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Removal of dianiline dithiophosphoric acid from wastewater by chelate precipitation

Xuanmin Jie, Hui Wang*, Yong Chen

Key Laboratory of Resources Chemistry of Nonferrous Metals, School of Chemistry and Chemical Engineering, Ministry of Education, Central South University, Changsha 410083, Hunan, China, Tel. +86 15200800027; emails: jxmerich@gmail.com (X. Jie), huiwang1968@163.com (H. Wang), 195073094@qq.com (Y. Chen)

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ABSTRACT

Dianiline dithiophosphoric acid (also referred as aniline aerofloat) is an effective collector for mineral flotation and is widely used in China. It causes significant pollution in flotation process, and the degradation characteristics of aniline aerofloat were investigated in this study. Removal of aniline aerofloat from flotation wastewater was studied through chelate precipitation with copper sulfate and polysilicate aluminum ferric (PSAF). Under optimum conditions of copper sulfate 20 mg/L, PSAF 150 mg/L, and pH 8.5, the removal rates of aniline aerofloat, chemical oxygen demand (COD), and total phosphorus of wastewater can be more than 86%, 83% and 88%, respectively. The pH, COD, and residual concentration of copper ions of the wastewater after treatment meet the standards of direct emission. The mechanism of chelate precipitation was further examined, and infrared spectra confirm that copper ions chelate with the two sulfur atoms of aniline aerofloat. This study provides a potential way for dealing with the comprehensive management of mining wastewater.

Keywords: Aniline aerofloat; Flotation wastewater; Chelate precipitation; Organic phosphorus

1. Introduction

Dianiline dithiophosphoric acid, also referred as aniline aerofloat, is a collecting reagent due to its excellent collectivity capacity; aniline aerofloat is widely used as a collector for flotation of Pb-Zn sulfide ore, especially in China [1]. Only a small portion of aniline aerofloat is adsorbed on the particles of flotation concentrates and tailings, the rest is discharged with flotation wastewater [2–5]. Due to its moderate toxicity, it can be toxic to aquatic plants and animals when the concentration is above 20 mg/L, and thus pollutes the environment [3]. In addition, as aniline aerofloat is a kind of organic phosphorus, it can increase the chemical oxygen demand (COD) and the total phosphorus (TP) concentration of flotation wastewater. The natural degradation rate of aniline aerofloat is very low; although degradation occurs under condition of strong acid or strong alkaline, it cannot be completely degraded to inorganics [6]. The hydrolysis product under strong alkaline condition is aniline which even has a greater toxicity. Therefore, it is necessary to treat flotation wastewater by other methods with respect to removal of aniline aerofloat.

Numerous studies have been carried out for aniline aerofloat wastewater (AAW) treatment,

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*Corresponding author.

including chemical, biological, and physical adsorption methods. Activated carbon adsorption can reduce the COD of wastewater containing aniline aerofloat to some extent, but the COD of the treated wastewater is still high. Although chemical coagulation experiments show good results when a high dosage of ferrous sulfate (700 mg/L) was added into wastewater samples, high reagent dosage may increase costs, and moreover, it leads to a high concentration of iron ions(Fe II) which can be easily oxidized to trivalent iron and thus, will increase the chroma of treated wastewater [7]. Sequencing Batch Reactor and Membrane Bioreactor systems have been used as biological methods for AAW treatment [3,8,9]. It was observed that aniline and a substance which was difficult to be biodegraded were produced during the biodegradation process of aniline aerofloat. Fenton reagent and NaClO oxidation methods need high amount of sodium hypochlorite (up to 100 g/L), and ozone oxidation method can also achieve certain effects. Although chemical oxidation methods have excellent COD removal ratios, organic phosphorus wase just oxidized to inorganic phosphorus, since aniline aerofloat is an organophosphorus compound, and high concentrations of total phosphorus could be found in the wastewater after treatment yet. It is very necessary to add a phosphorus removal process behind oxidation process. Most researches focus on the COD removal of AAW. The analysis shows that total phosphorus in the wastewater comes from aniline aerofloat during flotation process. In order to completely solve the pollution of aniline aerofloat, total phosphorus removal should be taken into consideration.

