Efficiency and Mechanism of Advanced Treatment for Phosphate Wastewater by High Efficiency and Low Consumption Coagulation and Phosphorus Removal System

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Abstract. Beaker coagulation experiments were carried out using polyaluminium chloride (PAC), polyferrie sulfate (FPS), polyacrylamide (PAM), polyaluminum chloride (PAFC), polyaluminum sulfate (PAFS) and polyacrylamide (PAFC). The phosphorus removal effects of several flocculants were compared. The best combination coagulant PAM-PAC/PFS with high efficiency and economy was selected. The best ratio of PAC/PFS is 1:1, and the dosage of PAM is 1mg/L. The experiment determined the optimal hydraulic conditions: fast agitation and addition of PAC/PFS at a speed of 400 r/min for 1 min. PAM was added during slow agitation at a speed of 100 r/min for 6 min. The phosphorus removal system has a good effect on the removal of total phosphorus and other water quality indicators in the mine drainage of many phosphate mines, and all of them can meet the discharge standards.

1. Introduction
Chemical phosphorus removal [1,2] refers to the addition of different kinds of chemical reagents in the sewage treatment stage to convert the soluble or granular phosphorus in the wastewater into insoluble precipitates, and finally the phosphate precipitates are discharged in the excess sludge situation [3-5]. The chemical phosphorus removal process does not require additional equipment, does not change the process, and is directly added. The phosphorus removal rate is high and the treatment effect is stable. And the sludge will not re-release phosphorus during the treatment and disposal process, causing secondary pollution [6-7].

This study mainly uses the complex coagulant PAM-PAC/PFS to construct a highly efficient coagulation and phosphorus removal system for the advanced treatment of phosphorus-containing mine wastewater. The results show that the system can not only achieve the treatment effect, improve the regional ecological environment, but also provide scientific and technical guidance and reliable reference for the phosphate mine enterprises to achieve wastewater discharge and advanced treatment. Therefore, the purpose of this study is to prepare a compound coagulant PAM-PAC/PFS and construct a highly efficient coagulation and phosphorus removal system. The precipitation time, the initial pH value, and the influence of temperature on the treatment process were investigated. Finally, the physical and chemical characterization of PAM-PAC/PFS was carried out, and the chemical mechanism of PAM-PAC/PFS treatment of phosphate rock wastewater was proposed.
2. Material and methods

2.1. Experimental Materials

2.1.1. Experimental water sample. Sewage produced by relevant phosphate mining enterprises in the east branch of A River, Yichang City, Hubei Province.

2.1.2. Experimental reagent. Polyaluminium chloride (PAC), polyferric sulphate (PFS), polyaluminum ferric chloride (PAFC), polyaluminum ferric sulphate (PAFS), polyacrylamide (PAM) and Polyaluminum silicate (PSAF).

2.2. Experimental method

The experiment adopted a program-controlled six-coupler, and the coagulation stirring experiment was carried out by setting different hydraulic conditions, and 1L uniform water sample was taken in a group of beakers. The beaker was then placed on a programmed coagulation experimental stirrer and subjected to a coagulation experiment at the set initial conditions of agitation. After the reaction was completed, the precipitate was allowed to stand for a certain period of time, and then an equal amount of supernatant was taken at about 2cm under each beaker liquid surface for water quality analysis.

Determination of total phosphorus by ammonium molybdate spectrophotometry; Determination of sedimentation volume of solids: the settled flocs were taken in a 10 ml measuring cylinder, and the sedimentation volume of the flocs was measured after precipitation for 12 hours.

3. Results and discussion

Figure 1 showed that the organic-inorganic compound coagulant PAM-PAC/PFS was used to coagulate the mine production wastewater with a total phosphorus concentration of 1.01 mg/L. The longer the sedimentation time, the better the phosphorus removal effect. Under the condition of the combined coagulant PAC/PFS dosage of 25 mg/L, the total phosphorus concentration of the treated sewage decreased to 0.48 mg/L when the precipitation time reached 15 min, which reached the first-level standard of comprehensive wastewater discharge. The phosphorus removal rate was 52.0%; Under the condition that the combined coagulant PAC/PFS dosage was 40 mg/L, the total phosphorus concentration of the treated sewage was reduced to 0.17 mg/L when the precipitation time reached 20 min, which met the requirements of surface water class III standard. The phosphorus removal rate rose to 83.6%.

Figure 1. Effect of different settling times on the removal of phosphorus under the condition of TP=1.01 mg/L

Figure 2 showed that the coagulation treatment of mine production wastewater with a total phosphorus concentration of 1.84 mg/L was carried out by an organic-inorganic compound coagulant
PAM-PAC/PFS. When the combined coagulant PAC/PFS dosage was 30 mg/L, the total phosphorus concentration of the treated sewage was reduced to 0.47 mg/L when the precipitation time reached 15 min, which met the first-level standard of comprehensive wastewater discharge, the total phosphorus removal rate reached 74.6%; Under the condition that the combined coagulant PAC/PFS dosage is 45 mg/L, the total phosphorus concentration of treated sewage water drops to 0.18 mg/L when the precipitation time reaches 20 min, which met the requirements of surface water class III standards. The total phosphorus removal rate rose to 90.0%.

