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Investigation on the simultaneous removal of COD and phosphorus from saponification effluent in rare-earth separating process by Fenton oxidation and chemical precipitation

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ABSTRACT

In general, the saponification effluent result from rare earth metallurgical process is often characterized by high chemical oxygen demand (COD) and high phosphorus and salt concentrations. This paper presents a method for simultaneously removing COD and phosphorus from saponification effluent via Fenton oxidation and chemical precipitation. A series of experiments were conducted to enhance the removal of COD and phosphorus from the effluent which contained 924 mg/L of COD and 15.5 mg/L of phosphorus. Experimental results showed that pH of the solution, reaction time, and H_2O_2 and Fe^{2+} concentrations exert significant effects on the removal of COD and phosphorus by Fenton oxidation and chemical precipitation, while a change of temperature makes no difference. Under optimal conditions with $[H_2O_2]$ = 11.9 g/L, $[FeSO_4 \cdot 7H_2O]$ = 4.8 g/L, pH of the solution = 3.0, and reaction time = 360 min, 82.3% of COD, and 72.3% of phosphorus were removed and the effluent was decolorized completely. The X-ray diffraction pattern of the precipitation indicated that the organic phosphorus in the saponification effluent had been changed into inorganic phosphorus and precipitated by calcium chloride. An economic evaluation indicated that it is more economic to adjust the pH with calcium oxide prior to the chemical oxidation process.

Keywords: Saponification effluent; Fenton oxidation; Chemical precipitation; COD and phosphorus removal

1. Introduction

Rare earth is widely used in military, chemistry, agriculture, and material areas [1]. In conventional rare earth metallurgical process, pure rare earth chloride solution is produced by solvent extraction, which holds a central position in the rare earth industry [2]. Nowadays, the most popular extraction agent used in rare earth metallurgical processes are phosphoric acid based alkyl phosphorus reagents such as di(2-ethylhexyl) phosphoric acid (P204) and 2-ethylhexyl-2-ethylhexylphosphonate (P507) [3,4]. But these extraction agents must be saponified first to avoid a large release of hydrogen ions in the extraction process, which would generate a large quantity of high-salinity organic effluent. In recent years, calcium oxide and magnesium oxide have been widely used as the saponifier in many factories in order to lower costs and avoid the production of ammonia–nitrogen wastewater [5]. However, this new saponification process often leads to an increase of chemical oxygen demand (COD) and phosphorus in the effluent because of the dissolution and entrainment of acidic phosphorus [6]. High COD and phosphorus concentrations in water would lead to excessive growth of algae and other microorganisms, resulting in dissolved oxygen depletion and fish toxicity [7]. Therefore, it is necessary to

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remove COD and phosphorus from saponification effluent before it is discharged.

Commonly, biological treatment is accepted as an economical and suitable process to remove phosphorus from some kinds of wastewater [8,9]. However, biological processes are not feasible in the treatment of saponification effluent because of latter's low biodegradability [10]. Although phosphorus may be efficiently removed from aqueous solutions by adsorption [11], it is difficult to remove phosphorus from the saponification effluent due to the complicated form of phosphorus that exists in the effluent. As an alternative, precipitation is often used to remove phosphorus from effluent [12–14]. Unfortunately, this process cannot remove phosphorus from the saponification effluent easily, because the phosphorus in the effluent is mainly in the form of organic phosphorus, which cannot be precipitated by calcium or magnesium salts. Therefore, before the chemical precipitation process, the organic phosphorus in the saponification effluent must be transformed into inorganic phosphorus, which is associated with the process of COD removal. So far, many methods have been used to remove COD from wastewater. Frequently used methods include flocculation precipitation [15], advanced oxidation [16–19], microorganism treatment [20,21], and absorption [22]. The COD in saponification effluent mainly originates from dissolution and entrainment of acidic phosphorus-containing extractant and kerosene, which is difficult to be decomposed by biological and physical/chemical processes. Fenton oxidation may be a good choice for many refractory organics [23]. Li et al. [24] studied the treatment of refractory organic matters in municipal solid waste landfill leachate. The results showed that 90% of COD and total organic carbon were removed by Fenton oxidative–coagulation and photo-Fenton. Park et al. [25] used Fenton oxidation to remove non-biodegradable organics and color in pigment wastewater. The results from their work reported that 58.9% of COD and 45.7% of color were removed for the final effluent. Thus, Fenton oxidation may be an effective technique for the removal of these recalcitrant organics in saponification effluent.