Dipropyl dithiophosphate has been synthesized by Xu et al. and was used as a metal chelator for heavy metal wastewater treatment; research shows that dipropyl dithiophosphate has a strong chelation ability with lead, cadmium, and copper ions [10,11]. Aniline aerofloat has a similar structure with dipropyl dithiophosphate, so it can also generate insoluble chelate salts with heavy metal ions, and it provides a new way for AAW treatment. Since mining production and electroplating industries will always produce wastewater with high concentration of heavy metals, use a copper mine stope, for example, its acidic wastewater can be as high as 101.4 mg/L copper ion concentration. This study tries to use a wastewater management to reduce these two kinds of pollutions at the same time. Taking into account the residual concentration of aniline aerofloat in actual flotation wastewater is usually less than 100 mg/L, at this concentration, although chelation reaction can occur, since the concentration is relatively low, it is difficult for the chelated product to precipitate itself, for it is most likely in the form of colloidal particles. So, same doses of coagulant should be added to accelerate the precipitation process. Currently, there have many types of coagulants, including inorganic salts (alum, ferrous sulfate, ferric chloride, potassium ferrate, etc.), inorganic polymer flocculant (poly aluminum chloride, poly silicate), and organic polymers flocculant (polyacrylamide, etc.) [12–14]. Poly silicate flocculant, especially poly aluminum ferric coagulation has a great advantage on costs and coagulate effects, and was more and more widely used in the field of water treatment in recent years [15,16]. For these reasons, this study used copper sulfate and polysilicate aluminum ferric to remove aniline aerofloat from flotation wastewater. Copper sulfate was used to take chelation reaction with aniline aerofloat, and then polysilicate aluminum ferric was added to precipitate the chelated product, and ultimately carry out the removal of aniline aerofloat, total phosphorus, and COD. In this paper, a comprehensive study of the optimal reaction conditions, including optimal pH and chemicals dosages, and the related reaction mechanism was initially revealed by infrared spectroscopy analysis.

2. Materials and methods

2.1. Materials

Aniline aerofloat and polysilicate aluminum ferric (PSAF) were of technical grade and were used without purification. PSAF was purchased from Hubei Shengshi Environmental Protection Technology Ltd, Co., China, and the purity was 65.5%. The solutions were prepared with distilled water. Copper sulfate and all other chemicals were of analytical grade.

Aniline aerofloat was purchased from Zhuzhou Flotation Reagents Factory, China. Considering the actual situation, aniline aerofloat solutions were prepared with the mass ratio of aniline aerofloat to sodium carbonate 1:3. The initial concentration of aniline aerofloat was 1.00 g/L, and then the solution was diluted into other levels. PSAF and copper sulfate solutions were used as soon as they were mixed. The pH of solutions was adjusted by H_2SO_4 or NaOH.

2.2. Methods

2.2.1. The standard curve of aniline aerofloat solution

Ultraviolet (UV) spectrophotometry was determined with a UV–vis spectrophotometer UV-2450 (Shimadzu Corporation, Japan). The standard curve of aniline aerofloat solution was prepared in advance using UV spectrophotometry at the wavelength of 232 nm, where aniline aerofloat solution has a strong absorbance. Through linear fitting by Origin 8.0 software, the standard curve of aniline aerofloat solution was shown in Fig. 1, it can be seen that the relationship between the absorbance and the concentration of aniline aerofloat solution can be shown as the linear regression equation of $Y = 0.01202 + 0.0418X$, where X is the mass concentration of AAW, mg/L; Y is the corresponding absorbance, cm^{-1}. When an absorbance value is known, the concentration of aniline aerofloat can be calculated based on the above equation.

