation, washed with deionized water for three times and dried in an oven. The specific surface area of residual RM was determined by the N_2 adsorption-desorption at 77 K using an accelerated surface area and porosimetry (Micromeritics ASAP 2000).

2.4. Phosphate removal experiments

Coagulation tests were conducted to investigate the performance of the prepared coagulants and 200 ml solution of KH_2PO_4 was employed in the investigation. All coagulation tests were conducted using a six-jar tester (JTY-6 Laboratory Stirrer) at room temperature. The jar test procedure was as follows: rapid stirring at 200 rpm for 3 min, followed by slow stirring at 70 rpm for 15 min and sedimentation for 30 min. The effect of pH, initial phosphate concentration, coagulant dosage and settling time on phosphate removal efficiency was studied. The coagulant dosage expressed in mg l^{-1} referred to the dry weight of coagulants. The pH was adjusted to prescribed values using 1 mol l^{-1} HCl or NaOH after the coagulant was dosed. The settling time was determined by measuring interface height of the clarification zone of the coagulated suspensions at specified time intervals after slow stirring ceased [17]. After sedimentation, an aliquot of supernatant sample was withdrawn at 1 cm below the liquid surface. The sample was directly used for zeta potential measurements using a Malvern Zetasizer 2000 (Malvern Co., United Kingdom). The phosphate concentration of the sample was measured using the ascorbic acid method with a spectrophotometer (HACH DR-5000) according to APHA standard method [18]. The phosphate removal efficiency (η,%) was calculated according to Eq. (5):

$$\eta = \frac{(C_i - C_e)}{C_i} \times 100(\%) \tag{5}$$

where C_i is the initial phosphate concentration (mg l^{-1}), C_e is the phosphate concentration of the supernatant samples (mg l^{-1}).

3. Results and discussion

3.1. Preparation of RMPACl

3.1.1. Effect of RM/ACl ratio

The effect of RM/ACl ratio (w/v) on phosphate removal efficiency and basicity of the coagulant was shown in Fig. 1. It was indicated that RM effectively adjusted basicity. Basicity value increased from 2.1% to 77.3% as RM/ACl ratio increased from 0 to 0.5. Phosphate removal efficiency increased with the increase in RM/ACl ratio (from 0 to 0.25), and then decreased when RM/ACl ratio was higher than 0.25. The maximum phosphate removal efficiency was obtained when RM/ACl ratio was 0.25.

Generally, basicity and dissolved metal content increased with the increase in RM/ACl ratio, resulted in an increase of polymerization extent and coagulation performance of the coagulant. Phosphate removal efficiency increased with the increase in RM/ACl ratio (from 0 to 0.25). However, if RM/ACl ratio continuously increased, basicity of the coagulant would further increased, the metals such as Al^{3+} and Fe^{3+} might easily hydrolyzed and precipitated, leading to a decrease of the metal content of the coagulant, and thus a decrease in coagulation performance [15,19]. The RM/ACl ratio (w/v) of 0.25 was determined as the optimum ratio for further investigations.

3.1.2. Effect of reaction time

The effect of reaction time was investigated and the results were shown in Fig. 2. Basicity rapidly increased to 32.3% within 1 h reaction and remained steadily around 33% after 2.5 h reaction. Similarly, phosphate removal efficiency rapidly increased from 90.4% to 93.1% within 1 h reaction, and then slowly increased from 93.1% to 94.9% with the increase in reaction time. The increase of reaction time resulted in an increase in basicity and the metal content of the coagulant. Thus, phosphate removal efficiency slowly increased with the increase of reaction time. The longer the reaction time, the higher the utilization of RM. Four hour reaction time was determined for further investigations.

