



Research article

Efficient removal of copper from wastewater by using mechanically activated calcium carbonate

Huimin Hu^a, Xuewei Li^a, Pengwu Huang^a, Qiwu Zhang^{a,*}, Wenyi Yuan^{b,**}^a School of Resources & Environmental Engineering, Wuhan University of Technology, 430070 Wuhan, China^b Shanghai Collaborative Innovation Centre for WEEE Recycling, Shanghai Polytechnic University, 201209 Shanghai, China

ARTICLE INFO

Article history:

Received 18 January 2017

Received in revised form

24 July 2017

Accepted 25 July 2017

Keywords:

Copper removal

Chemical precipitation

Wet stirred ball milling

Calcium carbonate

ABSTRACT

Copper removal from aqueous solution is necessary from the stances of both environmental protection and copper resource recycling. It is important to develop a new chemical precipitation method suitable for removing copper particularly at low concentration as the case of waste mine water, with regards to the various problems related to the current precipitation methods by using strong alkalis or soluble sulfides. In this research, we studied a possible chemical precipitation of copper ions at concentration around 60 mg/L or lower by cogrinding copper sulfate in water with calcium carbonate (CaCO₃) using wet stirred ball milling. With the aid of ball milling, copper precipitation as a basic sulfate (posnjakite: Cu₄(SO₄)(OH)₆·H₂O) occurred at a very high copper removal rate of 99.76%, to reduce the residual copper concentration in the solution less than 0.5 mg/L, reaching the discharge limit, even with the addition amount of CaCO₃ as a stoichiometric ratio of CaCO₃/Cu²⁺ at 1:1. It is more interesting to notice that, at the same conditions, other heavy metals such as Ni, Mn, Zn and Cd do not precipitate obviously just with CaCO₃ addition at CaCO₃/M²⁺ at 1:1 so that the precipitate without the impurities can be processed as good source to recover copper. This newly proposed concept can be further developed to treat wastewaters with other metals to serve both purposes of environmental purification and resource recovery in a similar way.

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1. Introduction

Wastewater containing heavy metals from mining, mineral processing and many manufacturing industries is one of the trickiest water pollution to deal with, in which copper is an important constituent of these effluents (van Hille et al., 2005). Copper (Cu(II)) ion plays an important role in the development of enzyme synthesis, tissues and bones for humans (Akar et al., 2009). However, the excessive Cu(II) may cause many harmful damages for eye and liver and the imbalance in cellular processes causing the Menkes, Wilson, Alzheimer's, Parkinson's and prion diseases (Awual et al., 2013; Kozłowski et al., 2009; Multhaup et al., 1996; Ofomaja, 2010). World Health Organization (WHO) has defined the Cu²⁺ permissible limit of 1.5 mg/L in drinking water (Awual et al., 2016), and the discharge limit permissible of industrial effluents in China has been set as 0.5 mg/L (Dong et al., 2017).

Various techniques have been used to treat these copper contaminated wastewaters, including chemical precipitation (Lundström et al., 2016), absorption (Labidi et al., 2016; Mushtaq et al., 2016) and biosorption (Abdelfattah et al., 2016), membrane separation (Duan et al., 2017), bio-electrochemical systems (Ntagia et al., 2016), ion exchange (Ntimbani et al., 2016), and electrochemical (Lambert et al., 2014). Chemical precipitation treatment may provide a desired quality effluent at the required plant capacity with the most economical overall operation.

Neutralization by using strong alkalis of sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)₂) is the most commonly used removal practice (Heuss-Assbichler et al., 2016; Mokone et al., 2010). Although this process is operation-effective and can be applied to large operating units, it has quite a lot of problems to deal with. In most cases the optimum precipitation pH occurs at high values between 10 and 11 (van Hille et al., 2005), so that the corrosion of equipment is very serious and further acid used to neutralize the wastewater after heavy metal removal is necessary for final water discharge. Another widely

* Corresponding author.

** Corresponding author.

E-mail address: zhangqw@whut.edu.cn (Q. Zhang).

used chemical precipitation method is sulphide precipitation based on much lower solubility of metal sulphide precipitates, fast reaction rates, potential for selective metal removal, better settling properties (Lewis, 2010). However, many problems (Mokone et al., 2012) exist and require measurements to overcome: the difficulty to control the precipitation processes, the formation of aqueous polysulphide complexes and further use of oxidizer to remove the sulfide in the solution after the metal removal for final water discharge. It is also well known that the metal removal efficiency goes down normally with low concentration of the target metal (Bilal et al., 2013). It is highly required to develop a new method to maintain a high efficiency of metal removal even with quite low concentration and allow a direct water discharge after metal removal without any other treatment like the further neutralization in alkali precipitation or the oxidation of remaining sulfide.

On the other hand, as one of most important and widely used metal in many industries, copper consumption increases rapidly and it is not easy to ensure sufficient supply of copper source to keep the demanding amount (Janyasuthiwong et al., 2015; Lifset et al., 2012). Similar to the natural mineral sources, copper is found to coexist always with other heavy metals in many wastewaters such as electroplating, printing, mining and other industrial wastewater, increasing the difficulty of copper removal. A new chemical precipitation technology for treating low concentration copper wastewater will be more desirable if selective removal of copper from other heavy metals is possible. The precipitate sample will certainly serve as a good source for copper recovery to add a new supplying route for the continuous increasing copper demand.