2.2.2. Fourier transform infrared measurement

In order to examine the mechanism of chelate precipitation, Fourier transform infrared (FT-IR) measurement was conducted with a FT-IR spectrometer AVATAR360 (Nicolet Corporation, America). The chelated product was dried to a constant weight in a vacuum drying box at the temperature of 70°C and the dried chelated product was ground to 200 mesh, as well as the aniline aerofloat powder, then both of them were analyzed.

2.2.3. Chelating precipitation experiments

Aniline aerofloat water samples used in the chelating precipitation experiment were diluted from 1.00 g/L to 50 mg/L. Control pH value of wastewater and certain amount of copper sulfate solution was added into 400 mL aniline areofloat water samples under a stirring speed of 200 r/min for 10 min. Then certain amount of PSAF solution was added as coagulant and was stirred rapidly at 100 r/min for 30 min. All of the above processes were carried out in 500 mL beakers with several single-paddle gang stirrers at room temperature. After settling for 1 h, the supernatant was taken from beakers and further analysis was conducted.

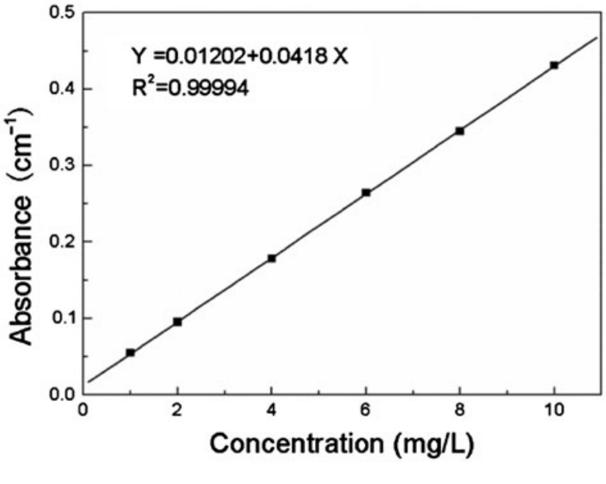

Fig. 1. The standard curve of aniline aerofloat solution.

Through the previous experiments, the optimal pH value of the chelating flocculation precipitation reaction has been found out. Then the optimal dosages of copper sulfate and PSAF were studied independently. Under the pH level of the optimal pH value, the doses of copper sulfate were maintained at 50 mg/L, while the doses of PSAF were changed with the dose values of 50, 100, 150, 200, 250, and 300 mg/L. After a detailed analysis and calculation, aniline aerofloat removal rate, COD removal rate, and TP removal rate could be worked out. The optimum dosage of PSAF could be known by comparing these results. Then the dose of PSAF at the optimum dosage was maintained, while the doses of copper sulfate of the five samples were set as 10, 20, 30, 40, and 50 mg/L, respectively. Not only the aniline aerofloat removal rate, COD removal rate, and TP removal rate, but also the residue content of Cu^{2+} was analyzed. By this way, an optimal dose of copper sulfate could be worked out.

Determinations of COD and TP were according to the methods of the China National Standards GB11914-89 and GB11893-89, and pH was analyzed by a portable PH meter PHB-4 (Shanghai Leici Corporation, China). Determination of the concentration of AAW was achieved by UV spectrophotometry using a UV–vis spectrophotometer UV-2450 (Shimadzu Corporation, Japan). And a copper ion water quality detection kit (Hangzhou Lu Heng Biological Technology Co., Ltd., China) was used to measure the residual concentration of Cu^{2+} roughly.