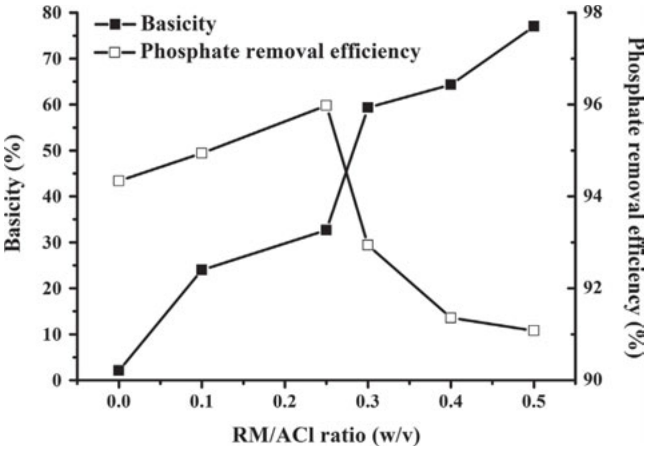

Fig. 1. Effect of RM/ACl ratio on basicity and phosphate removal efficiency.

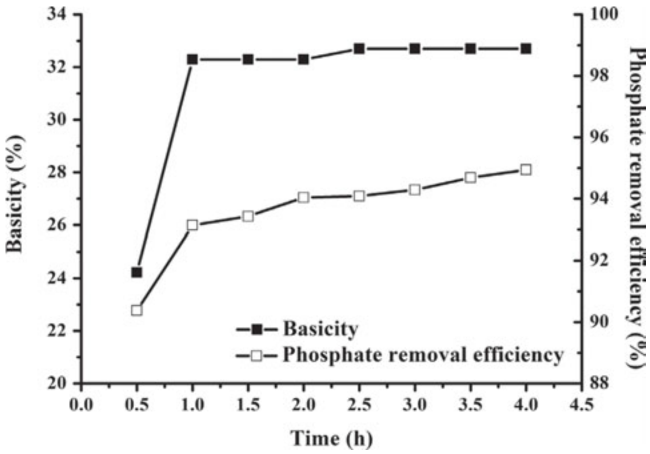

Fig. 2. Effect of reaction time on basicity and phosphate removal efficiency.

3.1.3. Effect of reaction temperature

The effect of reaction temperature was investigated and the results were shown in Fig. 3. Basicity increased from 24.1% to 33.2% with the increase in reaction temperature (from 25°C to 100°C). The removal of phosphate

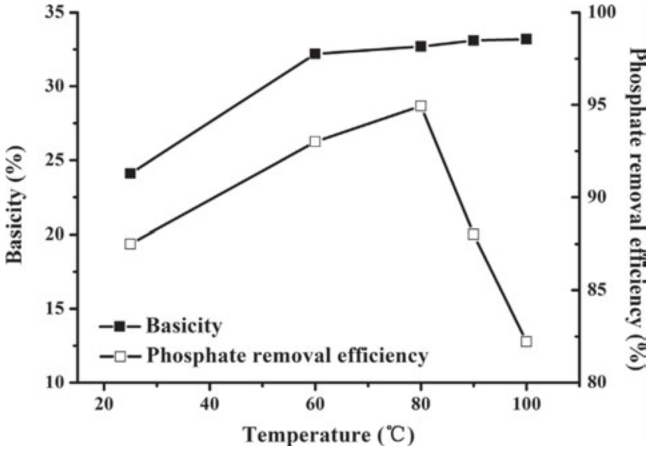

Fig. 3. Effect of reaction temperature on basicity and phosphate removal efficiency.

increased (from 87.5% to 94.9%) with the increase in reaction temperature (from 25°C to 80°C), and decreased when reaction temperature was higher than 80°C. The maximum phosphate removal efficiency was obtained at reaction temperature of 80°C. Reaction temperature greatly affected the dissolution of metals from RM to ACl. It was suggested that the higher the reaction temperature, the higher the reaction extent between RM and ACl. However, if reaction temperature continuously increased (higher than 80°C), residual RM particles became even smaller. The appearance of RMPACl was viscous. Metals easily hydrolyzed and precipitated, resulted in a decrease of phosphate removal efficiency [19]. 80°C was considered as the optimum reaction temperature for further investigation.