In many Chinese factories, the saponification effluent is conventionally treated by adding milk of lime to remove needless acids and salts [26], which produces a lot of waste and leave the acidic phosphorus and organic compound still in the effluent. This mishandled saponification effluent has led to water pollution in rivers near these factories. Thus, the feasibility of simultaneously removing COD and phosphorus from the saponification effluent by Fenton oxidation and chemical precipitation was investigated in this study. Laboratory-scale experiments were performed to investigate the effects of parameters such as pH, temperature, reaction time, ferric salt, and hydrogen peroxide dosage on the removal of COD and phosphorus, which will provide a guide for the harmless treatment of the saponification effluent.

2. Experimental

2.1. Materials and analysis

All the chemical reagents used in this study were analytical grade and de-ionized water was also used in the corresponding procedures during the experiments. The saponification effluent containing 2-ethylhexyl-2-ethylhexylphosphonate (P507) was obtained from Jiangsu Guosheng Rare Earth Co., Ltd., (Guangling Town, Taixing City, Jiangsu Province, China), and its main chemical composition is listed in Table 1. The most noticeable attribute of the effluent is the high content of calcium and chloride ions. This is due to a change of the saponification process where the traditional saponifier of ammonium hydroxide was replaced by calcium oxide [27]:

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \tag{1}$$

$$\mathrm{2(C_8H_{17})_2HPO_3 + Ca(OH)_2 \rightarrow Ca[(C_8H_{17})_2PO_3]_2 + 2H_2O} \tag{2}$$

$$\mathrm{Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O} \tag{3}$$

The total phosphorus concentration (P_T) of all samples, including aqueous solution, was analyzed by a bismuth-phosphomolybdenum blue spectrophotometric method (Model TU-1810, Beijing Puxi Science and Technology Instrument Co, Ltd., China) at $\lambda_{\max}$ of 700 nm with the blank sample containing only deionized water. Before being delivered for analysis, adequate nitric acid and hydrochloric acid were added to the water sample. Also, organic phosphorus was changed into inorganic phosphorus when the sample was boiled for about 30 min. COD was determined by the potassium iodide–alkaline potassium permanganate method, which was suitable for high-chlorine wastewater. Phase analysis of the precipitation was conducted by X-ray diffraction (XRD; Model D/max 2500 PC, Rigaku, Japan) with Cu K α radiation.

2.2. Experimental fundamental

In Fenton's reaction, hydroxyl radicals (•OH) are produced by interaction of hydrogen peroxide with ferrous salts according to Eq. (4) [28]. The hydroxyl radicals can attack and initiate the oxidation of organic pollutant molecule (R) by several degradation mechanisms as shown below [Eqs. (5)–(7)] [29,30]:

$$\mathrm{Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O} \tag{4}$$

$$\mathrm{{}^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O} \tag{5}$$

$$\mathrm{Fe^{3+} + R^{\bullet} \rightarrow R^+ + Fe^{2+}} \tag{6}$$

$$\mathrm{H_2O_2 + R^{\bullet} \rightarrow ROH + {}^{\bullet}OH} \tag{7}$$

After Fenton's reaction, the dissolved or entrained P507 in the effluent could be decomposed:

$$\mathrm{(C_8H_{17})_2HPO_3 + 49H_2O_2 \rightarrow 16CO_2 + H_2PO_4^- + 65H_2O + H^+} \tag{8}$$

According to Table 1, there is a lot of soluble calcium in the effluent. Therefore, the phosphorus would be precipitated by calcium ion as soon as the organic phosphorus was transferred into dissociative phosphate anion, and the reactions were expressed as follows:

$$Ca^{2+} + H_2PO_4^- + 2H_2O \rightarrow CaHPO_4 \times 2H_2O \downarrow + H^+ \quad (9)$$

$$Ca^{2+} + H_2PO_4^- \rightarrow CaHPO_4 \downarrow + H^+ \quad (10)$$

$$3Ca^{2+} + 2H_2PO_4^- \rightarrow Ca_3(PO_4)_2 \downarrow + 4H^+ \quad (11)$$

$$5Ca^{2+} + 3H_2PO_4^- + H_2O \rightarrow Ca_5(PO_4)_3OH \downarrow + 7H^+ \quad (12)$$

The degradation of organics and transformation of organic phosphorus would take place simultaneously when Fenton's reagent was added into the saponification effluent. The inorganic phosphorus would be precipitated by soluble calcium in the effluent. Therefore, simultaneous removal of COD and phosphorus from the saponification effluent would be realized in one step.