3. Results and discussion

3.1. Effect of pH on aniline aerofloat degradation

Fig. 2 shows the degradation ratios of AAW samples at pH 1.0–13.0. When the pH value is lower than 3.5, the resolution ratio of aniline aerofloat increases with the decrease in pH. Between the pH values of 3.5 and 2.5, changes are most intense, the resolution ratio of aniline aerofloat increases from 21.6 to 66.2%. When it comes to the range of $\text{pH} < 2.0$, the resolution ratio increases slightly from 68.2% at pH 2.0 to 70.6% at pH 1.0. In the case of strong alkaline condition, phenomena are similar. The resolution ratio of aniline aerofloat increases with the increase in pH, and it is up to 62.1% at pH 13.0. While when pH is between 4.0 and 11.0, aniline aerofloat shows a good stability. All of the resolution ratios were lower than 5%, especially when pH ranged from 6.0 to 10.0. It seems that aniline aerofloat can be removed from wastewater when treatment in strong acid or alkali condition, at some level.

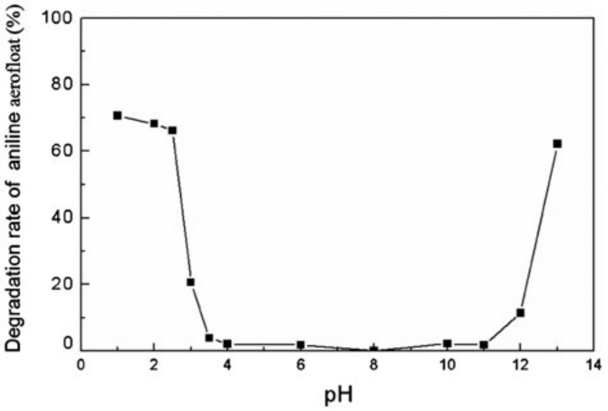

Fig. 2. Influence of pH values on aniline aerofloat degradation.

The structure of the sample which had been acid treated at a pH value of 2.0 was characterized by UV absorption spectrum, and the spectrogram is shown in Fig. 3(b). There is an absorbance maximum at 213 nm and it is different from the UV absorption spectra of aniline aerofloat solution, Fig. 3(a). Aniline aerofloat in the wastewater seems to be removed, but the removal is not incomplete, the product is still in the form of organic matter. And the total phosphorus of the waste water has no change, as no precipitate has been generated. Moreover, because of the excessive acidity or alkalinity, the wastewater after treatment cannot be emitted directly. So, other methods should be studied. The decomposition reaction equations of aniline aerofloat under strong acid and alkali conditions are likely as follows [17]:

$$2(C_6H_5NH)_2PSSH + 8H_2O \xrightarrow{H^+} 4C_6H_5NH_2 + 2H_2PO_4 + H_2S\uparrow \tag{1}$$

$$(C_6H_5NH)_2PSSH + 7NaOH \longrightarrow 2C_6H_5NH_2 + Na_3PO_4 + 2Na_2S + 3H_2O \tag{2}$$

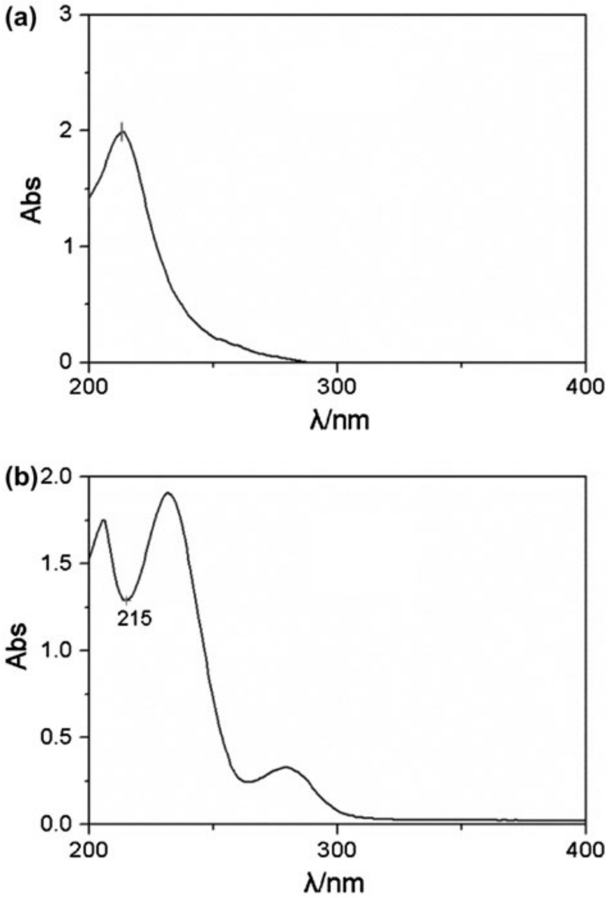

Fig. 3. UV absorption spectra of the treated sample (a) and aniline aerofloat (b).

