Minerals Engineering 128 (2018) 275–283

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Comparison of the reduction of chemical oxygen demand in wastewater from mineral processing using the coagulation–flocculation, adsorption and Fenton processes

Xiangsong Meng, Jiangqiu Wu, Jianhua Kang, Jiande Gao, Runqing Liu, Yuesheng Gao, Ruolin Wang, Ruiying Fan, Sultan Ahmed Khoso, Wei Sun*, Yuehua Hu*

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China

A R T I C L E I N F O

Keywords:
COD
Minerals processing wastewater
Coagulation–flocculation
Adsorption
Fenton

A B S T R A C T

The reduction of chemical oxygen demand (COD) from minerals processing wastewater (MPW[1]) was studied using the coagulation-flocculation (CF), adsorption, and Fenton processes. The effects of multiple parameters on COD reduction were evaluated in detail using polymeric ferric sulphate as coagulant, polyacrylamide as flocculant, granular activated carbon as adsorbent as well as H_2O_2 and $FeSO_4{\cdot}7H_2O$ as Fenton reagents. Results showed that the adsorption and Fenton processes can effectively reduce the COD of tailings dam wastewater (TDW[2]) from 183 mg/L to 51.9 mg/L and 50.0 mg/L, respectively, thereby satisfying the requirement of the emission standard (COD < 100 mg/L). The CF process is limited to reducing the dissolved COD in TDW and cannot meet the emission standards. Cost evaluation analysis showed that the cost of the adsorption process (3.57 US$/m^3) was much higher than that of the Fenton process (0.35 US$/m^3). Therefore, the Fenton process should be used in subsequent pilot experiments and industrial experiments. This study provided fundamental support for selecting an optimal technique in MPW treatment for practical applications to ensure the sustainable development of mines and environmental protection.

1. Introduction

Many types of industrial wastewater are produced with industrial development. These wastewaters usually contain a variety of pollutants (Meric et al., 2005), such as suspended solids, heavy metals, and chemical oxygen demand (COD). COD is an important indicator of water quality and is usually used to describe the degree of organic contamination in wastewater. The direct return of high-COD wastewater to industrial production has many negative effects (Ioannou-Ttofa et al., 2017; Klamerth et al., 2012; Pliego et al., 2014). High-COD wastewater can reduce the resin exchange ability by contaminating the ion exchange resin in a salt-removing system. High organic content in a circulating water system promotes microbial reproduction. High-COD wastewater can also seriously damage the ecosystem of a body of water. Therefore, suitable methods must be adopted to treat industrial wastewater to reduce COD.

Minerals processing wastewater (MPW) is an important part of industrial wastewater (Kang et al., 2017a). Ore beneficiation of nonferrous metals mainly adopts the flotation method (Liu et al., 2015; Yin et al., 2017a,b), which uses a considerable amount of water, and processing a ton of raw ore requires 4–7 m^3 of water. Various types of residual reagents may leave in MPW, such as collectors and frothers, which lead to a high COD. Hunan Shizhuyuan Nonferrous Metals Co., Ltd. (Hunan, China) is a large enterprise that mainly produces molybdenum concentrates, bismuth concentrates, wolframite and scheelite mixed concentrates, and fluorite concentrates (Han et al., 2017). A brief flow diagram of the ores flotation is shown in Fig. 1. The main organic reagents used in flotation include dithiocarbamate, pine oil, benzohydroxamic acid and oleic acid. Fig. 2 shows a schematic of the wastewater production. Lime is added to the tailings slurry and mixed in a

* Corresponding authors at: School of Minerals Processing and Bioengineering, Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China.
E-mail addresses: sunmenghu@csu.edu.cn (W. Sun), hyh@csu.edu.cn (Y. Hu).

[1] MPW: minerals processing wastewater.
[2] TDW: tailings dam wastewater.

https://doi.org/10.1016/j.mineng.2018.09.009
Received 5 January 2018; Received in revised form 3 September 2018; Accepted 5 September 2018
0892-6875/

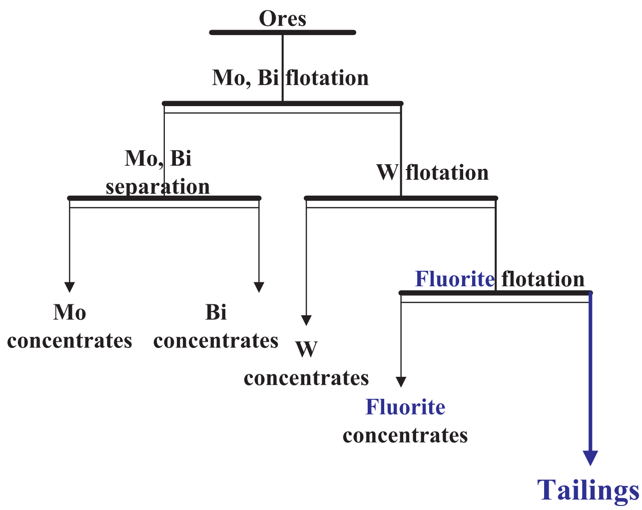

Fig. 1. Brief flow diagram of the ores flotation.

