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Approaching Zero-discharge with Cleaner Production: Case Study of a Sulfide Mine Flotation Plant in China

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ABSTRACT: In order to decrease the discharge from sulfide mine flotation plants, treatment and reuse approaches based on our previous wastewater monitoring experiments were explored in these plants. The flotation wastewater was collected from the case plant and was treated with coagulation sedimentation and activated carbon adsorption. Then, the effluent was examined for reuse in the flotation process. Furthermore, the effluent was also treated with sodium hypochlorite oxidation to avoid pollution in case effluent happened to be discharged accidently. The results showed that flotation wastewater pollutants could be eliminated effectively and reuse of the effluent did not cause adverse effects, during the six-year application of this procedure. In addition, flotation reagent consumption was greatly reduced, since the effluent containing mostly foaming agents could be reused. Thus, this method proved to be environmentally friendly due to the decreased use of fresh water as well as being economically beneficial.

Key words: Cleaner production, Zero-discharge, Sulfide mine flotation wastewater, Coagulation sedimentation, Activated carbon adsorption

INTRODUCTION

The sulfide mine flotation process consumes large amounts of fresh water and requires many chemical materials such as depressants and foaming agents. As a result, the process produces vast quantities of wastewater and the discharge contains complex chemicals which causes heavy pollution (Tu, 1998). Furthermore, the components of the wastewater vary a lot depending on the specific mine components. Usually it consists of gangue and product condensing water, where various organic and inorganic constituents are brought into contact in order to separate different products.

The discharge is characterized by high organic load, high-suspended solids, and intense foamability. In addition, conventional environmental technologies can easily be applied (Xie *et al.*, 2005). Many methods have been used for the treatment of sulfide mine flotation wastewater (Rubio *et al.*, 2007; Wei and Zhou, 2007; Zheng and Bin, 1998; Li *et al.*, 2009). The most common method is coagulation-flocculation followed by gravity sedimentation (Mackie *et al.*, 2009; Eilbeck and Mattock, 1987; Wang, 2000; Chong *et al.*, 2009; Olga and Helen, 2002; Haydar and Aziz, 2009). Less commonly applied methods include adsorption (Haydar and Aziz, 2009; Jagtoyen *et al.*, 1991; Wei *et al.*, 1994; Asubiojo and Ajelabi, 2009; Rivera-Utrilla *et al.*, 2009) and biodegradation (Chen *et al.*, 2009; Zhang et al., 2009; Yang *et al.*, 2009). Some advanced treatment methods such as chemical oxidation (Qiu *et al.*, 2006), and electrochemical oxidation (Mahmoud, 2009; Ataei *et al.*, 2009) have been explored. However, up until now no general rules have been safely established and each particular wastewater should be handled individually.

Due to low treatment cost and operation complexity, coagulation is a widely used method to remove turbidity and suspended solids (Wang, 2000; Biati *et al.*, 2010; Saeedi *et al.*, 2007). Coagulants are ionic in nature and can enhance aggregation by destabilizing the electrostatic forces of the suspension. Many soluble inorganic salts can be used as coagulants. However, only some, such as aluminum and iron salts, are used in full-scale operations. Polymerized forms of iron and aluminum salts are also used, including polyaluminum chloride (PACl). More

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recently, organic coagulants have largely replaced traditional inorganic agents. Most commercial polymeric flocculants (polyelectrolytes) are either cationic copolymers of acrylamide with a monomer or ammonium-based polymers, with charges randomly distributed along the backbone chain. Anionic and nonionic (polyacrylamides) are also used.

Furthermore, the pH value of the water for the flotation process needs to be between 11.0-11.7. If the pH of the discharge is adjusted to about 7 in the treatment, then it would have to be readjusted again when it is reused for the flotation process. As a result, the treatment cost would increase a lot and the treatment process would become more complex and difficult to control. Therefore, the study described herein does not change the pH value except for the oxidation process. According to our previous research results on wastewater modeling, pollutants such as chemical oxygen demand (COD) of the discharge of the sulfide mine flotation process can be treated effectively using coagulation sedimentation and activated carbon adsorption. The effluent can be reused completely in the flotation process (Yang et al., 2008; Yuan et al., 2002). In order to ensure this technology can be applied successfully in practice, the same treatment technology was carried out and analyzed on wastewater from a state-owned sulfide mine flotation plant in Jiangsu province (China) for more than six years with a treatment capacity of about 3500 tons of flotation wastewater per day.