2.3. Experimental procedure

Fenton's reaction mainly depends on four factors: reaction time, pH of the solution, hydrogen peroxide concentration, and Fe^{2+} concentration [31]. Therefore, the four factors were investigated. The pH of the saponification effluent was adjusted to a predetermined value (1.0, 2.0, 3.0, 4.0, and 5.0, respectively) by a sodium hydroxide solution before the chemical oxidation process. A 100 mL sample was placed in a 300 mL conical flask, submerged in a temperature controlled water bath, and allowed to attain the preset experimental temperature. Then, $FeSO_4{\cdot}7H_2O$ was added to reach the desired Fe^{2+} concentration (the addition of $FeSO_4{\cdot}7H_2O$ was 0.29, 0.35, 0.38, 0.48, and 5.9 g, respectively). Finally, desired H_2O_2 (30% (w/v)) was carefully added to start the Fenton's reaction (the addition of H_2O_2 was 2.4, 2.6, 2.9, 3.1, 3.3, 3.5, 3.7, 4.0, 4.2, and 4.4 mL, respectively). The aqueous solution of Fenton's reagent and wastewater were magnetically stirred with the speed of 550 rpm during the reaction period. After the required time (60, 120, 180, 240, 300, and 360 min, respectively), the effluent was vacuum filtered immediately. The filtrate was collected and analyzed for COD and P_T. The residue was washed with deionized water before it was dried and sent for phase analysis. The removal efficiency of COD or P_T was defined as follows:

$$\text{Removal efficiency } (\%) = \left(1 - \frac{C}{C_0}\right) \times 100\% \quad (13)$$

where C_0 is the initial concentration of COD or P_T in the saponification effluent, and C is the concentration of COD or P_T after Fenton's reaction.

3. Results and discussion

3.1. Effect of temperature and pH

The effect of temperature on COD and phosphorus removal efficiency was tested at room temperature (25°C) and 60°C, and the results are shown in Table 2. There was no significant difference in the COD and phosphorus removal efficiency for the tested temperatures. Some research results indicate that the temperature of the effluent hardly affects the efficiency of COD removal in Fenton's oxidation [32]. In addition, high temperatures would enhance the decomposition of hydrogen peroxide. Thus, all further experiments were carried out at room temperature for practical and economic reasons.

The pH of the effluent is an important parameter for Fenton's oxidation process, which controls the production rate of the hydroxyl radical and the concentration of Fe^{2+}. In order to find the optimal pH for the COD and phosphorus removal from the effluent in Fenton's oxidation process, a series of experiments were conducted at different pH values of 1.0, 2.0, 3.0, 4.0, and 5.0. The results are illustrated in Fig. 1. The results indicate that the maximum removal efficiency in COD (79.6%) and phosphorus (61.3%) was achieved in Fenton's oxidation of saponification effluent at pH 3.0. Many studies have revealed that the degradation of organics in water by Fenton's oxidation was strongly affected by the solution pH and the optimal solution pH values were close to 3.0 [33]. Lower values of pH result in a decline of $Fe(OH)^{2+}$ and hydroxyl radicals concentration, while higher pH values results in the hydrolysis of ferric ion and slow formation of hydroxyl radicals [34,35], both negatively influencing the degradation of organics. Meanwhile, the rate of undesirable H_2O_2 decomposition shows the lowest value at pH 3.0 [36]. Therefore, the experimental results are in accord with previous research findings [33] and pH of 3.0 was chosen as the optimal solution pH in Fenton's oxidation of saponification effluent.