3.2. Treatment of AAW

Different from the preparation of chelating precipitation, the AAW solution used in this part was prepared with a mass concentration of 50 mg/L rather than 1.0 g/L, which was similar to the actual situation. In high concentration, precipitation will be easily settled. But when the concentration is reduced to a level of dozens of ppm, things become different. A dose of 50 mg/L copper sulfate, which means 50 mg copper sulfate addition for per liter wastewater, was added into the AAW. As soon as copper sulfate was added, the color of the solution turned from colorless to light brown, and without obvious precipitation or turbidity. After several hours stewing, no change was happened at all. It is obvious that the chelate in the solution is in the form of colloidal particles, a simple stewing is useless, and destabilization is needed. PSAF was added as a coagulant to destabilize colloids in the following experiments. Full dose of PSAF was added into the treated wastewater soon under a stirring speed of 100 r/min for 30 min. Desired performance is obtained from the experimental results, and colloidal solution could be destabilized easily. After 30 to 60 min stewing, pale brown flocculent precipitate appeared in the bottom of beaker, and the supernatant turned to be colorless.

3.2.1. Effect of pH on COD removal ratios

Several groups of AAW samples were prepared with the pH values from 5.0 to 10.0. After treated by copper sulfate and PSAF, the detection result of the supernatant of each sample is shown in Fig. 4. The COD removal ratio increases with the decrease in pH when the pH value is between 5.5 and 8.5, from almost zero at pH 5.5 to a COD removal ratio of 87.4% at pH 8.5. Other results are as follows: 9.1% at pH 6.0 (±0.1), 18.4% at pH 6.5, and 56.6% at pH 7.0. When the pH value is higher than 8.5, opposite results are worked out, in other words, the COD removal ratio decreases with the decrease in pH, for a COD removal ratio of 71.0% at pH 9.1 and 31.6% at pH 10. The COD concentration of original wastewater sample is 76 mg/L; after treatment it will decrease to 10 mg/L at pH 8.5. Therefore, the optimal pH value is 8.5.

3.2.2. *Effect of PSAF addition on wastewater treatment*

The effect of PSAF on COD, TP, and the aniline aerofloat removal ratio was investigated under conditions of pH 8.5 and copper sulfate concentration of 50 mg/L, and the results are shown in Fig. 5. When dose level is between 50 and 200 mg/L, the removal ratio of aniline aerofloat in the wastewater sample increases with the PSAF addition. But when the PSAF addition further increases, it presents a little change with an aniline aerofloat removal ratio of 88% at 200 mg/L PSAF addition and 86% at 250 mg/L. The results of COD removal show similar patterns, the removal ratio of COD increases with the increasing dose of PSAF, from 73.0% at 50 mg/L to 85.5% at 150 mg/L. When it comes to the dose above 200 mg/L, the removal ratios of COD have plateaued, for 85.0% at 200 mg/L and 85.5% at 250 mg/L. TP removal is similar to the case of COD removal. The TP concentration of the original sample is 1.98 mg/L, and when the PSAF addition changes from 50 to 250 mg/L results are as follows: 0.60 mg/L TP concentration at 50 mg/L PSAF, 0.50 mg/L at 100 mg/L, 0.22 mg/L at 150 mg/L, 0.22 mg/L at 200 mg/L, and 0.22 mg/L at 250 mg/L. And the pH values of the wastewater sample after treatment are all around 7.0. All things considered, the optimal dose of PSAF is 150 mg/L, and at which point the concentrations of aniline aerofloat, COD, and TP decrease from 50, 76, and 1.98 mg/L to 6.5, 11, and 0.22 mg/L, respectively, and the pH of treated sample is 6.9. Contents of pH, TP, and COD in the wastewater after treatment meet the concentration limit stipulated in *Lead-zinc Industry Integrated Wastewater Discharge Standard* (GB25466-2010).

