

ENHANCING PHOSPHATE REMOVAL BY COAGULATION USING POLYELECTROLYTES AND RED MUD

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ABSTRACT

Phosphate removal by chemical precipitation remains the leading technology today. In this research, phosphate removal using polyaluminium chloride (PAC) alone and in the presence of polydiallyldimethylammonium chloride (PDADMAC) and red mud were investigated. The results showed that PAC was effective in phosphate removal by coagulation via charge neutralization and adsorption of polymeric hydroxyl complexes. For synthetic wastewater, the phosphate removal efficiency reached 94.6% and for raw wastewater, the total phosphorus removal efficiency was as high as 96.6%. PDADMAC was not efficient in removing phosphate when used alone, at dosages of 0.1-0.3 mg/L, and it had little effect on enhancing phosphate removal by PAC as a coagulation aid, even when the dosage of PDADMAC was increased from 0.1 mg/L to 2 mg/L. Red mud, a by-product of bauxite processing in the alumina manufacturing industry, served as “nuclei for coagulation” resulting in large, rapid-settling flocs. When 40 mg/L red mud was added, the phosphate removal efficiency of 3.18, 4.76 and 6.35 mg Al³⁺/L PAC increased by 15.1, 20.5 and 13.0%, respectively. Adsorption and desorption experiments of phosphate on flocs after coagulation showed that the addition of red mud not only decreased the required PAC dosage but also enforced the phosphate adsorption on flocs.

KEYWORDS: phosphate; coagulation; polyaluminium chloride (PAC); red mud; polydiallyldimethylammonium chloride (PDADMAC)

INTRODUCTION

Phosphate removal from wastewater has received considerable attention in response to the issue of eutrophication. Surface waters receiving excess phosphate may be susceptible to algal and hydrophytic blooms as well as rapid deterioration of water quality. Removal was initially achieved by chemical precipitation, which remains the leading technology today [1]. Chemical removal techniques, using metal

salts (iron, alum and lime) are reliable and well-established processes [1-3]. However, compared with the conventional salts, few investigations focused on phosphate removal by polyelectrolytes which are highly effective in coagulating and flocculating process.

Polyaluminium chloride (PAC), an inorganic polyelectrolyte, has the advantage of being effective within a broader pH range and rapid aggregation velocity [4, 5]. Polydiallyldimethylammonium chloride (PDADMAC), the important commercial polymer of the allyl monomers, is a cationic functional polymer that has outstanding utility in many flocculation applications [6-8]. Sometimes, metal coagulants are used together with organic polyelectrolytes to improve efficiency and flocs characteristics [9].

Red mud is waste by-product during bauxite ore processing in Bayer Process of Alumina Manufacturing Industry. Due to its large quantities generated and high alkaline nature, this solid waste causes a significant impact on the environment and needs a “search out” for proper disposal techniques [10-13]. In recent years, lot of research has been done to utilize red mud as a coagulation aid and adsorbent for gas cleaning and wastewater treatment as well as catalyst for some industrial processes [12, 14-17].

In this research, phosphate removal of PAC, alone or in the presence of PDADMAC, red mud or red mud and PDADMAC together, was investigated. In addition, the flocs after coagulation with and without red mud were also examined to further illustrate that phosphate removal was enhanced by red mud added.

MATERIALS AND METHODS

Materials

Polyaluminium chloride (PAC) was supplied by Dagan Reagent Plant, Tianjin, China. The basicity ($B = [\text{OH}]/[\text{Al}]$) of PAC was 2.4 and its Al₂O₃ content was 30%. PAC was dissolved in deionized water to obtain a solution of 5 wt.%. A 40 wt.% of polydiallyldimethylammonium chloride (PDADMAC) aqueous solution was purchased from Hangzhou Yinhu Chemical Co., Ltd., China. This solution was diluted with deionized water to obtain a final concentra-

tion of 0.1 wt.%. The two kinds of solutions were prepared freshly before each set of experiments for consistency.