Table 2
Effect of temperature on COD and phosphorus removal efficiency

Temperature	COD		Phosphorus	
	25°C	60°C	25°C	60°C
Removal efficiency (%)	73.5	72.8	61.3	63.1

Table 1
Main composition of saponification effluent

Parameter	H^+ (mol/L)	Ca^{2+} (g/L)	Cl^- (g/L)	P_T (mg/L)	COD (mg/L)	Absorption value*
Value	0.56	39.5	94.39	15.5	924	0.23

*Absorption value was obtained at 460 nm.

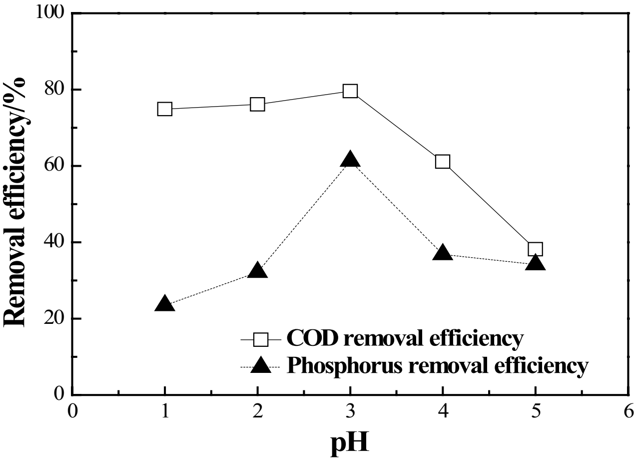

Fig. 1. Effect of pH on COD and phosphorus removal (reaction conditions: [$FeSO_4·7H_2O$] = 3.8 g/L, [H_2O_2] = 10.6 g/L, T = 25°C, and reaction time = 360 min).

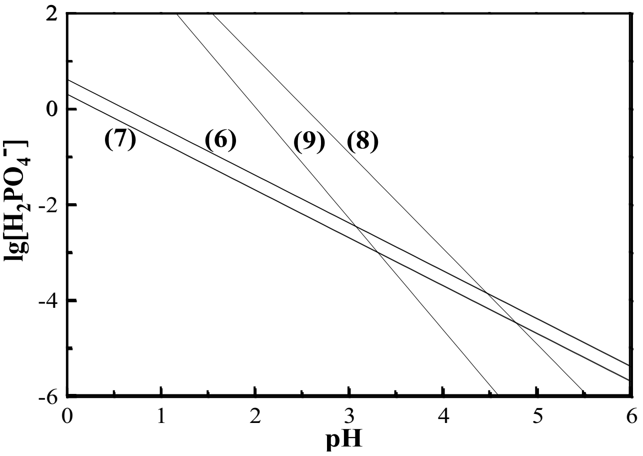

Fig. 2. Effect of pH on phosphorus concentration according to the results of thermodynamic calculation (T = 25°C, [Ca^{2+}] = 39.5 g/L).

We also find from Fig. 1 that the removal efficiency of phosphorus is very low at pH 1.0 and 2.0, which is inconsistent with the higher removal efficiency of COD. This may be attributed to the dissolution of calcium phosphate at low pH levels. According to the thermodynamic calculation [37] results of Eqs. (6)–(9), the effect of pH on phosphorus concentration in the effluent is shown in Fig. 2. As can be seen, phosphorus concentration in the effluent is obviously influenced by the solution pH, and the phosphorus concentration decreases quickly as the solution pH increases. The residual phosphorus concentration in the effluent is higher at low solution pH, which means that the phosphorus in the effluent could not be precipitated by calcium ion even if the organic phosphorus is transformed into inorganic phosphorus. So, it is not difficult to illuminate why the removal efficiency of phosphorus is very low at pH 1.0 and 2.0.

Therefore, further experiments were conducted at an initial pH of 3.0 by adding NaOH solution for pH adjustments before the progress of the Fenton's oxidation.