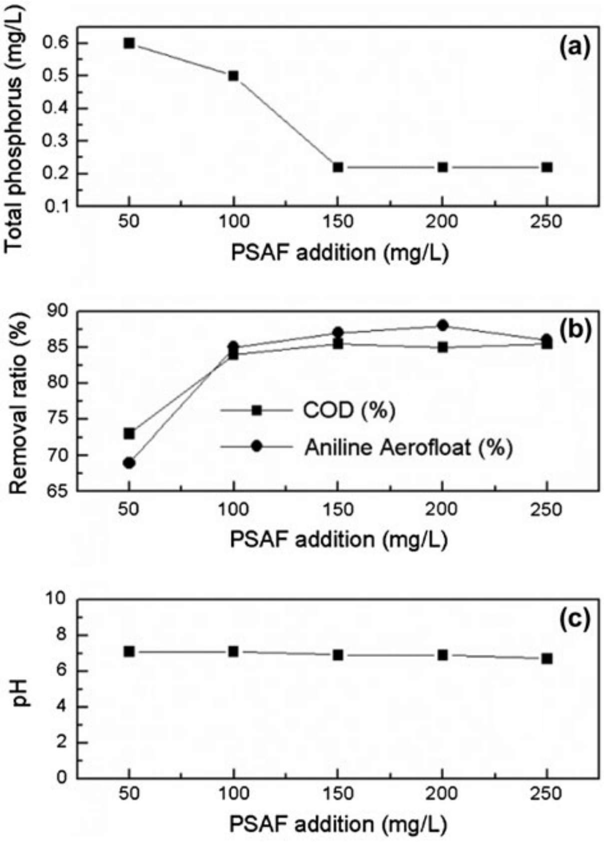

Fig. 5. Influence of PSAF addition on TP (a), COD and aniline aerofloat removal ratios (b), and pH (c).

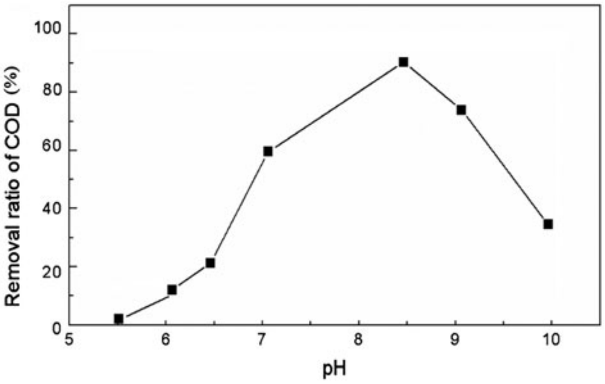

Fig. 4. Influence of pH values on COD removal ratios.

The effect of pH on aniline aerofloat removal when PSAF added only was been studied. A ose of 200 mg/L PSAF was added into five groups of wastewater samples. As shown in Fig. 6, no matter how the pH changes, the removal ratio of aniline aerofloat is always below 15%. Although the removal ratio of aniline aerofloat increases with the increase in pH, results are still unsatisfactory with a highest removal rate of 12% at pH 4.0–12.0.

