

Study on treatment of ultra-high concentration phosphorus-containing wastewater

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Abstract—An efficient combined treatment process, lime-electrolysis was developed to treat the Ultra-high concentration phosphorus-containing Wastewater. The experimental results show that the removal rates of COD and TP are 86.4%, 69.9%, respectively. The results indicated that the optimal conditions are: lime dosage was 2g, pH 8.5, mixing rate 2.5 (equivalent units) and reaction time 20min, sedimentation time 10min; using the soluble iron plate and carbon rod as electrode plate, electrolysis pH 7, electric current 0.4 A, reaction time 80 min, exchange electrode reaction 2min per 12min. The biodegradability of the wastewater was improved evidently. This combined process provides instructive example for efficient treatment of Ultra-high concentration phosphorus-containing Wastewater.

Index Terms— lime electrolysis Phosphorus removal

I. INTRODUCTION

There have been reports about treating high concentration phosphorus-containing wastewater with coagulation sedimentation, electrolysis and other technologies, some of which have been used in practical application^[1, 2]. However, few studies have focused on the ultra-high concentration phosphorus-containing wastewater treatment.

Electrolysis can be used for a variety of industrial wastewater treatments^[3-5], but its application is limited by high running costs. As a traditional method for phosphorus removal, calcium lime method has advantages such as high phosphorus removal efficiency, simple operation, but there are still some problems to be solved^[6].

This study focused on treating ultra-high concentration phosphorus-containing wastewater with lime-electrolysis combined process, and investigated dosage, pH value and other factors on influencing the treatment efficiency, also provided a basis for better handling of ultra-high concentration phosphorus-containing wastewater in future.

II. METHODS AND MATERIALS

A. Experimental water quality

Experiment wastewater was the actual production wastewater. Water quality shown that the mass concentration of TP and COD are 18265mg/L, 255218mg/L, respectively, pH 3.0.

B. Methods

lime method: took 50ml pharmaceutical wastewater in 200ml beaker. Regulated pH using 16mol/L NaOH. Beaker was placed on a magnetic stirrer after cooled, then added the lime,

kept the stirrer agitating at a constant speed of 2.5 (equivalent unit), and then the beaker was standing for several minutes for settling. The reaction solution was filtered. The colature was used to measure the concentration of remaining phosphorus.

Electrolysis method: The electrolysis device was a 100ml electrolyzer. The size of soluble iron electrode plate was 20 mm×40 mm×1 mm. The carbon rod electrode was 5 mm in diameter and 40mm in length. Took 100ml water sample treated by cooling crystallization into the electrolyzer, regulating pH with dilute sulfuric acid and NaOH, then kept the magnetic stirrer agitating at a constant speed of 1.5 (equivalent unit) to blend it well. kept the plate distance at 3.5cm.

C. Analytical methods

The Phosphorus concentration were analyzed by ammonium molybdate spectro-photometry. pH was measured by pH meter.

III. RESULTS AND DISCUSSION

A. Results of phosphorus removal by lime

1) Effect of pH on phosphorus removal.

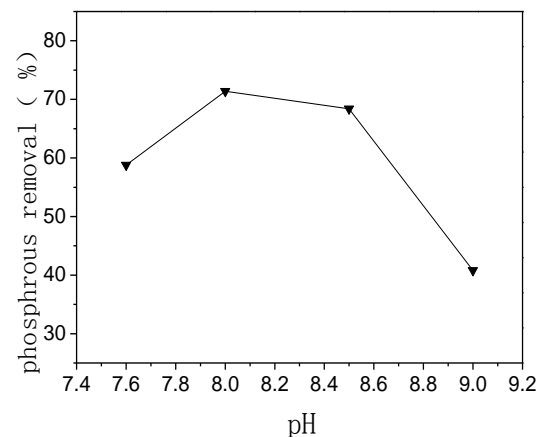


Fig.1 Effect of pH on phosphorus removal

With the solution alkalinity increased, phosphorus removal rate increased from less than 45% to over 70% (pH=8.5). Phosphorus removal reaction by lime was more thorough under alkaline conditions, for the abundant presence of Ca^{2+} and OH^- stimulated the reaction in the direction of precipitation. However, when pH was too high (more than 8.5), phosphorus removal rate decreased for the reason that excessive OH^- competed with phosphate anion to combine with calcium ion, leading to 1

ess calcium phosphate product. At the same time, sedimentation performance of the wastewater deteriorated, decreasing the phosphorus removal rate by less phosphate precipitation.