MATERIALS & METHODS

Raw wastewater was collected from the case flotation plant effluent. Pollution load in the wastewater was expressed in terms of chemical oxygen demand (COD), lead (Pb) concentration, and foamability. Foamability was expressed in terms of COD because foaming agents are organic. Amounts of suspended solids (SS), pH, turbidity (NTU), and sulfate ion (SO_4^{2-}), copper (Cu), chloride ion (Cl^-), and zinc (Zn) concentrations were measured as well. Inorganic pollutants were expressed as Pb concentration because the product qualities would worsen if the treated water was reused for the flotation process. The characteristics of the wastewater used in this study are presented in Table 1.

Table 1. Wastewater characteristics

Parameter	Range
pH	11.0-11.7
Chemical oxygen demand (mg/L)	380-400
Lead (mg/L)	60-90
Suspended solids (mg/L)	380-410
Turbidity (NTU)	210-230
Sulfate ion (mg/L)	900-1000
Copper (mg/L)	0.1-0.2
Chloride ion (mg/L)	60-70
Zinc (mg/L)	2.0-4.0

Analytical grade $KAl(SO_4)_2 \cdot 12H_2O$ (Alum, Linyi Jinhuang Chemical Co., Ltd), polyacrylamide (Shanghai Yi-heng Chemical Co., Ltd), powdered activated carbon (Shanghai Jinhu Activated Carbon Co., Ltd), and sodium hypochlorite (Tiankai Chemical Co., Ltd) were used. Their characteristics are reported in Table 2. Their concentrations are based on 100% active material. Coagulation effectiveness on flotation wastewater was established through on-site jar tests. A jar test unit with a seven-paddle-stirrer, manufactured by Shenzhen, Guohua, China, was used for the coagulation experiments. The following test procedure was used: homogenization in 1000 L beakers, rapid mixing with addition of coagulant at 100 rpm for 1 min, polyacrylamide addition without stopping mixing for 1 min, flocculation at 25 rpm for 5 min, and settling for 30 min. The optimum coagulation dose was based on the quality of the treated wastewater parameters, while the optimum coagulant dose corresponded to either the quantity of chemical where the minimum values of residual Pb and COD were obtained (as in the case of the polyacrylamide application) or to the quantity of chemical beyond which no significant amelioration was achieved (as for the rest of the chemicals used).

The adsorption effectiveness and adsorption time were established through jar tests on the coagulation effluent. The following test procedure was used: rapid mixing with addition of powdered activated carbon at 60 rpm for 10 min and settling for 30 min. The optimal adsorption agent dose and adsorption time were determined using the coagulation process procedure. The optimal sodium hypochlorite dose, pH, and oxidation time were established through jar tests on the coagulation effluent. The following test procedure

Table 2. Characteristics of the reagents used in this study

Reagent name	Molecular weight	Concentration (%)	Molecular formula
Alum	378	99.0	$KAl(SO_4)_2 \cdot 12H_2O$
Polyacrylamide	10 million	-	$(CH_2)_2CONH_2$
Powdered activated carbon	12.01	-	C
Sodium hypochlorite	56.5	99.5	NaClO

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was used: rapid mixing with adjustment of pH with vitriol and sodium hydroxide at 40 rpm for 30 min, and filtering. The optimum sodium hypochlorite dose was determined as above.

The pH measurements were conducted using a PHS-3 portable glass electrode pH meter (Shanghai LEICI Instrument Factory, Shanghai, China). COD was measured using a spectrophotometer (model 721, Third Analytical Instrument Factory of Shanghai, China) and a COD Reactor (Chengde Environmental Protection Instrument Factory, Hunan, China). The metal concentrations were measured using an atomic absorption spectrometer (HITACHI, Hitachi, Japan). Suspended solids (SS) were measured according to APHA-AWWA-WPCF (Clesceri, *et al.*, 1998).

