Experimental Study on Treatment of High-concentrated Sulfur Wastewater by Process of Depositing Natrojarosite and Its Environmental Significance

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Abstract: High-concentrated sulfur wastewater with sodium and COD (chemical oxygen demand) up to 26000 mg/L from a chemical plant, Jiangsu Province of China has been treated by deposition of natrojarosite in lab. The results indicated that the COD of the wastewater was decreased sharply from 26000 mg/L to 1001 mg/L, with removal rate of COD up to 96% by twice precipitations of natrojarosite and twice oxidation of H₂O₂. The treated sulfur wastewater reached the requirement of subsequent biochemical treatment to water quality. The optimal operational parameters should be controlled on pH value between 2.50 and 3.20 and 50 g FeCl₃·6H₂O solid added in per liter wastewater and proposed a new mineralogical method on treatment of other wastewaters. Depositing process of jarosite and its analogs should be able to be used to treat wastewater from mine and other industries to remove S, Fe and other toxic and harmful elements, such as As, Cr, Hg, Pb, etc. in the water.

Key words: natrojarosite, high-concentrated sulfur wastewater, COD, environmental significance

1 Introduction

A great mass of sulfur wastewater is often yielded from the producing processes of many industries such as oil refinery, chemical works, pharmaceutical factory and tannery and so on, which threats seriously public health and the environment due to toxicity, corrosiveness and stink of the sulphide in the wastewater. Therefore, these sulfur wastewaters must be properly treated. Generally, various methods of treatment were adopted in the light of different source and concentration of the wastewater. At present, main techniques treating the sulfur wastewater included oxidation, neutralization, precipitation, gas stripping, etc., in which general oxidation could not provide high treating rate, neutralization and gas stripping could cause the second pollution due to their subsidiary SO₂, SO₃, H₂S products and wet air oxidation is hardly wide-ranging spread because of its expensive operating costs and difficult operation (Jiang et al, 2004; Yu et al, 2003). So there is an urgent need to develop effective methods to control the sulfur wastewater.

High-concentrated sulfur wastewater with a great deal of

Na⁺, S²⁻, S₂O₃²⁻, SO₄²⁻ has being yielded from the producing processes of a certain chemical plant, Jiangsu Province. The wastewater was alkaline with pH value 13.3 and orange in color and its COD value gets to 26000 mg/L. Moreover, there existed a reaction equilibrium of low-valence S and high-valence S (S₂O₃²⁻, S²⁻) \leftrightarrow SO₄²⁻ + ne- in the wastewater. If this high-concentrated sulfur wastewater was managed together with other industry organic wastewater directly, the cost and difficulty of subsequent process would be augmented. Therefore, it was better to pre-treat the sulfur wastewater by itself. However, it was very difficult to reduce COD of the high-concentrated sulfur wastewater with conventional methods mentioned above.

The method of depositing jarosite or its analogs has become a mature technology removing iron since the 1960s (Zou, 1998). The technique is that under a certain temperature, acidity and existence of ammonium or alkaline metal cations, Fe^{3+} in solution is combined into minerals of jarosite or its analogs and precipitated down. Jarosite or its analogs are indissoluble in thin acids and easily deposited, washed and filtered. Consequently, Fe^{3+} can be easily removed from soak solution.

In fact, minerals of jarosite group which may fix Fe³⁺ and

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Fig. 1. Effect of pH on the COD removal rate.

 SO_4^{2-} distribute widely in the zone of weathering of the Earth. Simulating their natural forming process should have potential important role in treatment of high-concentrated sulfur wastewater. This paper proposed a new technology treating high-concentrated sulfur wastewater by using the process of formation and precipitation of jarosite and its analogs, which provides theoretical basis and experimental parameters for engineering design of the sulfur wastewater treatment.

2 Experiment Method

The wastewater samples with COD 26000 mg/L and pH value 13.3 for experiment were from industrial wastewater yielded from a chemical plant, Jiangsu Province of China.

In the experiment, a certain quantity of sulfur wastewater was taken to make up experimental solutions in conical flasks in which a certain quantity of FeCl₃ solutions, which made up by HCl solutions with pH value about 1 and FeCl₃·6H₂O (analytical reagent) solids were added. The pH value of the solutions was adjusted by 0.5M KOH solutions. After shaking well and reacting for 6-8 hours at room temperature, the solutions were filtered to get the filtrates and COD values of filtrates were determined. Furthermore, 30% hydrogen peroxide was added to the filtrates, and the pH values of the filtrates were adjusted to 3.0. After reacted for 1 hour with magnetic stirring at room temperature, the filtrates were filtered again and get the second filtrates, then the COD values of the second filtrates were measured. The precipitates obtained were dried naturally and analyzed by XRD to determine their components.