2) Effect of dosage on phosphorus removal.

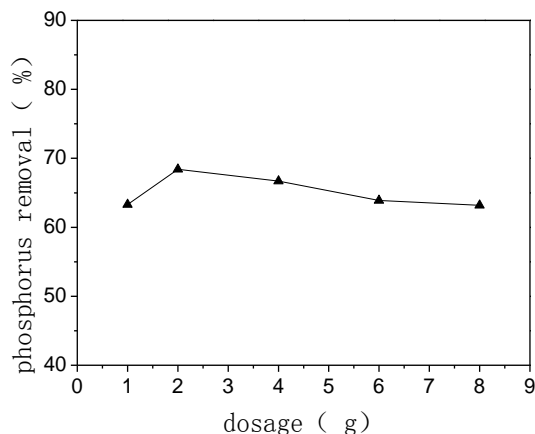


Fig. 2 Effect of different dosages on phosphorus removal

With the increase of lime dosages, phosphorus removal rate was declined as a whole. The phosphorus removal rate was 71.4% when adding 2g lime. Ca^{2+} and PO_4^{3-} react step by step. The increase of Ca^{2+} can ensure that Ca^{2+} is sufficient in reaction system, The excess Ca^{2+} and OH^- would promote the reaction $3PO_4^{3-} + 5Ca^{2+} + OH^- = Ca_5(PO_4)_3OH$, which was good for getting rid of PO_4^{3-} in the sewage. However, too much lime led phosphorus removal rate decreased, mainly due to the interference effect of ions, suspended solids and crystal. Which making it difficult for the combination of free Ca^{2+} and P.

3) Effect of reaction time on phosphorus removal.

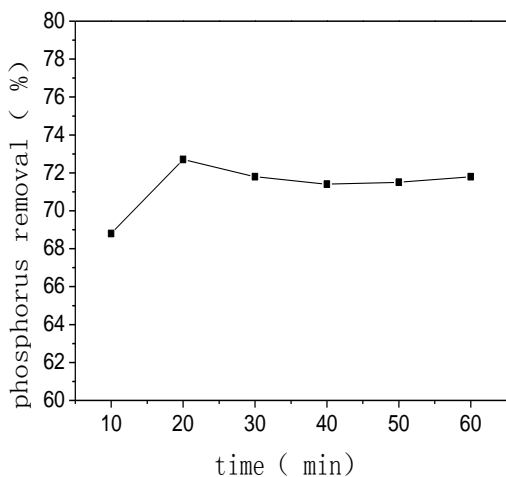


Fig. 3 Effect of reaction time on phosphorus removal

Figure 3 showed the phosphorus removal rate under different reaction time. The phosphorus removal rate increased rapidly from 0min to 20min. The phosphorus removal rate reached 72.4% when the reaction time was 20min. However, the rate

increased slowly when the reaction time continued to be extended. Therefore, considering the economic benefits, the optimal electrolytic time was 20min.

Taking both the removal rate and operating cost into consideration, the optimal conditions was pH 8.5, 2g lime/50mL wastewater, mixing rate 2.5(equivalent units) and reaction time 20min, sedimentation time 10min. Under this condition, the removal rates of COD and TP are 52.3%, 50.9%, respectively.

B. Results of phosphorus removal by electrolysis

The electrolytic experiment used iron-carbon electrodes. Electrolysis can both remove the phosphorus and lower the chroma by a large margin. Using the single factor experiment to investigate the effect of different factors (including pH, electric current, plates interval and electrolytic time) on phosphorus removal after cooling crystallization, meanwhile investigated the electrode passivation phenomenon.