RESULTS & DISCUSSION

Coagulation Sedimentation Tests

The dose response curves of Alum on Pb concentration and COD removal are presented in Fig. 1. A dose of 20 mg/L of Alum was adequate to substantially reduce the Pb concentration. The efficiency of Pb removal was 98%, while that of COD was only 13.16%. Thus, Alum was found to be an exceptionally effective coagulant under the natural pH value of 11.43. In order to improve the Pb removal efficiency, an additional treatment with a combination of Alum and a flocculent aid was used in this study.

In this experiment, Alum was used as the primary coagulant and polyacrylamide was used as the flocculant aid. The coagulation experiments were carried out at 20 mg/L of Alum, while the polyacrylamide concentration was varied, and the results are shown in Fig. 2. A dose of approximately 0.2 mg/L of polyacrylamide was determined to be optimal in terms of the cost of polyacrylamide and its effect. Thus, Alum was found to attain generally high Pb removal and COD efficiencies and polyacrylamide was determined to be an effective flocculants aid, when Alum was used as the primary coagulant.

For the adsorption and oxidation tests, pollutants were expressed using only COD because the Pb concentration was very low throughout the coagulation process. The flotation indices were not affected if the effluent was reused for the flotation process. The most important role of the oxidation process was to remove the foamability of the effluent, which was expressed in terms of COD.

The powdered activated carbon efficiencies on COD concentration are presented in Fig. 3. A dose of 100 mg/L of powdered activated carbon was determined to be adequate for a substantial reduction in COD. However, the efficiency of COD removal was only 41.18%.

To find the proper adsorption time, experiments were carried out on the coagulation effluent using 100 mg/L of powdered activated carbon. A time of 30 min was chosen as the appropriate adsorption time, based on the results shown in Fig. 4.

The dose response curve showing the effectiveness of sodium hypochlorite on COD removal by wastewater oxidation is presented in Figure 5. A dose of 110 mg/L of NaClO was found to be adequate to substantially reduce the COD concentration, and the efficiency of COD removal was determined to be 26.37%.

To find the proper oxidation time, experiments were carried out on the adsorption effluent using 110 mg/L of NaClO and the results are shown in Fig. 6. The optimum oxidation time was determined to be approximately 30 min.

To determine the proper pH for wastewater oxidation, experiments were carried out using 110 mg/L of NaClO and an oxidation time of 30 min. The results are shown in Fig. 7. NaClO was shown to be a rather effective oxidation agent and the optimum pH for oxidation was determined to be approximately 10.5. The treatment technology was applied to wastewater from a case plant with a treatment capacity of 3,000 tons of wastewater per day. The average values of flotation products in 2002 are shown in Table 3 and those for 2008 are shown in Table 4.

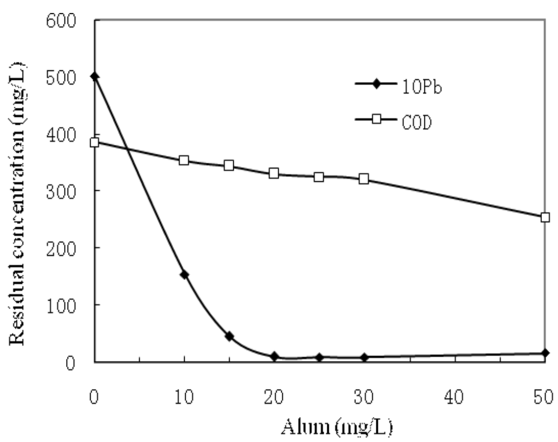

Fig. 1. Dose response curves of Alum on efficiency of wastewater coagulation

Note: 10Pb means that the Pb concentrations were 10 times the value indicated.

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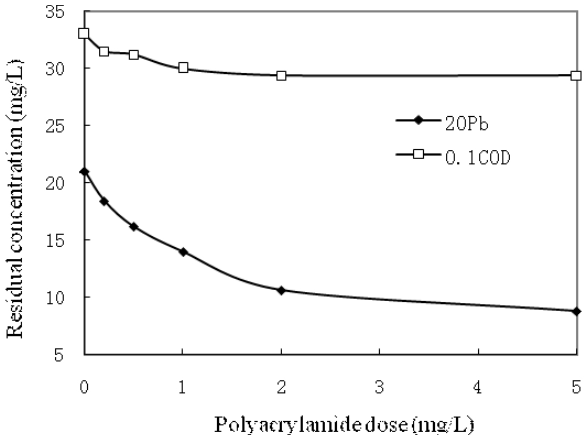

Fig. 2. Effect of polyacrylamide on coagulation efficiency using Alum

Note: 20Pb means that the Pb concentrations were 20 times the value indicated and 0.1COD means that the COD concentrations were one tenth the value indicated.