Red mud was obtained from Shandong Aluminium Industry Co. Ltd., China. The powder placed in porcelain dishes was heat-treated at 700 °C for 2 h in an oven [16]. At the end of the treatment, the red mud was ground in a mortar and sieved. The particles smaller than 180 mesh were kept for further consideration in the trials. The red mud after heat-treatment had the following main composition: SiO₂, 22.45%; Fe₂O₃, 13.05%; Al₂O₃, 8.06%; CaO, 45.23%; MgO, 1.14%; TiO₂, 4.25%; K₂O, 0.64%; Na₂O, 1.86%.

Preparation of wastewater

Two kinds of wastewater were used in this study. One was synthetic wastewater, which was prepared by adding selected quantities of KH₂PO₄ to the tap water. The tap water was from the municipal water supply system of Beijing, China. The initial pH of the synthetic wastewater was adjusted to 8.0 by the addition of 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Another was raw wastewater, collected from the Small Moon River, an eutrophication river, in Beijing's suburb. The quality characteristics of raw wastewater were as follows: COD, 60-62 mg/L; TP, 0.74-0.82 mg/L; Turbidity, 15-40 NTU; pH, 7.7-8.2.

Coagulation experiments

The coagulation experiments were carried out in 1-L cylindrical containers using a jar tester (Model JTY-6, Daiyuan Co. Ltd., Beijing, China). The process of coagulation involved rapid mixing (300 rpm, 2 min), slow mixing (50 rpm, 10 min), and sedimentation (30 min). Following sedimentation, a sample was taken from 2 cm below the surface of the solution for residual phosphate measurement using the ascorbic acid method with a HACH DR/4000U spectrophotometer. At the beginning of rapid mixing, the added order of coagulant and aids was red mud, PAC and PDADMAC [9].

Adsorption and desorption experiments of phosphate on flocs

The flocs with and without red mud addition after coagulation experiments were collected from 4 cylindrical containers into 1 container. The volume of solution was adjusted to 1 L, and the initial phosphate concentration was measured. To start the adsorption experiment, 1 ml 1.00 mg/ml fresh phosphate solution was added and the flocs were stirred continuously at 20 rpm for 24 h. The residual phosphate in the two kinds of wastewater solutions were measured 30 s, 15 min, 30 min, 1 h, 2 h, 4 h and 24 h after the fresh phosphate was added.

The pH of the wastewater solutions after 24 h was used as the initial pH for desorption experiments. The pH was gradually decreased by the addition of 0.1 mol/L HCl to bring about phosphate desorption from flocs. During the process, residual phosphate of the wastewater solutions was obtained at different pH values.

RESULTS AND DISCUSSION

Phosphate removal by PAC and PDADMAC

Phosphate removal by PAC alone, PDADMAC alone, and both polyelectrolytes together from two kinds of wastewater were investigated. The effect on phosphate removal from synthetic wastewater having the initial pH of 8.0 with 2.0 mg/L PO₄³⁻-P is shown in Fig. 1A. The removal efficiency of phosphate increased remarkably from 28.5 to 90.4% when the dosage of PAC increased from 1.59 to 11.9 mg Al³⁺/L. With PAC dosage further increased to 23.8 mg Al³⁺/L, the phosphate removal efficiency increased slightly to 94.6%. The result also showed that PDADMAC was ineffective in removing phosphate at dosage of 0.1-0.3 mg/L. When PAC was used alone, the removal efficiency was 59% at a dosage of 4.76 mg Al³⁺/L. However, the phosphate removal efficiency was less than 59% when PAC and PDADMAC were used together, even when the dosage of PDADMAC increased from 0.1 to 2 mg/L.

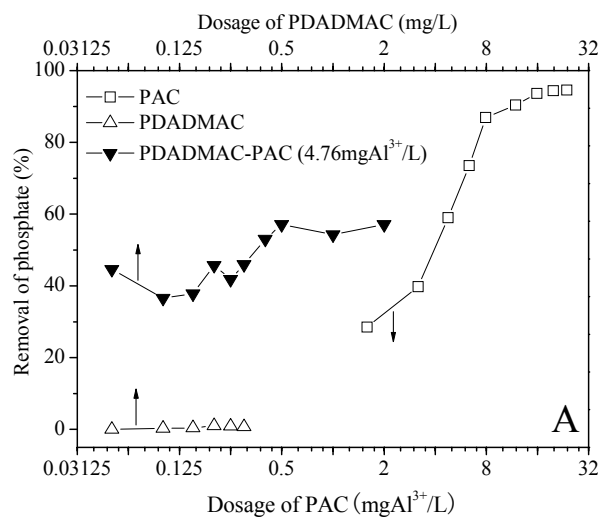


FIGURE 1A - Phosphate removal by PAC and PDADMAC from synthetic wastewater.