buffer pool, and then the slurry is pumped to a tailings dam in which the solid particles are deposited. Approximately 20,000 m^3/d of tailings dam wastewater (TDW) is generated. At present, other streams of clean water, possibly from rainwater and/or from the mountains, flow into the TDW, thereby diluting the TDW and causing COD reduction. Therefore, the COD of the outlet wastewater (which is typically 70–120 mg/L) is lower than that of the inlet (which is typically 150–200 mg/L). A total of 2000–5000 m^3/d of the outlet wastewater is recycled to the mineral processing plant and the rest is discharged. The COD of the outlet wastewater is sometimes over the Chinese "Integrated wastewater discharged standard (GB 8978–1996)" (COD < 100 mg/L) (China-MEP, 1996), in which case the Shizhuyuan company needed to shut down production. Otherwise, the company will face large fines when encountering the inspection of the environmental protection department. This situation strongly threatens the sustainable development of the company. In addition, the local government requests the company to construct facilities to realize separation of rainwater and wastewater, thereby indicating that clean water from the mountains cannot flow into the TDW and the COD of the outlet wastewater will be higher than that of the current in the future. Therefore, the COD will be above the emission limit (COD < 100 mg/L) frequently. This situation urges the company to search for a proper technology to treat the wastewater. Many other countries also stipulate COD emission limit values of wastewater, such as 100 mg/L in Singapore (Singapore-NEA), 120 mg/L in Japan (Japan-MOE, 2015), 125 mg/L in the European Union (European-commission, 1991), and 150 mg/L in Pakistan (Pakistan-MOCC, 1993). Among these standards, the Chinese standard is relatively more stringent.

A number of studies have been reported using coagulation–-flocculation (CF) (Michael et al., 2014), adsorption (Álvarez-Torrellas et al., 2017), Fenton process (Villegas- Guzman et al., 2017; Wen et al., 2017), chemical sedimentation (Kang et al., 2017b), membrane filtration (Zhang et al., 2015), and aerobic or anaerobic digestion technology (Rajbhandari and Annachhatre, 2004) processes for industrial wastewater treatment. Different species of wastewater can be treated with different optimum processes. For MPW, with a large amount of wastewater and a relatively lower COD than other industrial wastewater, finding an economical and effective treatment process is necessary. CF, adsorption and the Fenton process are three common methods used to reduce the COD of wastewater. However, to the best of our knowledge, no studies currently apply these three processes to one wastewater, especially comparative studies about the COD reduction of MPW.

CF is a relatively simple physical–chemical technique that may be successfully used for the treatment of industrial wastewater and is especially effective in removing suspended solids and colour from wastewater. O.S. Amuda and A. Alade investigated the treatment of abattoir wastewater that used alum, ferric chloride and ferric sulphate to achieve TSS and TP removal efficiencies of 65% and 32% respectively (Amuda and Alade, 2006). Its main mechanism for removing pollutants from wastewater can be summarized as charge neutralization, sweeping and bridging (Aguilar et al., 2003; Aguilar et al., 2005; Ayekoe et al., 2017). The CF process is effective at removing COD when the COD is caused by insoluble solids. Sajjad et al. studied tannery wastewater using a combination of alum with cationic and anionic polymers by CF and found that coagulation–flocculation–sedimentation removed all particulate COD, and only soluble COD remained (Haydar and Aziz, 2009). The CF process can also remove some soluble COD possibly because the metal ions ionized by the coagulant react with some organic matter in the wastewater to generate insoluble precipitation. Therefore, organic matter is removed from wastewater and the COD is reduced. However, other dissolved organic matter does not react with the coagulant to form a precipitate, and the ability of the coagulant to reduce the COD is not evident. Commonly used coagulants include iron salts and aluminium salts (Aber et al., 2010). The most widely used flocculant is polyacrylamide. Recent works clearly reveal that iron salts are more efficient than aluminium ones in COD reduction of wastewater (Amor et al., 2015). Wei et al. used coagulants including aluminium sulphate, ferric chloride, polyaluminium and polymeric ferric sulphate (PFS) to treat stabilized landfill leachate, thereby demonstrating that PFS had the highest COD removal efficiency (70%) (Li et al., 2010).

Adsorption is a process by which a substance is transferred from the liquid phase to the surface of a solid. The adsorption mechanisms between adsorbents and adsorbates are physisorption, chemisorption and/or ion exchange adsorption (Albadarin et al., 2014; Khosravi et al., 2014; Lee et al., 2017). Physisorption is caused by van der Waals forces, which are relatively weak, between adsorbents and adsorbates (Lima et al., 2015; Sophia and Lima, 2018). Chemisorption involves the formation of chemical bonds between adsorbents and adsorbates, which is relatively strong (Harja and Ciobanu, 2018; Tian et al., 2017). Ion exchange adsorption refers to the replacement of some ions in the water with other ions that were previously fixed to the adsorbents (Chen et al., 2014; Zhao et al., 2017). Granular activated carbon (GAC) is one of the best adsorbents for removing various organic contaminants because of its large surface area and microporous structure (Thankappan et al., 2015; Xing et al., 2008).

For the Fenton process, Fe^{2+} catalyses H_2O_2 under acidic conditions producing $^{\cdot}OH$ with powerful oxidizing abilities to degrade organic substances (RH). The reaction mechanisms are as follows (Herney-Ramirez et al., 2010; Kang and Hwang, 2000; Li et al., 2012b; Rodriguez-Chueca et al., 2014):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \quad (1)$$

$$RH + \bullet OH \rightarrow R\bullet + H_2O \quad (2)$$

$$R\bullet + Fe^{3+} \rightarrow product + Fe^{2+} \quad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \bullet HO_2 \quad (4)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet HO_2 \quad (6)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (7)$$

Therefore, the present study aimed to investigate and compare the performance of the CF, adsorption and Fenton processes on the reduction of COD from MPW with the goal to reach the legal limits of release into natural waters (specifically COD < 100 mg/L). In the CF process, the effect of PFS dosage on COD reduction was studied. In the adsorption process, the effect of contact time, pH and GAC dosage on COD reduction were studied. In the Fenton process, the effects of reaction time, reaction pH, H_2O_2 dosage and $FeSO_4{\cdot}7H_2O$ dosage (H_2O_2/Fe^{2+}