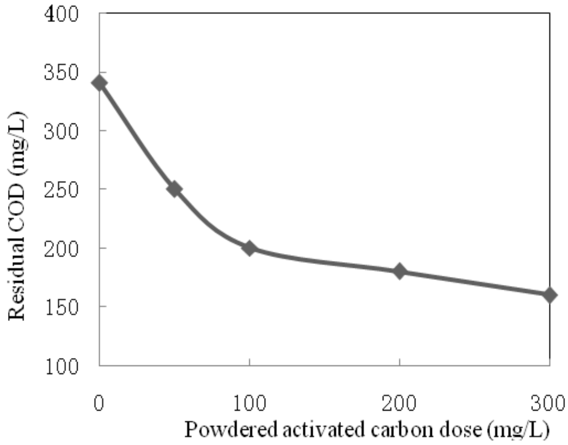

Fig. 3. Dose response curve of powdered activated carbon on COD removal efficiency

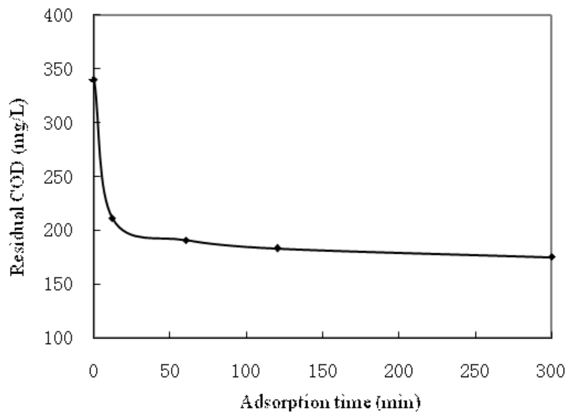

Fig. 4. Effect of adsorption time on efficiency of adsorption

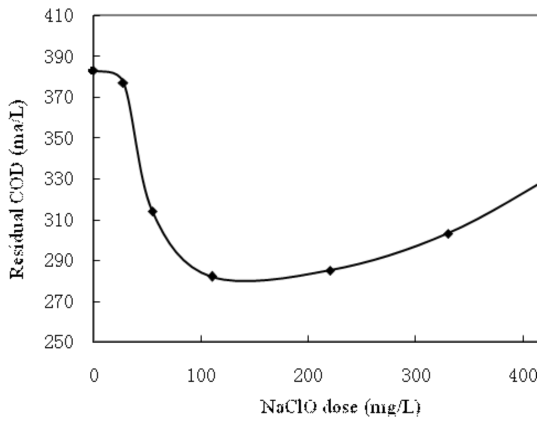

Fig. 5. Dose response curve of NaClO on the efficiency of wastewater oxidation

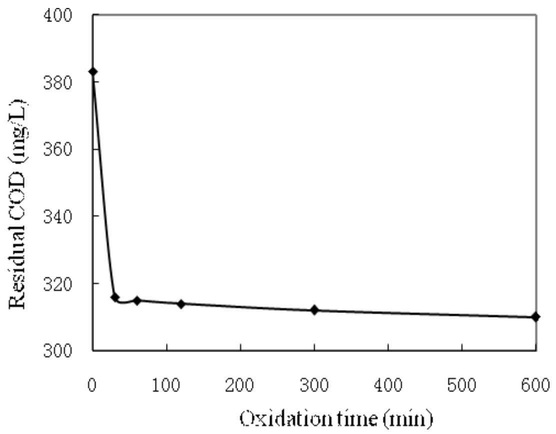

Fig. 6. Effect of time on oxidation efficiency

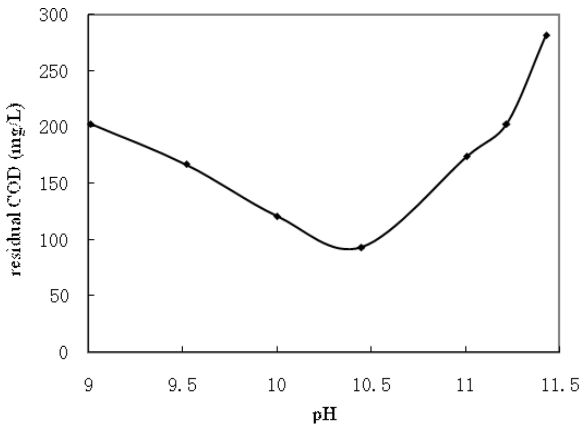

Fig. 7. Effect of pH on oxidation efficiency

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Table 3. Operation performance without the reuse of wastewater (2002)

	Product grade (%)				Rates of recycled metals (%)			
	Pb	Zn	S	Ag (g/t)	Pb	Zn	S	Ag(g/t)
Pb	60.77	5.66	18.63	979.55	88.801	4.078	4.841	55.524
Zn	1.38	53.10	30.77	115.56	4.787	90.673	18.945	15.525
S	0.44	0.91	46.42	81.70	4.098	3.468	70.082	26.909
Gangue	0.22	0.40	3.52	5.37	2.314	1.781	6.131	2.042

Table 4. Operation performance with the reuse of treated wastewater (2008)

	Product grade (%)				Rates of recycled metals (%)			
	Pb	Zn	S	Ag(g/t)	Pb	Zn	S	Ag (g/t)
Pb	65.64	5.67	16.97	628.61	89.371	3.751	4.595	50.731
Zn	1.37	53.88	30.43	95.18	4.911	92.103	21.352	19.817
S	0.52	0.94	45.85	61.28	3.872	2.844	67.298	26.523
Gangue	0.19	0.32	3.18	4.39	2.103	1.295	6.831	2.857

By comparing Table 3 and 4, it was concluded that the lead product grade improved from 60.77% to 65.64%, and the rate of recycled metal increased from 88.801% to 89.371% by reusing the treated wastewater. At the same time, zinc product recovery improved from 53.10% to 53.88%, and the rate of recycled zinc increased from 90.673% to 92.103%. In addition, the concentration of silver in the sulfur product increased and the grade of metal products in the gangue decreased.

The described procedures are beneficial for resource conservation. Moreover, the amount of flotation reagent decreased a lot, especially the foaming agents, which are not commonly used in the lead flotation process. Furthermore, the flotation process could be controlled by adjusting the amount of powdered activated carbon.