Additionally, the effect of calcination treatment on RM at different temperatures (100°C, 300°C, 500°C, 700°C) was also carried out before RM was reacted with ACl. Calcination treatment on RM could dehydrate the residual water in the capillary of RM, thus more RM and alkali was applied in the preparation of the coagulant. Results showed that basicity increased when RM went through calcination treatment. Basicity slightly decreased when calcination temperature was higher than 300°C. Calcination of RM seemed to be a proper treatment to increase basicity and activate RM. However, there was no significant increase of phosphate removal efficiency of the prepared coagulant when calcination treatment on RM was carried out (data not shown). Therefore, the effect of calcination treatment on RM was discussed without further consideration in this study.

3.2. *Removal of phosphate*

3.2.1. *Effect of dosage and initial phosphate concentration*

The effect of dosage and initial phosphate concentration was investigated and the results were shown in Fig. 4. Phosphate removal efficiency increased with the increase in dosage of both coagulants. The dosage fundamentally depended on the concentration of phosphate. Higher coagulant dosage was required for removal of phosphate from solution with higher initial phosphate concentration. Phosphate removal efficiency decreased with the increase in initial phosphate concentration at the same dosage of coagulants. At the dosage of 60 mg l^{-1} for RMPACl, phosphate removal efficiency was 97.0% for 1 mg l^{-1} phosphate solution, while the removal efficiency was 75.7% for 5 mg l^{-1} phosphate solution. Accordingly, at the dosage of 87.5 mg l^{-1} for PACl, phosphate removal efficiency was 89.0% and 79.4% for 1 mg l^{-1} and 5 mg l^{-1} phosphate solution, respectively. It was indicated that phosphate removal efficiency of RMPACl was slightly higher than that of PACl. High phosphate removal efficiency (>94.9%) was achieved by dosing RMPACl at the dosage of 147.5 mg l^{-1}. In addition, RMPACl was prepared from RM and ACl, the amount of coagulant dosage saved by having residual RM particles remained in the coagulant. As RM was one kind of industrial waste, RMPACl was considered as a cost-effective coagulant for removal of phosphate.

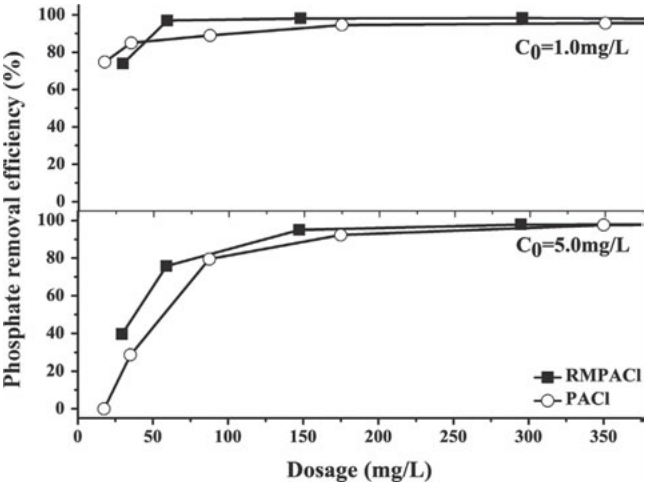

Fig. 4. Effect of dosage and initial phosphate concentration on phosphate removal efficiency (C_0 = 1.0 mg l^{-1} and 5.0 mg l^{-1}, 25°C).

The advantage of RMPACl on the removal of phosphate was not only due the increase of basicity and metal content of the coagulant, but also the adsorption of phosphate on residual RM particles. It was reported that the specific surface area of raw RM was in the range of 10–21 $m^2 g^{-1}$ [20], and in this study, the specific surface area of residual RM separated from RMPACl was 36.9 $m^2 g^{-1}$. The phosphate adsorption capacity of residual RM could be increased with the increase of specific surface area.