1) Effect of pH on phosphorus removal.

pH determine the product of this experiment by affecting the existence and transformation of ferric hydroxide and ferrous hydroxide, so it has great influence on the phosphorus removal rate. Under the initial condition (electric current is 0.4A, phosphorus concentration is 5203mg/L), the experiment was carried out under different pH values (pH=5, 6, 7, 8) for 30min. Taking the electrode passivation into consideration, we designed another group of experiment under the same conditions except that the reaction time is 10min followed by 2min of electrode exchanging. The result is showed in Fig.1.

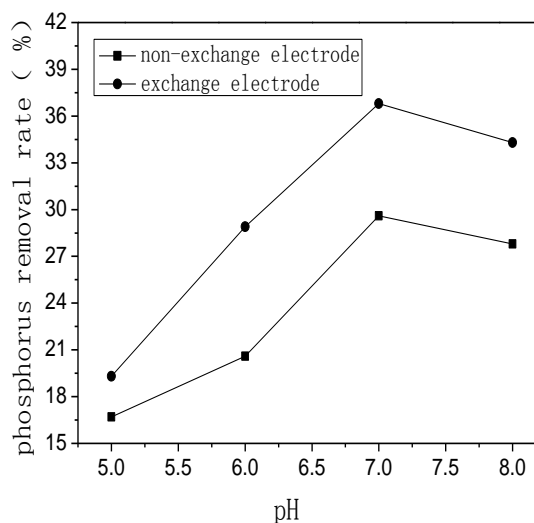


Fig.4.Effect of pH on phosphorus removal

Figure 4 showed that when the electrodes were not exchanged, the phosphorus removal rate raised and then decreased when the pH continued to become higher. When the pH equals 7, the phosphorus removal rate reached the peak, 29.6%; when the pH was low, the phosphate removal rate was about 20%, which was a very poor effect; under basic conditions,

the phosphorus removal rate was lowered due to the production of ferric hydroxide and ferrous hydroxide; the neutrality condition was best for phosphorus removal because the concentration of ferric ion and ferrous ion were high instead of developing into ferric hydroxide precipitate or ferrous hydroxide precipitate, at the same time, the orthophosphate concentration was high to produce precipitate more easily.

White precipitate appeared on the electrode surface after the experiment was conducted for a period of time which indicated the phenomenon of electrode passivation. The electrode passivation was more serious when the pH was higher. After the exchanging of electrodes, the phosphorus removal rate increased by 2.6%, 8.3%, 7.2%, 6.5%, respectively. After the electrodes exchanging, the carbon electrode was anode and the iron electrode was cathode, hydrogen was produced from the cathode and served to break the passivation layer and clean the surface of the electrode, this contributed to a higher phosphorus removal rate.

2) Effect of electric current density on phosphorus removal

The key factor whether phosphate precipitate can be produced is the concentration of ferric ion in the solution, changing the concentration of ferric ion by adjusting the electric current, the phosphorus removal rate increased when the integration rate of ferric ion and dissolved phosphate was increased. But at the same time, it increases the energy consumption of the current and the plate, so to determine the best current has a double meaning in obtaining ideal phosphorus removal rate and saving electrolytic energy consumption. Adjusting pH =7, reaction and sedimentation time was 30min, 20 min. setting current of 0.2A, 0.3A, 0.4A, 0.5A, 0.6A, respectively, exchange electrode reaction 2min per 12min. The result is showed in Figure 4.