Chemical oxygen demand (COD) and pH values of experimental samples were measured by a CTL-12 type COD Tester and a pHs-2C type digital pH Meter, respectively. A HJ-6 type multi-point heating magnetic stirrer were used to stir samples. The precipitates were identified using a high-power (1200KV) rotating anode Xray diffractometer (RIGAKU-RA) made in Japan in the College of Chemistry and Molecular Engineering, Peking University, with analysis conditions: CuK radiation, scan range $20: 2.6^{\circ}-75.0^{\circ}$ and scan rate $8^{\circ}/\text{min}$.

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3 Experimental Result

3.1 Effect of pH on COD removal rate of the wastewater

At room temperature, a series of 100 mL actual sulfur wastewaters were put in seven 250 mL conical flasks in which 100 mL 0.5 M FeCl₃ solutions were added in each flask. The flasks were shaken continuously so that the solutions get homogeneous. At this time, the pH value of the solutions was at 0.81. Then using 0.5 M KOH solution, the pH values of solutions in six flasks were adjusted to 1.50, 2.40, 2.75, 2.84, 3.18 and 3.54, respectively. When the pH values of the mixed solutions was at 0.81 and 1.50, there hardly were precipitates occurring and the color of the solutions turned dark to some extent. With increasing pH value of the solutions, the solutions got turbid gradually. There occurred some precipitates on the bottom of the flasks after standing. After standing for 8 hours, the solutions were filtered and the COD values of the filtrates were determined. The COD removal rates of the wastewaters under different pH values are shown in Fig. 1.

From Fig. 1, it can be seen that while the pH value of the solutions were between 0.8–2.0, COD removal rates of the wastewater was about 40% by precipitating treatment and its change is very little, and while the pH value were between 2.5–3.2, the COD were dropped over 50%, with the highest removal rate up to 54.6% at pH 2.75. In the experiments, KOH solution was used to adjust the pH value of the wastewater, since jarosite forms more easily than natrojarosite and could be the seed to fasten the speed of precipitation (Dutrizac, 1996).

3.2 Effect of quantities of FeCl₃ on the COD removal rate

At room temperature, a series of 100 mL actual sulfur wastewaters were put in 7 conical flasks of 250 mL, in which 50 mL FeCl₃ solution dissolving 2.0 g, 2.5 g, 4.0 g, 5.0 g, 6.0 g, 7.0 g and 8.0 g of analytical grade $FeCl_3 \cdot 6H_2O$ solid reagent were added respectively. Dilute hydrochloric acid was used to dissolve FeCl₃·6H₂O as the solvent and the pH values of the experimental solutions were adjusted to about 2.75 by 0.5M KOH solution. After shaken well, the solutions got turbid suspension. After standing for half an hour, the solutions turned clear and a number of precipitates occurred on the bottom of the flasks. After standing for 8 hours, the solutions were filtered and the CODs of the filtrates were measured, with the results of 15756, 14950, 13364, 12376, 12272, 12194 and 11908 mg/L respectively. The COD removal rate of the wastewaters under different FeCl₃·6H₂O solid contents were illustrated in Fig. 2.

Table 1 Kemoval fatt of COD after deposition and oxidation				
	First deposition	First oxidation	Second deposition	Second oxidation
Reaction time (h)	8	1	8	1
Concentration of COD (mg/L)	15028	8023	3825	1001
Removal rate of COD (%)	42.20	69.14	85.29	96.15

 Table 1 Removal rate of COD after deposition and oxidation



Fig. 2. Effect of quantities of $FeCl_3 \cdot 6H_2O$ solid reagent on the COD removal rate.

Figure 2 showed that the more quantity of the FeCl₃· $6H_2O$ was added, the higher the COD removal rate of the wastewater was. While the FeCl₃· $6H_2O$ content added was within 2.0–5.0 g, the COD removal rate had a rapid increase, whereas the FeCl₃· $6H_2O$ content within 5.0–8.0 g, the increase of the rate trended to slow. So, in the interest of economy, 5.0 g FeCl₃· $6H_2O$ added in 100 mL wastewater would have a good comprehensive effect and the COD removal rate could be up to 52.4%.