3.2. Effect of H_2O_2 concentration

In order to elucidate the role of the concentration of H_2O_2 on the removal of COD and phosphorus from the saponification effluent by Fenton's oxidation, a series of experiments were conducted with different [H_2O_2] ranging from 7.3 to 13.2 g/L. Fig. 3 shows the effect of [H_2O_2] on the removal of COD and phosphorus by Fenton's oxidation. The results in Fig. 3 indicate that higher [H_2O_2] generated more hydroxyl radicals, which improved the COD and phosphorus removal efficiency. With an increase of [H_2O_2] from 7.3 to 11.9 g/L, the COD removal efficiency increased from 31.4% to 81.5% and the phosphorus removal efficiency increased from 16.8% to 64.5%. However, with a further increase of the [H_2O_2] to 12.5 and 13.2 g/L, the phosphorus removal efficiency remained nearly unchanged and the COD removal efficiency reduced slightly. This may be explained by the fact that the reactive $^{\bullet}OH$ radical could be consumed by excess H_2O_2 and results in the generation of less reactive $^{\bullet}OOH$ [38]. In addition, high [H_2O_2] would also result in increase of treatment cost. Hence, 11.9 g/L was considered as appropriate concentration of H_2O_2 in Fenton's oxidation of saponification effluent.

3.3. Effect of Fe^{2+} concentration and H_2O_2/Fe^{2+} ratio

Ferric ion is the catalyst which plays an important role in Fenton's oxidation process. The effect of [$FeSO_4·7H_2O$] on the removal of COD and phosphorus by Fenton's oxidation is shown in Fig. 4. As can be seen, the removal of COD and phosphorus are remarkably dependent on the [$FeSO_4·7H_2O$] at fixed [H_2O_2] and solution pH. The removal efficiency of COD and phosphorus were 47.9% and 35.5%, respectively at a low [$FeSO_4·7H_2O$] (2.9 g/L). Both COD and phosphorus removal efficiency were increased with the increase of [$FeSO_4·7H_2O$], and the removal efficiency of COD and phosphorus were 81.5% and 64.5%, respectively, when the [$FeSO_4·7H_2O$] was increased to 3.8 g/L. This is because more $^{\bullet}OH$ radicals are produced with an increase of [$FeSO_4·7H_2O$] according to Eq. (1). When we continue increasing the [$FeSO_4·7H_2O$], the removal efficiency of COD was mostly the same, while there was a small increase in phosphorus removal efficiency. The increase in phosphorus removal may be attributed to the absorption of phosphorus by flocculent ferric hydroxide [39,40].

Actually, the H_2O_2/Fe^{2+} ratio changes when varies the addition of H_2O_2 and $FeSO_4·7H_2O$ in the saponification effluent. There exists optimal H_2O_2/Fe^{2+} ratio when Fenton's oxidation process is employed for organics degradation [41]. While, the optimal H_2O_2/Fe^{2+} ratio is significantly varied when different type of organics are decomposed. And the optimal H_2O_2/Fe^{2+} ratio can vary from 1.5 to 329 when different wastewater was mineralized [42,43]. Fig. 5 shows the different removal efficiency of COD and phosphorus when the H_2O_2/Fe^{2+} ratio changes in oxidation of saponification effluent. It can be seen that the removal efficiency of COD and phosphorus reaches a maximum when the H_2O_2/Fe^{2+} ratio is 12.3. Thus, the optimal H_2O_2/Fe^{2+} ratio for Fenton oxidation of saponification effluent is 12–13.

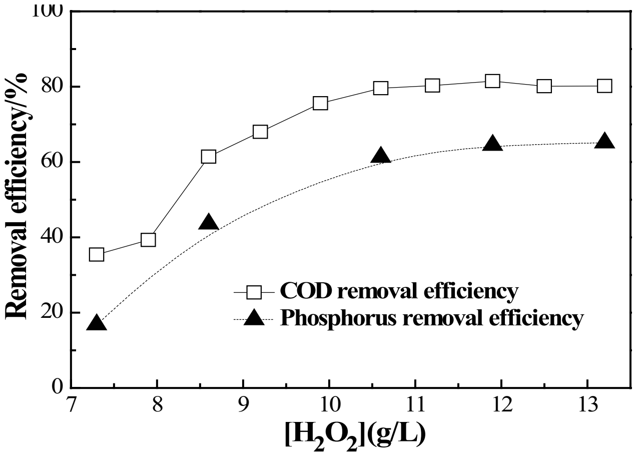

Fig. 3. Removal efficiency of COD and phosphorus with varying H_2O_2 concentration (reaction conditions: $[FeSO_4·7H_2O]$ = 3.8 g/L, pH = 3, T = 25°C, and reaction time = 360 min).