Figure 2. Effect of different settling times on the removal of phosphorus under the condition of TP=1.84 mg/L

Figure 3 showed that the organic-inorganic compound coagulant PAM-PAC/PFS was used to coagulate the mine production wastewater with a total phosphorus concentration of 3.10 mg/L. Under the condition that the combined coagulant PAC/PFS dosage was 30 mg/L, the total phosphorus concentration of the treated sewage water was 0.48 mg/L when the precipitation time reached 15 min, which met the first-level standard of comprehensive wastewater discharge, the total phosphorus removal rate reached 84.3%; Under the condition that the combined coagulant PAC/PFS dosage was 50 mg/L, the total phosphorus concentration of treated sewage water was 0.18 mg/L when the precipitation time reached 20 min, which met the requirements of surface water class III standard. The phosphorus removal rate rose to 94.0%.

Based on the analysis of the experimental results of Figure 1, Figure 2 and Figure 3, it can be seen that under the optimal dosage of PAM-PAC/PFS and the optimal coagulation hydraulic pressure. When the precipitation time increased from 0 min to 20 min, the phosphorus removal effect of the compound coagulant PAM-PAC/PFS increased greatly, and the total phosphorus removal rate increased significantly. When the precipitation time exceeded 20 min, the phosphorus removal effect did not change much, which indicated that the compounding coagulant PAM-PAC/PFS phosphorus removal process was efficient and rapid. After the mine production wastewater was treated with the compound coagulant PAM-PAC/PFS, it was best to meet the optimal dosage of the coagulant PAC/PFS required to meet the first-level standard of comprehensive wastewater discharge, the best precipitation time was 15 min; The optimum precipitation time was 20 min under the condition that the total phosphorus concentration of the effluent reaches the optimum dosage of the coagulant PAC/PFS required for the surface water class III standard.
Figure 3. Effect of different settling times on the removal of phosphorus under the condition of TP=3.10 mg/L

According to the constructed PAC-PAC/PFS phosphorus removal system, the total phosphorus content of the treated effluent met the first-level standard of comprehensive wastewater discharge and the standard conditions of surface water, respectively [8-10]. The relationship between the initial total phosphorus concentration of the mine production wastewater and the dosage of the required coagulant to determine the optimal dosage, as shown in Table 1.

Table 1. Deal with different initial total phosphorus concentration of mine effluent to meet the emission standards for the dosage of PAM-PAC/PFS

| Standard                        | TP (mg/L) | Optimal dosage (mg/L) |
|--------------------------------|-----------|-----------------------|
| Primary discharge standard for wastewater | 1.10 2.01 2.53 3.15 3.75 |                      |
| Surface water class III standard | 25 25 30 30 30 |                      |

The relationship between the relevant production standards and the amount of sludge produced by the total phosphorus in the mine production wastewater with different initial total phosphorus concentrations after treatment with the compounded coagulant PAM-PAC/PFS was linear. Fit and determine the relevant rules as was shown in Table 2.

Table 2. The relationship between the concentration of different initial total phosphorus and the amount of mud produced by the relevant standard

| Standard                        | Mud yield (y) & TP (x) | Correlation coefficient |
|--------------------------------|------------------------|-------------------------|
| Primary discharge standard for wastewater | y = 0.0056x + 0.211 | R² = 0.9548 |
| Surface water class III standard | y = 0.0124x + 0.2151 | R² = 0.9935 |

It can be seen from Table 2 that after the mine production sewage was treated with the compounding coagulant PAM-PAC/PFS, Under the condition of meeting the first-level standard of comprehensive wastewater discharge, the relationship between different initial total phosphorus concentrations (x, mg/L)
and mud production (y, g/L) satisfied $y = 0.0056x + 0.211$ (R$^2 = 0.9548$); When the surface water III standard was met, the relationship between different initial total phosphorus concentrations (x, mg/L) and mud yield (y, g/L) satisfied $y = 0.0124x + 0.2151$ (R$^2 = 0.9935$).

4. Conclusion
A new complex coagulant PAM-PAC/PFS has been first successfully prepared for the efficient and economical phosphorus removal of wastewater from phosphate mines. The results of characterization analysis indicated that the surface of the dephosphorization floc of the compound coagulant PAM-PAC/PFS was rough and porous, and had a strong condensed state. During the precipitation process, the fine phosphorus-containing particles in the sewage were caught and adsorbed, so that the poorly soluble substances in the sewage were rapidly gathered and swept to form a precipitate. The characterization analysis of PAM-PAC/PFS revealed that the composite coagulant PAM-PAC/PFS and phosphorus removal floc had no obvious diffraction peaks of crystals containing phosphorus, which indicated that the composition was in amorphous form. Combined with the results of characterization analysis, there were a large number of active groups in the compounding coagulant which contributed to coagulation, such as Si-O-Si, Fe-OH, Al-OH, H-OH. When the coagulant was added to water, a polyhydroxy complex ion such as Fe$^{3+}$ (OH)$^{2+}$, Al$^{n+}$ (OH)$_{m(3n-m)}$ was formed by hydrolysis reaction. Since their hydroxyl groups were unsaturated, these complexes required hydroxyl groups to be obtained from water, and strongly adsorb to colloidal particles such as polyphosphates in water. This method has been shown to significantly improve the removal efficiency of P. Due to its simplicity and low cost, it is a promising coagulant for the efficient treatment of mine wastewater.

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