3.3 Effect of twice deposition and oxidation on the COD removal rate

200 mL high-concentrated sulfur wastewater was put into a conical flask in which then 50 mL FeCl₃ solution made up by dulite HCl solution with pH value lower than 1 and 0.5 g FeCl₃·6H₂O (analytical reagent) was added. The pH value of the experimental wastewater solution was adjusted to 2.50–3.20 by 0.5M KOH solution. The flask was shaken continuously until the solution was homogeneous. After standing and reacting for 6–8 hours, the solution was filtered and the COD of the filtrate was determined. Next, 30% hydrogen peroxide was added to the filtrate in volume ratio 1/20 and the pH value of the filtrate was adjusted to 3.0. After reacting for 1 hour on the magnetic stirrer, the filtrate was filtered again and COD value of the second filtrate was measured.

After that another 50 mL FeCl₃ solution dissolving 5.0 g FeCl₃·6H₂O solid reagent was put in the second filtrate and the second filtrate was stood and reacted for 6–8 hours. Then the second filtrate was filtered and the COD of the third filtrate obtained was analyzed. Next, 30% hydrogen peroxide was added to the third filtrate in volume ratio 1/40 again and the pH value of the third filtrate was adjusted to 3.0. After reacting for 1 hour with magnetic stirring at room

temperature, the COD of the wastewater was determined again.

Through twice precipitation and oxidation, the COD of the original sulfur wastewater up to 26000 mg/L was dropped down to 1001 mg/L. The experimental results are listed in Table 1.

The first precipitation dropped the COD concentration of the wastewater from 26000 mg/L to about 15000 mg/L and got the COD removal rate at about 42.20%. In order to transform more low-valence S ($S_2O_3^{2^-}$, S^{2^-}) to SO₄^{2⁻}, the wastewater filtrate was oxided using H₂O₂ before the second precipitation. The filtrate after the second precipitation had its COD value at 3825 mg/L and the removal rate of COD was up to 85.29%. Through the second oxidation, the COD of the wastewater was dropped to 1001 mg/L and the total removal rate of COD was up to 96.15%.

The experimental results indicated the twice precipitation and oxidation had a better effect on the treatment than only one time, which lowered greatly the COD of the wastewater and made the wastewater meet the requirement of subsequent biochemical treatment.

3.4 Component identification of precipitates

The precipitates obtained by precipitation and filtration were dried under room temperature and XRD analysis was carried out on them. The representative XRD pattern was illustrated in Fig. 3. The results indicated that the precipitates were made up of major natrojarosite NaFe₃ $(SO_4)_2(OH)_6$ and minor hydronium jarosite $(H_3O)Fe_3(SO_4)_2$ $(OH)_6$ (Wang et al., 1987).

4 Discussion

The experimental treatment of high-concentrated sulfur wastewater containing sodium from a chemical plant, Jiangsu Province by precipitating natrojarosite indicated that the precipitation method could help to lower the COD of the sulfur wastewater and made it meet the requirement of subsequent biochemical treatment. The experiment of the effect of pH value revealed that natrojarosite precipitated easily and its precipitation could yield a positive disposal effect of SO₄²⁻ and the COD of the wastewater in pH value between 2.5–3.2 at room temperature, which was consistent with the studies of Chen et al. (1991) that the pH value for forming jarosite



Fig. 3. X-ray diffraction pattern of precipitate. $a-NaFe_3(SO_4)_2(OH)_6; b-(H_3O)Fe_3(SO_4)_2(OH)_6.$

precipitation was between 2.0–3.0 at 20°C and 1.0–2.3 at 100°C. When the pH value was higher than 3.2, more Fe^{3+} tended to be precipitated as $Fe(OH)_3$, which decreased the removal rate of SO_4^{2-} and accordingly also affected the COD removal rate of the solution.

The wastewater had high concentration of Na⁺, SO₄²⁻, and furthermore the concentration of SO₄²⁻ in the wastewater was so high that the low-valence S (S₂O₃²⁻, S²⁻) could not go on transforming to SO₄²⁻, which led to so high COD in the wastewater that it was descended difficultly. In the light of the principle of iron removal by jarosite and its analogs, just the suitable amount of Fe³⁺ was added into the wastewater with highly-concentrated Na⁺ and SO₄²⁻ and made these ions precipitating down as natrojarosite NaFe₃ (SO₄)₂(OH)₆ in the experiment, using the properties of jarosite and its analogs to be precipitated and separated easily from the solutions. The reaction is shown as the following:

 $Na^{+} + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow NaFe_3(SO_4)_2(OH)_6 + 6H^{+}$

The precipitation of natrojarosite broke directly the equilibrium of low-valence S and high-valence S (S $(S_2O_3^{2^-}, S^{2^-}) \leftrightarrow SO_4^{2^-}$ +ne-) existing in the wastewater, which caused the high COD of the wastewater difficulty to be lowered. The decrease of $SO_4^{2^-}$ in solution made low-valence S $(S_2O_3^{2^-}, S^{2^-})$ go on transforming to $SO_4^{2^-}$, and then the COD of wastewater was dropped down. Oxidation of H₂O₂ further increased the transformation from S $(S_2O_3^{2^-}, S^{2^-})$ to $SO_4^{2^-}$ and reduced the COD of the wastewater.