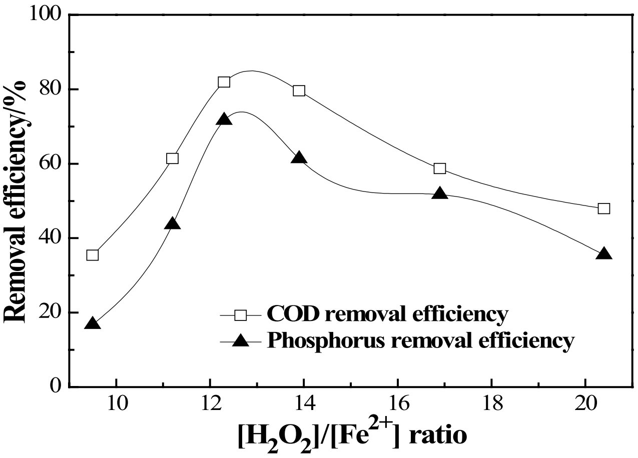

Fig. 5. Effect of H_2O_2/Fe^{2+} ratio on COD and phosphorus removal (reaction conditions: pH = 3, T = 25°C, and reaction time = 360 min).

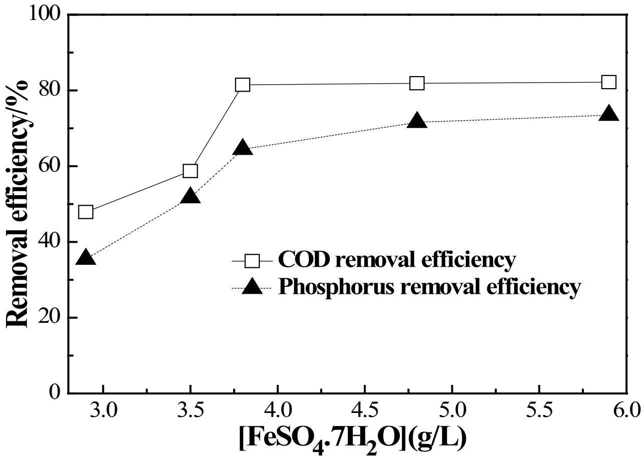

Fig. 4. Removal efficiency of COD and phosphorus with varying $FeSO_4·7H_2O$ concentration (reaction conditions: $[H_2O_2]$ = 11.9 g/L, pH = 3, T = 25°C, and reaction time = 360 min).

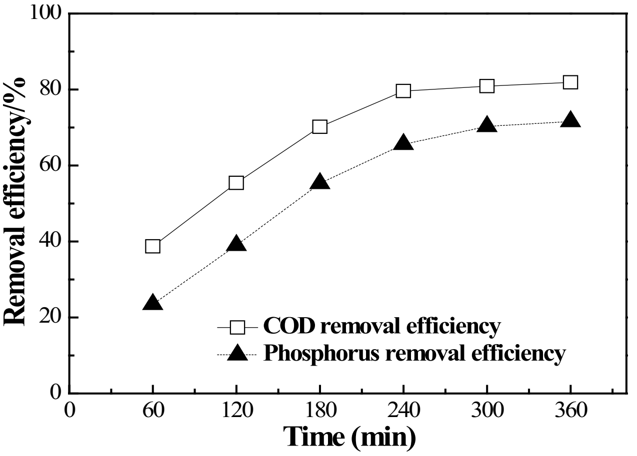

Fig. 6. Effect of time on COD and phosphorus removal (reaction conditions: $[FeSO_4·7H_2O]$ = 4.8 g/L, $[H_2O_2]$ = 11.9 g/L, pH = 3, and T = 25°C).

Considering the above-indicated results, the optimal $[FeSO_4·7H_2O]$ and H_2O_2/Fe^{2+} ratio were selected as 4.8 g/L and 12.3, respectively for the Fenton's oxidation of saponification effluent.