CONCLUSION

Alum was found to effectively reduce the pollution load of sulfide mine flotation wastewater without pH adjustment. The efficiencies of coagulation sedimentation varied between 69.26% and 97.98% in terms of heavy metals, and 6.84% and 15.79% in terms of suspended solids. The optimal Alum concentration was about 20 mg/L and the optimal polyacrylamide concentration was about 0.2 mg/L. The powdered carbon adsorption process was shown to efficiently remove COD and reduce the foamability of the coagulation effluent. Although the COD of the adsorption effluent was still high, the treated wastewater could be reused for the flotation process and did not negatively affect the flotation performance of the sulfide mine. The optimal powdered carbon concentration was about 100 mg/L, and the optimal adsorption time was approximately 30 min. The adsorption efficiencies varied between 26.47% and 52.94% in terms of COD. The results of the sodium hypochlorite oxidation on coagulation effluent showed that the COD of the oxidation process effluent was lower than standards for industrial wastewater discharge. The optimal sodium hypochlorite concentration was about 110 mg/L, and the fitting oxidation time was 30 min with pH at about 10.5.

This technology has been used successfully in a state-owned sulfide mine plant in Jiangsu, China, for six years. The results of this study showed that the treated wastewater could be reused for the flotation process and did not result in adverse effects. At the same time, the decrease of fresh water and flotation reagents created an economic benefit for the company. Furthermore, adjusting the powdered carbon concentration, which regulates wastewater foamability, easily controlled the flotation effect. Cleaner production and zero discharge from the sulfide mine flotation process were realized.

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