Phosphate removal from wastewater by PAC is a complex coagulation process which appears to be largely a result of a complexation driven by specific interactions [1, 2]. Once added into water, the hydrolysis of PAC could produce a series of products ranging from monomers, oligomers to polymeric hydroxyl complexes. Most of them are positively charged and can interact with negatively charged phosphate ions in solution that is charge neutralization by ligand competition. Another main interaction is the adsorption of phosphate ions onto the outer sphere of polymeric hydroxyl complexes during the process of phosphate removal [18]. The purpose of adding PDADMAC is to enhance the polymer bridging interaction and form larger flocs during flocculation process. However, the results show that the phosphate removal efficiency is decreased compared to PAC used alone. A possible reason is that the pyrrolidinium rings of PDADMAC, connected with -CH₂-CH₂-bridges in the 3,4-position, and its pendant double bonds

formed by linear chain propagation of the monomer, may interact with $-OH$ in $Al_x(OH)_y^{(3x-y)+}$, the hydrolysis products of PAC, which retards the reaction of aluminum species with the phosphate ions [7, 19].

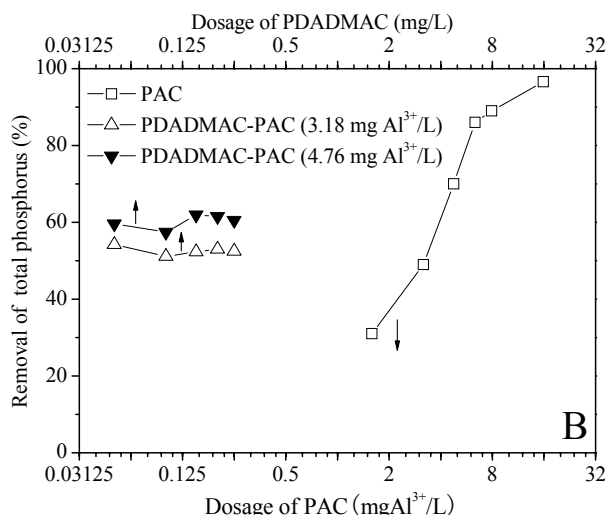


FIGURE 1B - Phosphate removal by PAC and PDADMAC from raw wastewater.

For the raw wastewater from an eutrophication river, PAC was also effective in total phosphorus removal. It is shown in Fig. 1B that the removal efficiency of total phosphorus increased with increasing dosage of PAC. The efficiency was as high as 96.6% at PAC dosage of 15.9 mg Al³⁺/L, and the residual total phosphorus was less than 0.02 mg/L, which is the critical phosphorus concentration of eutrophication in waters. According to the removal curves of PAC and PDADMAC used together, PDADMAC was not efficient in enhancing total phosphorus removal of PAC at the PAC dosages of 3.18 mg Al³⁺/L and 4.76 mg Al³⁺/L.

Phosphate removal by PAC and red mud

At 2.0 mg/L PO₄³⁻-P initial concentration, the effect of red mud as a coagulant aid on the phosphate removal with PAC from synthetic wastewater was studied. As can be seen from Fig. 2, the phosphate removal efficiency of PAC at 3.18, 4.76 and 6.35 mg Al³⁺/L increased with increase of dosage of red mud. The efficiency of 4.76 mg Al³⁺/L PAC increased to 73%, with the addition of 20 mg/L red mud, which was nearly the same as the efficiency of 6.35 mg Al³⁺/L PAC used alone. Thus, red mud addition could decrease the PAC dosage to be added. When red mud increased to 40 mg/L, the phosphate removal efficiency of 3.18, 4.76 and 6.35 mg Al³⁺/L PAC was increased by 15.1, 20.5 and 13.0%, respectively. After that, the removal efficiency increased slightly when the red mud further increased. For the raw wastewater, the total phosphorus efficiency also increased by 2-10% after 20-100 mg/L red mud added with PAC (data not shown).