3.2.2. *Effect of pH*

In the coagulation process, pH is considered as an important and prerequisite factor. The effect of pH was investigated and the results were shown in Fig. 5. It was suggested that pH had an important effect on phosphate removal efficiency. Under acidic conditions (pH <5.0), phosphate removal efficiencies of RMPACl and PACl were rather low. At the pH range of 5.0–6.0, aluminum salt was rapidly hydrolyzed to form amorphous aluminum hydroxides. Amorphous aluminum hydroxides, which were positively charged colloidal particles, could adsorb phosphate. Phosphate removal efficiency increased significantly during this pH range, which indicated that the formation of amorphous aluminum hydroxide was one of the mechanisms of the coagulation. The optimum coagulation pH range of RMPACl was found to be 6.0–8.5, which was slightly wider than that of PACl (6.0–8.0). Phosphate removal efficiencies all decreased obviously under the alkaline conditions

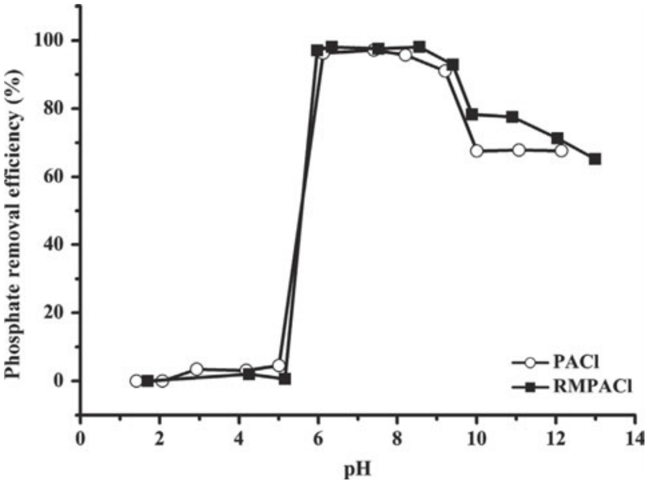

Fig. 5. Effect of pH on phosphate removal efficiency of RMPACl and PACl (C_0= 5.0 mg l^{-1} P, 25°C).

(pH >8.5), which was due to the competition of phosphate and OH^- on the colloidal particles surface. At the pH range of 8.0–12.0, phosphate removal efficiency of RMPACl was slightly higher than that of PACl. It was suggested that the dissolved calcium in RMPACl increased the removal of phosphate at the alkaline pH range [21]. Moreover, residual RM particles, which adsorb phosphate under the alkaline conditions, also improved the removal of phosphate [8,9].

The effect of pH on zeta potentials of RMPACl and PACl was also investigated. As can be seen from Fig. 6, zeta potentials of RMPACl and PACl decreased with increasing pH. Compared with PACl, RMPACl had a high absolute value of zeta potential, which might be due to the relatively low basicity of RMPACl. pHpzc value of the coagulant was between 7.5 and 8.5, which was in agreement with the optimum pH range for removal of phosphate. As pH increased above the pHpzc, zeta potentials of the coagulant became negative, the adsorption of phosphate decreased. The results indicated that charge neutralization was the main mechanism of RMPACl for phosphate removal.

3.2.3. Effect of settling time

In the coagulation process, settling time is important since it influences the overall cost and efficiency of coagulation. Fig. 7 showed the interface height of the clarification zone as a function of settling time. The minimum interface height by dosing RMPACl was obtained for 10 min, while it took 15 min to reach the minimum height by dosing PACl. It was indicated that settling time was short by dosing RMPACl. The effect of settling time was mainly due to the change in floc density. When RMPACl was dosed, aluminum salt was rapidly hydrolyzed to form positively charged amorphous aluminum hydroxides, which could be electrostatically adsorbed on the negatively charged surfaces of residual RM particles. RM-aluminum hydroxides resulted in the formation of dense flocs, thus aluminum hydroxide coated RM particles coagulated and settled quickly [22].

For the prepared coagulant, mechanisms for removal of phosphate could be a combination of coagulation and adsorption. Coagulation generally involved hydrolysis, adsorption, and precipitation processes. When coagulant was dosed into water, aluminum salt rapidly hydrolyzed, formed a range of hydrolysis species, and ultimately, amorphous aluminum hydroxide, which could adsorb phosphate. Phosphate was removed through charge neutralization coagulation [15,23].