Calcium carbonate (CaCO_3) is one of the most easily available minerals all around the world. As used in the alkali precipitation treatment, Ca(OH)_2 has been prepared from CaCO_3 . CaCO_3 itself is too stable to be used directly for the chemical precipitation of heavy metals, although the use of CaCO_3 as an adsorbent for metal removal is not new. One concept is to activate it and raise its reactivity to a high level as that of Ca(OH)_2 so that similar chemical precipitation by using the activated one may occur rather than a physical adsorption with large amount consumption of CaCO_3 for quite small amount of metal removal. Mechanical activation as a major means of material activation has received wide attention and been applied to many aspects (Li et al., 2017b; Sasai et al., 2008; Sepelak et al., 2013; Takacs, 2013; Wang and Forssberg, 2006; Balaz et al., 2013; Balaz and Sedlak, 2010), with a high-intensity dry grinding operation generally involved. As to the treatment of wastewater, wet stirred ball milling at relatively low intensity of grinding operation is considered, and the usually reported particle aggregation and welding of the particles can be prevented and small milling beads are favorable to efficiently generate fresh surfaces (Romeis et al., 2016) which have predominantly a radical nature (Molchanov and Buyanov, 2000). Experiments on the reaction between the activated calcium carbonate and sulfate salts of copper and nickel by using a planetary ball mill with relatively high intensity of milling operation have been successfully reported (Li et al., 2017a).

In this paper, activating calcium carbonate by means of wet stirred ball milling to remove copper from the solution with low copper concentration as model sample of some copper contaminated or mining related wastewater has been investigated and the fundamental data are reported. The influences of reaction time, dosages of CaCO_3 , and initial concentration of copper, on the removal efficiency have been carefully studied, together with the selective precipitation of copper from other coexisting heavy metals.

2. Materials and methods

2.1. Reagents and instruments

All reagents ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, CaCO_3) used in this investigation were analytical grade chemicals purchased from Sinopharm Chemical Reagent Co., Ltd, China and used as received without further treatment. Distilled water was used to prepare solutions with metal concentrations at 0.001 mol/L, around 60 mg/L for Cu, Ni, Mn, Zn and 112 mg/L for Cd or even lower for the experiments.

Milling operation was performed in a lab-scale stirred ball milling equipment (Changsha Tianchuang Powder Technology Corporation, YS7124-JM-1L, China). The cylindrical chamber (total volume 1000 mL) with diameter of 115 mm, height of 120 mm and the inner wall was lined with Al_2O_3 material of 10 mm thickness. The used balls were yttrium-stabilized zirconia milling beads of 3 mm in diameter.

2.2. Procedure

First, 300 mL copper solution, certain volume of milling beads, and CaCO_3 were added in the grinding chamber for milling operation with parameters of milling speed, milling time, the starting Cu (II) concentration, Ca/Cu molar ratio changed. After the run, 10 mL suspension was centrifuged for 5 min at 8000 rpm to obtain the supernatant for the pH and remaining metal concentrations measurement, and the rest suspension was filtered to collect the precipitated phase and the products were dried at 80 °C for 24 h for further analyses. All the experiments were performed at room temperature.

2.3. Characterizations

The pH of all the samples were measured by a pH meter (METTLER TOLEDO FE20-FiveEasy™, Switzerland). The concentrations of metal ions in the supernatant were determined by atomic absorption spectrophotometer (AAS: SHIMADZU AA-6880, Japan), X-ray diffraction (XRD: RU-200B/D/MAX-RB RU-200B, Japan) and thermogravimetric (TG-DSC: STA449F3, NETZSCH, Germany) analysis were performed to identify the phases in the precipitated samples.

The removal rates of Cu (II) and other metals were calculated by the following equation:

$$\eta = \frac{(C_0 - C_e)}{C_e} \times 100\%$$

In the formula, C_0 represents the initial concentration and C_e the concentration after treatment. The unit of C_0 and C_e are mg/L.

3. Results and discussion

3.1. Cu (II) removal experiments

Experiments on the effects of the milling time and molar ratio of $\text{CaCO}_3/\text{Cu}^{2+}$ were carried out at fixed Cu (II) initial concentration of 0.001 mol/L (equivalent to 63.55 mg/L), the volume ratio of milling balls to the used solution at 10% and the milling speed at 200 rpm. The molar ratio of $\text{CaCO}_3/\text{Cu}^{2+}$ was varied at 0.5:1, 0.8:1, 1:1, 1.2:1, 1.5:1 and 2:1. The changes in Cu removal rate and the pH after the treatment are shown in Fig. 1. From (a), the removal rate increased sharply during the milling time up to 90 min and tended to be levelled off after 90 min with all the molar ratios of $\text{CaCO}_3/\text{Cu}^{2+}$. It is understood that 90 min milling operation was long enough to raise

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