In the experiment, oxidation and deposition promoted each other. Unreacted Fe³⁺ in the first depositing process would catalyze subsequent oxidation of H₂O₂, which accelerated the reaction and shortened the time of oxidation (Peng, 1985). Moreover, H₂O₂ with strong oxidation would transform low-valence S to SO₄²⁻ and lead the increase of SO₄²⁻ concentration in the wastewater in turn, which would be advantageous to the second precipitation and cut down effectively the COD in the wastewater. The study of Lu et al. (1994) revealed that H_2O_2 had the best disposal effect on COD and the oxidizing reaction need to last the shortest time under the conditions of pH value at 3.0 and the existence of Fe³⁺ as catalyzer; besides, higher concentrated Fe³⁺ was advantageous to the increase of reaction speed, whereas lower ones stayed the decomposing rate of H_2O_2 and prolonged the time of reaction. Therefore, precipitation should be carried out firstly and followed by oxidation of H_2O_2 in the treatment experiment and pH value should be adjusted to about 3.0 in the oxidizing treatment.

The treatment of precipitation and oxidation not only lowered effectively COD of the sulfur wastewater from Jiangsu and made it meet the requirement of subsequent biological treatment for water quality, but also deposited and fixed sulfur as natrojarosite, which laid a foundation for retrieving of S in the wastewater. In addition, industrial level FeCl₃ solution would be considered to utilize in order to reduce the cost of treatment of the wastewater during large-scale industrial process.

As far as jarosite is concerned, the main chemical composition is Fe and K besides SO_4^{2-} , with a chemical formula of KFe₃[SO₄]₂(OH)₆. There often are Na⁺, NH₄⁺, Ag^+ , H_3O^+ , Tl^+ and so on to substitute K and Cr^{3+} , V^{3+} , even lanthanides occurring in the Fe site. Furthermore, besides respective univalent and trivalent cations substitute each other in the K and Fe sites, there are still bivalent ions Ca^{2+} , Ba²⁺, Pb²⁺, Hg²⁺, etc. occurring in the K site (Dutrizac et al., 1996). At this case, for the balance of electrovalence, there would be some bivalent cations substituting trivalent cations or vacant sites in the K site. Moreover, $[SO_4]^{2-}$ can also be substituted partially by complex anions $[SeO_4]^{2-}$, [CrO₄]²⁻, [PO₄]³⁻, [AsO₄]³⁻, [CO₃]²⁻, [SbO₄]³⁻, [SiO₄]⁴⁻, etc. (Baron and Plamer, 2002; Courtin-Nomade et al., 2003; Drouet et al., 2003; Prieto et al., 2002). Therefore, the formation of jarosite and its analogs should be able to be used to fix and remove many harmful elements, such as S, As, Cr, Hg, Pb, etc. in wastewater because of their widerange and strong isomorphism. A good chromium removal effect have been got using the formation of jarosite and ammoniojarosite to treat simulated chromium wastewater (Wang et al., 2006).

5 Conclusions

The experimental studies on the treatment of highconcentrated sulfur wastewater with sodium and COD up to 26000 mg/L from a chemical plant, Juangsu Province by deposition of natrojarosite showed that through twice precipitations of natrojarosite, adding twice oxidation of H_2O_2 , the COD of the wastewater was decreased sharply from 26000 mg/L to 1001 mg/L, with the COD removal rate up to 96%. The treated sulfur wastewater met the requirement of subsequent biochemical treatment to water quality. The optimal operational parameters should be controlled on pH value between 2.50 and 3.20 and 50 g FeCl₃·6H₂O solid added in per liter wastewater.

The study provided an experimental basis for a pretreatment of high-concentrated sulfur wastewater and proposed a new mineralogical method on the treatment of other wastewaters. Depositing process of jarosite and its analogs should be able to be used to harness wastewater from mine and other industries to remove S, Fe and other toxic and harmful elements, such as As, Cr, Hg, Pb, etc. in the water.

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