The adsorption of phosphate by residual RM was considered as another mechanism. It was reported that

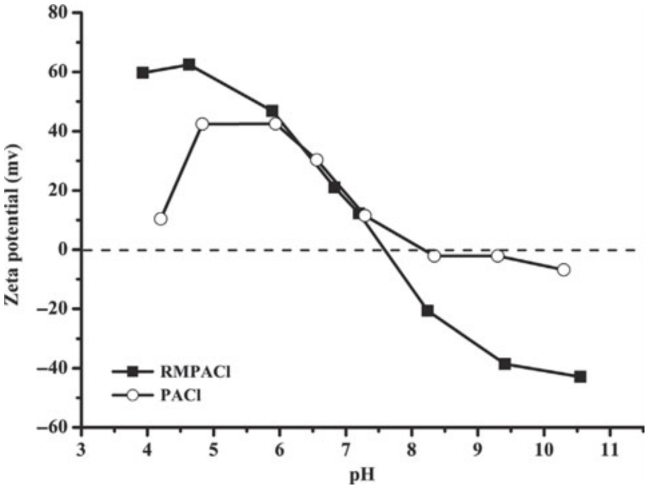

Fig. 6. Effect of pH on zeta potential of RMPACl and PACl (C_0 = 5.0 mg l^{-1} P, 25°C).

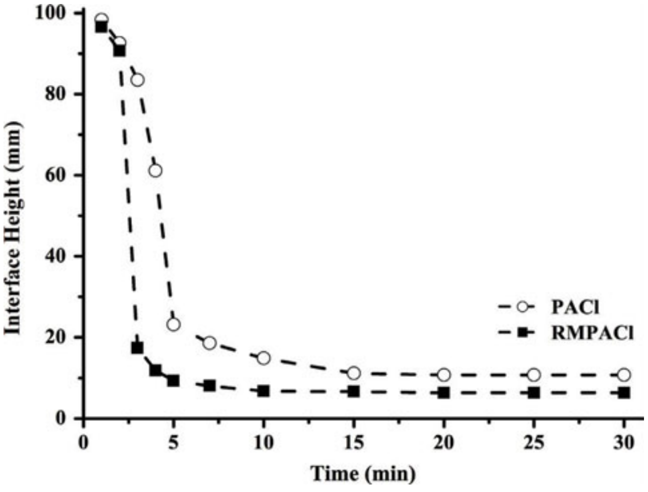

Fig. 7. Effect of time on interface height by dosing RMPACl and PACl (C_0 = 5.0 mg l^{-1} P, 25°C).

RM exhibited certain adsorption of phosphate for its component of metal oxides and specific surface area [8–10]. In this investigation, metal oxides on the surface of RM partially dissolved in acidic ACl. The pore volume and specific surface area of residual RM increased, resulted in an increase in phosphate adsorption capacity [24].

In addition, residual RM acted as seeds to precipitate during coagulation. It was reported that enhancing phosphate removal was obtained by coagulation with PACl and RM [25]. Dosing RM in PACl coagulation enhanced the adsorption of phosphate by flocs, increased the density of flocs, reduced the final volume of sludge. In this study, residual RM of RMPACl increased the particle density of flocs and the probability of collision, enhanced the heterogeneous coagulation, thus resulted in an increase in phosphate removal efficiency.

4. Conclusions

In this study, RMPACl was prepared from RM and ACl for removal of phosphate from water. Experiments were carried out to investigate the effect of RM/ACl ratio, reaction time, and reaction temperature on phosphate removal efficiency and basicity value of the coagulant. The results showed that RM effectively adjusted basicity, which increased from 2.1% to 77.3% as RM/ACl ratio increased from 0 to 0.5. It was indicated that RM could be employed as a low-cost alkali for preparation of coagulants. RMPACl showed better coagulation performance than PACl for removal of phosphate, in terms of optimum pH range, initial phosphate concentration, coagulant dosage, and settling time. Based on the results, it was suggested that RMPACl was considered as a cost-effective coagulant for removal of phosphate.

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Author Disclosure Statement

No competing financial interests exist.

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