The results demonstrated that phosphate removal of PAC was enforced in the presence of red mud. One reason

is that red mud removes phosphate from aqueous solution by adsorption [16, 17]. Red mud, as a waste product of the alumina manufacturing industry, has high aluminium, iron and calcium contents which are active components for the adsorption of phosphate, and red mud has a large specific surface area which is suitable for increasing the touching chance between the phosphate in solution and red mud [10, 13 and 20]. Another important reason is that red mud serves as "nuclei for coagulation" and increases collision frequency of fine particles, resulting in the formation of larger, rapid-settling flocs.

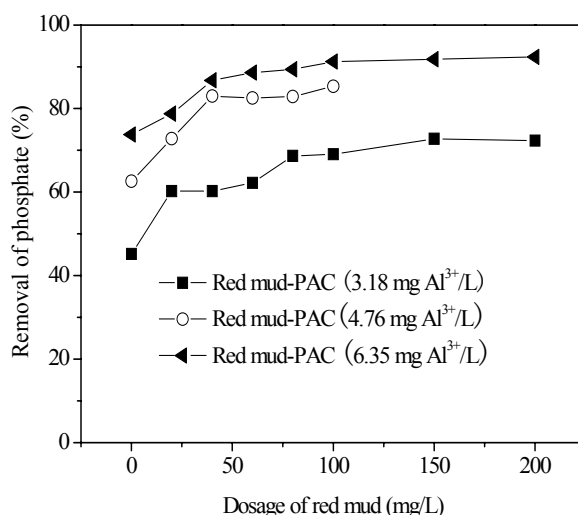


FIGURE 2 - Phosphate removal by PAC and red mud.

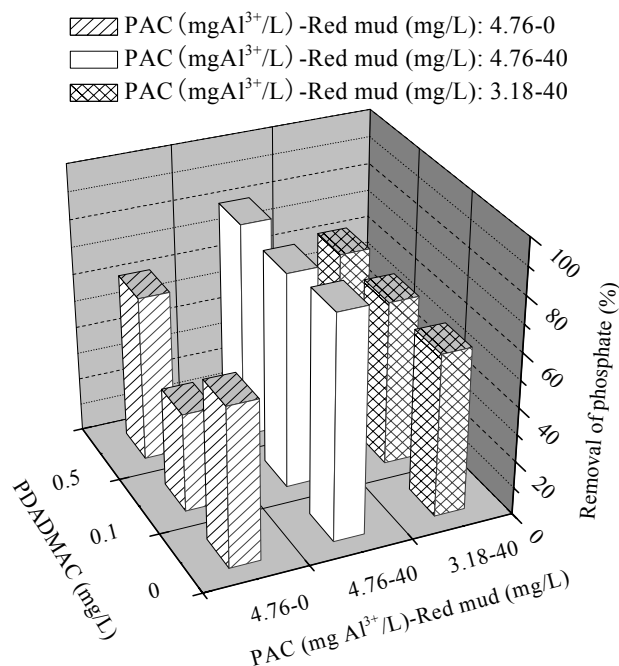


FIGURE 3 - Phosphate removal by PAC, PDADMAC and red mud.

Phosphate removal by PAC, PDADMAC and red mud

To examine the effect of PAC, PDADMAC and red mud used together on phosphate removal, studies were

done with the synthetic wastewater of 2.0 mg/L $\text{PO}_4^{3-}\text{-P}$. According to the results in Fig. 3, there were two factors that impact on phosphate removal efficiency. One was red mud addition. Compared with 4.76 mg Al^{3+} /L PAC and PDADMAC used together, the average phosphate removal efficiency reached to 80.8% from 52.2%, with 40 mg/L red mud added. Another factor was PAC dosage. The average removal efficiency increased by 19.7% with PAC dosage increasing from 3.18 mg Al^{3+} /L to 4.76 mg Al^{3+} /L. In addition, PDADMAC, at dosages of 0.1 mg/L and 0.5 mg/L, had little effect on enhancing phosphate removal when used together, which was the same as with PAC and PDADMAC used together.

Phosphate adsorption and desorption on flocs

The adsorption and desorption of phosphate from the synthetic wastewater by flocs with and without red mud after coagulation experiments were investigated as a function of time (30 s-24 h) and pH (3-8). The results are shown in Figs. 4 and 5.