3.4. Effect of reaction time

Fig. 6 shows the results of the Fenton's oxidation test obtained by varying the reaction time from 60 to 360 min. During the experiment, it was found that once the hydrogen peroxide was added into the saponification effluent under stirring, the pale yellow solution was turned into claybank quickly with lots of bubbles and some precipitation. This indicated that the hydrogen peroxide was first decomposed by Fe^{2+} to form $^{\bullet}OH$ and Fe^{3+} according to Eq. (1). Then, the organics in the effluent would be attacked and degraded by $^{\bullet}OH$ to produce CO_2 which is the source of bubbles. Meanwhile, it can be observed from the experiments that the bubbles were not reduced until 180 min. This phenomenon was in accord with the experiment results. As can be seen from Fig. 6, only 38.7% of COD and 23.5% of phosphorus was removed within 60 min. As reaction time increased, the removal efficiency of COD and phosphorus increased quickly. When the reaction time was 240 min, the removal efficiency of COD and phosphorus increased to 79.6% and 65.6%, respectively. Further increase of reaction time did not increase the removal efficiency of COD but gave a slow increase in the removal efficiency of phosphorus. This is because the precipitation of phosphorus lags behind the decomposition of organics. Therefore, the reaction time of 360 min was advisable for the Fenton's oxidation of saponification effluent.

3.5. Experiment results obtained at optimum conditions

According to the results of previous experiments, the optimum conditions for removing COD and phosphorus from saponification effluent were confirmed. A confirmatory experiment under the optimum conditions was repeated and the results are shown in Table 3. The results show that 82.3% of COD and 72.3% of phosphorus is removed under optimum conditions. Meanwhile, the residual concentration of COD and phosphorus in treated effluent are 164 and 4.3 mg/L, respectively, which means a good performance for COD and phosphorus removal.

The picture of saponification effluent before and after Fenton's oxidation is shown in Fig. 7. It can be seen clearly from the picture that the effluent was decolorized completely after Fenton's oxidation and the treated effluent was a clean and transparent solution without peculiar smell. This would benefit from the complete decomposition of P507 and kerosene contained in the saponification effluent. Fig. 8 shows the XRD pattern of the precipitation obtained under the optimum conditions. It can be seen from Fig. 8 that there are two main crystal phases in the precipitation, namely, calcium sulfate ($CaSO_4$), and tricalcium phosphate [$Ca_3(PO_4)_2$]. The calcium sulfate resulted from the precipitation reaction between calcium chloride in the saponification effluent and ferrous sulfate added into the saponification effluent ($CaCl_2 + FeSO_4 = CaSO_4\downarrow + FeCl_2$). The emersion of tricalcium phosphate indicated that the organic phosphorus in the saponification effluent had been changed into inorganic phosphorus and was precipitated by calcium chloride in the saponification effluent according to Eq. (9). This is also in accord with the decrease of phosphorus concentration in the effluent during the Fenton oxidation process.

3.6. Operational costs and economic evaluation of the Fenton oxidation and chemical precipitation process

In the scope of this study, the operational costs of removing COD and phosphorus from saponification effluent through rare-earth separating process by Fenton oxidation and chemical precipitation was estimated. To simplify the calculation, the manpower costs were not taken into consideration and only the costs of chemicals were included in the calculation. The requirements and market prices of the chemicals are listed in Table 4. As shown in Table 4, the highest costs come from the consumption of sodium hydroxide which is the most expensive chemical in this process. The treatment cost would decrease from 12.26 to 3.44 $/m^3 if the sodium hydroxide was replaced by calcium oxide to change the pH value. Therefore, it is more economic to change the pH with calcium oxide before chemical oxidation process.

After Fenton oxidation and chemical precipitation process, the phosphorus concentration in the effluent decreased to 4.3 mg/L which is lower than the requirements of Chinese emission standard of pollutants for rare earths industry (P: 5 mg/L, GB 26451-2011). But the COD still exceed the limit of the standard (COD: 100 mg/L, GB 26451-2011). Therefore, the effluent needs further treatment to decrease the COD. Generally, the biodegradability of the organics in effluent improved significantly after the Fenton oxidation process [43]. Thus, the biological treatment will be a good choice for further decreasing the COD of the effluent

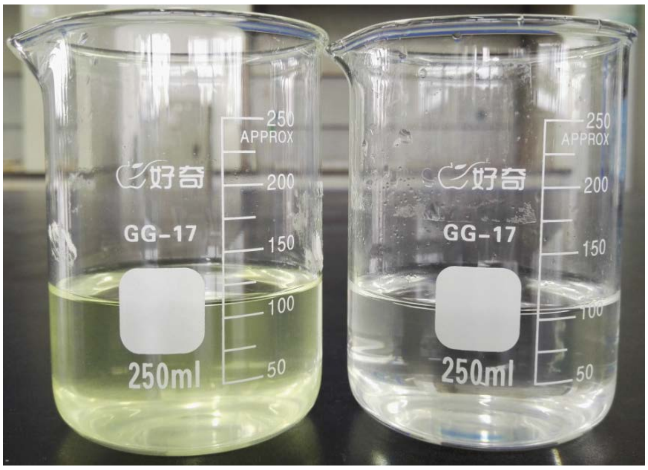

Fig. 7. Saponification effluent before and after Fenton's oxidation.