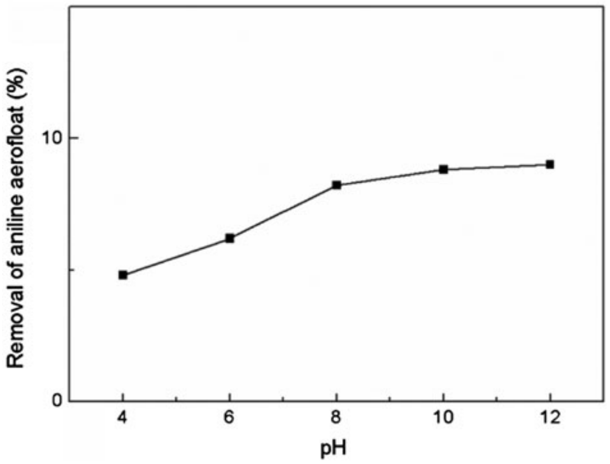

Fig. 6. Influence of pH on aniline aerofloat removal when PSAF was added alone.

This indicates that aniline aerofloat cannot be effectively removed by adding PSAF only. It is likely because that aniline aerofloat solution has a strong thermodynamic stability, and it was not in the form of colloidal particles but a smaller dispersion system or even ions. And a mere adsorption by the flocs formed by PSAF hydrolyzing cannot work effectively for aniline aerofloat removal.

3.2.3. *Optimization of copper sulfate addition*

In order to decrease the secondary pollution caused by copper sulfate, the optimal dose of copper sulfate was further studied. The dose of PSAF was fixed at 150 mg/L, while the doses of copper sulfate were ranged from 10 to 50 mg/L. Fig. 7 shows that when the dose of copper sulfate is lower than 20 mg/L, the removal of aniline aerofloat increases with the increase in copper sulfate. When it is higher than 20 mg/L, changes tend to be at stabilized level. It can be seen that when the dose of copper sulfate is 10 mg/L, the removal ratios of COD and aniline aerofloat are 40 and 36%, respectively, and the concentration of total phosphorus is 1.02 mg/L, which does not meet the standards (GB25466-2010). Table 1 shows the residual concentrations of copper ion and pH after treatment under different copper sulfate doses, from which it can be observed that all the pH values are with little

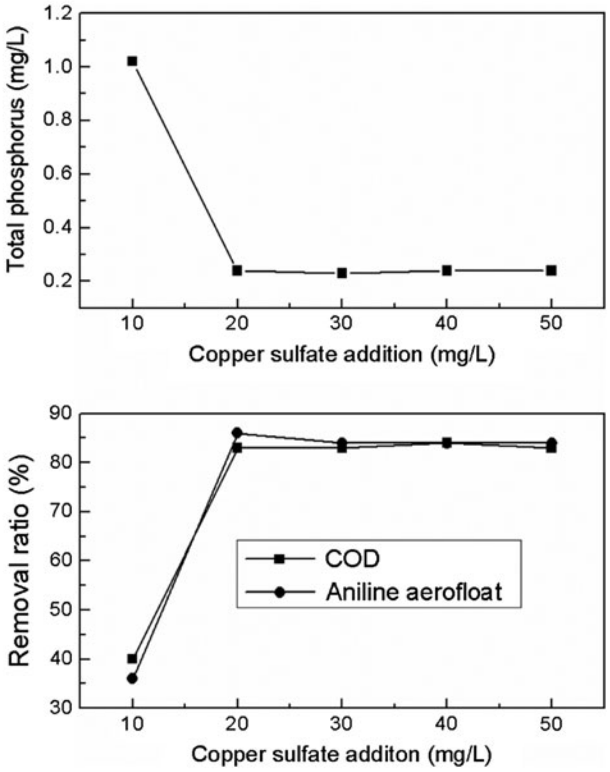

Fig. 7. Influence of copper sulfate on removals of COD, TP, and aniline aerofloat.