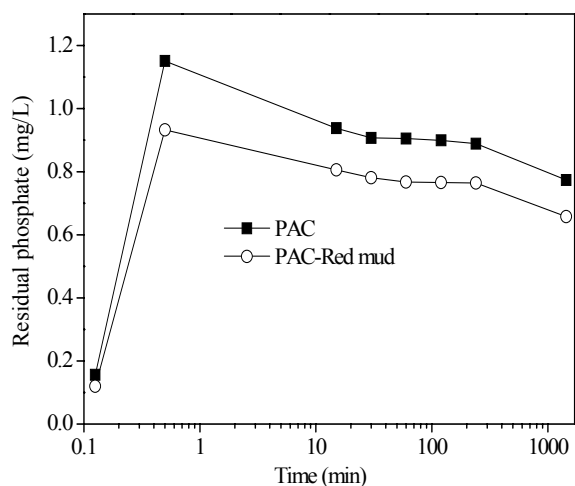


FIGURE 4 - Effect of time on phosphate adsorption by flocs.

As can be seen from Fig. 4, the initial phosphate concentration of solution with and without red mud, after the solution volume adjustment to 1 L, was 0.12 mg/L and 0.16 mg/L. About 30 s after the addition of 1 ml 1.00 mg/ml fresh phosphate solution, the residual phosphate of the solution with red mud dramatically decreased to 0.93 mg/L while it was 1.15 mg/L without red mud. Red mud addition reduced the quantity of PAC needed, and the excess PAC hydrolysis products in solution reacted with phosphate ions immediately when fresh phosphate solution was added. With the time increasing, the phosphate concentration was decreasing and phosphate was removed by adsorption of flocs. In addition, the residual phosphate of solution with red mud added was always lower than that of PAC used alone.

The pH of the solution with and without red mud was about 8.0 after phosphate adsorption for 24 h. This pH was used as the initial one for desorption experiment. The re-

sidual phosphate concentration in the supernatant is shown in Fig. 5 when pH decreased to 7, 6, 5, 4, and 3. As the pH decreased to 5 from 8, a gradual decrease in phosphate concentration was observed, and phosphate ions were further adsorbed on flocs. The phosphate concentrations of solution with and without red mud were 0.33 mg/L and 0.23 mg/L, respectively, at pH 5. When pH decreased to 4, some phosphate ions were desorbed from the flocs without red mud, and the phosphate concentration increased to 0.77 mg/L. However, phosphate ions were still adsorbed by flocs with red mud and the concentration decreased to 0.11 mg/L. The phosphate desorption of flocs with red mud happened until pH was reduced to 3. The results indicated that phosphate adsorption on flocs was enforced by the addition of red mud.

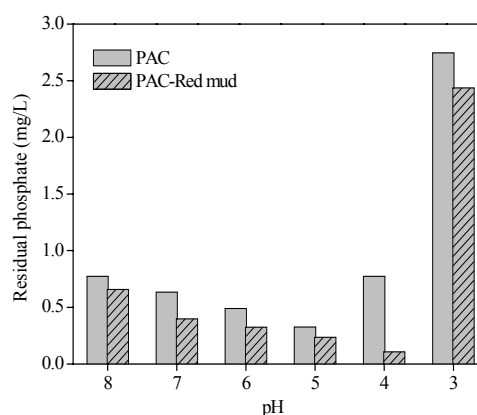


FIGURE 5- Effect of pH on phosphate adsorption by flocs.

CONCLUSIONS

The results of this investigation on enhancing phosphate removal by coagulation using PAC, PDADMAC and red mud supported the following conclusions:

PAC was effective in the removal of phosphate from synthetic wastewater and total phosphorus removal from raw wastewater; whereas PDADMAC was not efficient in removing phosphate when used alone, and it had little effect on enhancing phosphate removal of PAC.

The phosphate removal efficiency of PAC increased significantly in the presence of red mud. Red mud served as “nuclei for coagulation” resulting in the formation of large, rapid-settling flocs, and phosphate was adsorbed onto the flocs and settled with them. Addition of red mud not only decreased the required PAC dosage but also enforced the phosphate adsorption on flocs.

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