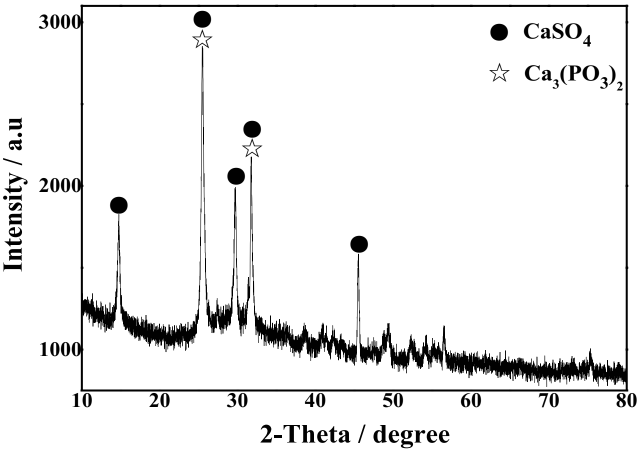

Fig. 8. XRD pattern of the precipitation obtained under the optimum conditions.

Table 3
Results of confirmatory experiment under the optimum conditions (reaction conditions: [$FeSO_4 \cdot 7H_2O$] = 4.8 g/L, [H_2O_2] = 11.9 g/L, pH = 3, T = 25°C, and time = 360 min)

Experimental index	Removal efficiency (%)		Residual concentration in effluent (mg/L)		Absorption value*
	COD	Phosphorus	COD	Phosphorus	
Results	82.3	72.3	164	4.3	0.04

*Absorption value was obtained at 460 nm.

Table 4
Operational costs in Fenton oxidation and chemical precipitation process

Chemicals	Market price ($/kg)	Requirement (kg/m^3 wastewater)	Treatment cost ($/m^3 wastewater)
$FeSO_4·7H_2O$	0.07	4.76	0.32
H_2O_2	0.18	11.9	2.19
NaOH (CaO)	0.42 (0.06)	22.9 (16.1)	9.73 (0.91)
Mixing energy			0.014
Final cost ($/m^3 wastewater)		12.26 (3.44)	

to meet the criterion [18]. While, the cost of the biological treatment is often very low and the total cost of the whole process is acceptable for the manufacturer of rare earth.

4. Conclusions

Fenton oxidation and chemical precipitation were used to remove COD and phosphorus from saponification effluent produced in rare metals metallurgical processes. The removal of phosphorus was closely linked with the degradation of organics because the phosphorus would be precipitated by calcium ion in the effluent after the organic phosphorus was transferred into dissociative phosphate anion. The experimental results showed that degradation of organics and precipitation of phosphorus were strongly influenced by the pH of the solution. The $Fe(OH)^{2+}$ and hydroxyl radicals concentration would reach the peak at pH 3.0, which was beneficial for the degradation of organics and precipitation of phosphorus. The reaction time, H_2O_2 and Fe^{2+} concentration were also important for the removal of COD and phosphorus. Under the optimal reacting conditions with $[FeSO_4·7H_2O]$ = 4.8 g/L, $[H_2O_2]$ = 11.9 g/L, pH of the solution = 3.0, and reaction time = 360 min, 82.3% of COD, and 72.3% of phosphorus were removed and the effluent was decolorized completely. Meanwhile, the COD and phosphorus concentration was reduced from 924 and 15.5 mg/L in saponification effluent to 164 and 4.3 mg/L in treated effluent. This means that the acidic phosphorus-containing extractant in the saponification effluent has been degradated and the organic phosphorus has been changed into inorganic phosphorus and precipitated by calcium chloride.

Acknowledgments

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