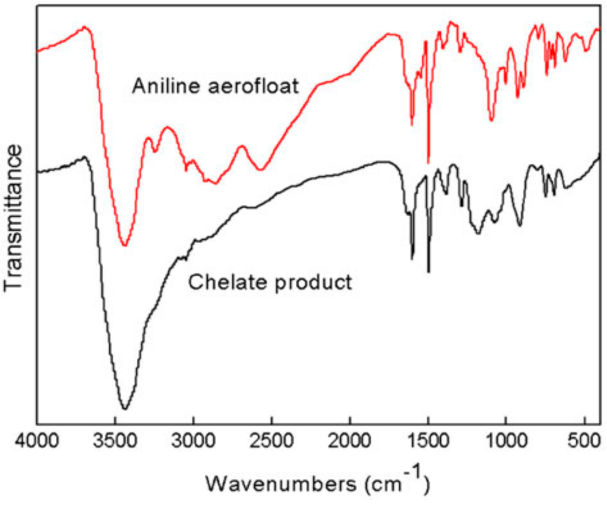

Fig. 8. FT-IR spectra of chelate product and aniline aerofloat.

Table 1
Effects of copper sulfate on pH and copper ion of treated samples

$CuSO_4$/(mg/L)	10	20	30	40	50
pH after treatment	7.7	7.6	7.4	7.2	6.8
Residual of Cu^{2+}/(mg/L)	<0.05	<0.05	<0.05	<0.05	>0.10

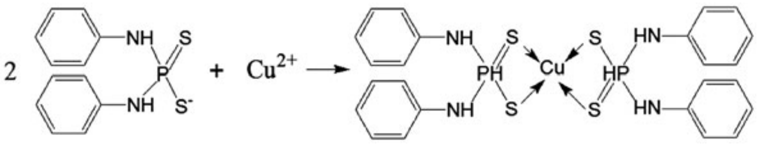

Fig. 9. The mechanism of chelate precipitation.

difference, and they are all around 7.0. When the doses of copper sulfate are 10, 20, 30, and 40 mg/L, the copper ion residual concentrations of the samples after treatment are all below 0.05 mg/L, but 0.10 mg/L or more copper residual will be found at a level of 50 mg/L copper sulfate addition. Although it has reached the maximum removal ratio of aniline aerofloat at 20 mg/L copper sulfate, copper ions residual does not increase with increasing of the copper sulfate. This is most likely because PSAF can reduce the residual concentration of copper ions in a certain extent.

3.3. The mechanism of chelate precipitation

Fig. 8 shows the FT-IR spectra of aniline aerofloat powder sample and chelating product. The stretching vibration frequencies of aniline aerofloat are as follows: Ar–NH 3,430, –SH 2,560, P=S 688, and P–S 550 cm^{-1} [18]. Results are roughly similar, when it comes to the FT-IR spectra of copper chelate, except in some respects, for the characteristic peaks of –SH at 2,560, P=S 688, and P–S 550 cm^{-1} decrease or even disappear. It indicates that Cu^{2+} will make chelate precipitation with the two sulfur atoms of aniline aerofloat, which causes the decrease in the characteristic peaks of –SH and P=S, and the chelate mechanism is shown in Fig. 9 [11].

4. Conclusions

The removal rates of aniline aerofloat, COD, and TP of wastewater treated by copper sulfate and PSAF can be more than 86, 83, and 88%, respectively. The mechanism can be explained that Cu^{2+} will make chelate precipitation with the two sulfur atoms of aniline aerofloat even in a concentration of ppm level, and PSAF facilitates the coagulation sedimentation of colloidal chelate product. The optimum doses of copper sulfate addition and PSAF addition are 20 and 150 mg/L, respectively, and the optimum pH is 8.5. When the copper sulfate doses changes from 20 to 40 mg/L, the residual concentrations of copper ions all meet emission standards, and it will provide a better evidence for removing aniline aerofloat from flotation wastewater by copper wastewater in the actual conditions. Contents of pH, TP, COD, and copper ions in the wastewater after treatment satisfy the concentration limit stipulated in *Lead-zinc Industry Integrated Wastewater Discharge Standard* (GB25466-2010), and the concentration of aniline can be reduced to a level which has no damage with hydrophytes and environment.

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