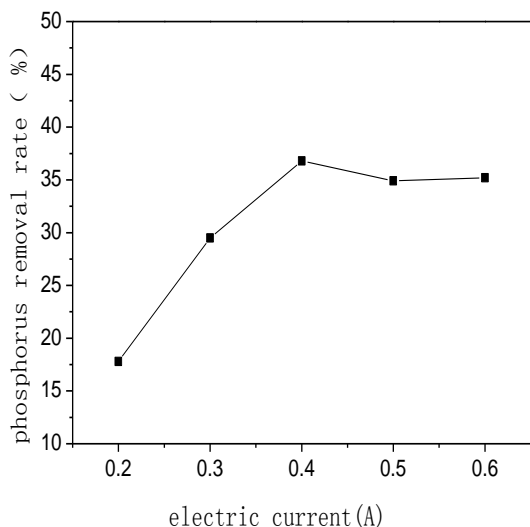


Fig.5 Effect of electric current density on phosphorus removal

Figure 5 showed that with the increase of electric current,

the phosphorus removal rate increased rapidly, the removal rate reached 36.8% when the electric current was 0.4A. But when the electric current continued to raise, the removal rate increased very slowly, the effect of electric current on phosphorus removal was no longer significant. When the current density was lower than 0.4A, the system was not capable of producing enough Fe^{2+} , so the increased current density can help increase the dissolve rate of Fe^{2+} , the phosphorus removal rate increased as a result. When the current went on increasing, the energy consumption of phosphorus removal increased, so the optimal condition was achieved when electric current was 0.4A

3) Effect of electrolytic time on phosphorus removal

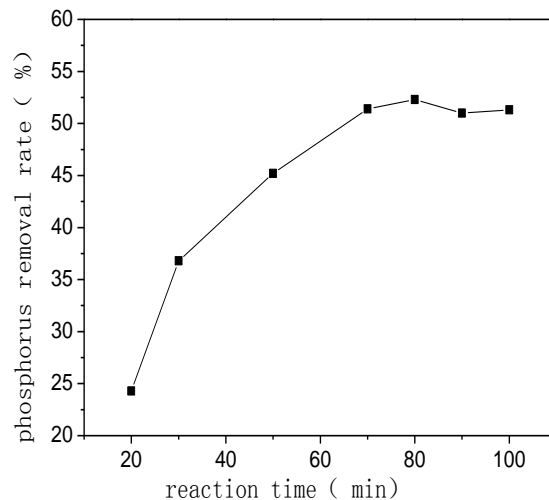


Fig.6 Effect of electrolytic time on phosphorus removal

Figure 6 showed the phosphorus removal rate under different reaction time. The phosphorus removal rate increased gradually when the electrolytic time extended. The phosphorus removal rate reached 52.3% when the electrolytic time was 80min, however, the rate increased slowly when the reaction time continued to be extended. Therefore, considering the economic benefits, the optimal electrolytic time was 80min. The electrolytic time had direct influence on the phosphorus removal rate, under the same operating conditions, the phosphorus removal rate was higher when the electrolytic time extended. This was due to the fact that when the electrolytic time was longer, the iron ion dissolved in the water sample was more, then more floc unit were produced which contributes to a better removal result. At the same time, the floatation effect was better thanks to the more tiny bubbles emerged from the cathode. When the electrolytic time was much longer, however, the electrode passivation effect was intensified and led to excessive energy consumption.

Taking both the removal rate and operating cost into consideration, the optimal conditions are pH 7, electric current 0.4 A, reaction time 80 min, exchange electrode reaction 2min

per 12min. Under this condition, the removal rates of COD and TP are 52.3%,50.9%,respectively.

IV. CONCLUSIONS

The results indicated that the optimal conditions are: lime dosage was 2g, pH 8.5,mixing rate 2.5(equivalent units)and reaction time 20min, sedimentation time 10min; using the soluble iron plate and carbon rod as electrode plate, electrolysis pH 7, electric current 0.4 A, reaction time 80 min, exchange electrode reaction 2min per 12min.

The experimental results show that the removal rates of COD and TP are 86.4%, 69.9%,respectively. TP decreased from 18256mg/L to 2482mg/L.COD decreased from 255218mg/L to 76816mg/L.

Lime- electrolysis was developed to treat the Ultra-high concentration phosphorus-containing Wastewater, the combined process not only can effectively remove TP, but also improve water biodegradability which is conducive to the subsequent process.

ACKNOWLEDGMENT

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