Leaching of Cu from malachite using $\text{Fe}_2(\text{SO}_4)_3$ solution as the leaching agent

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ABSTRACT: $\text{Fe}_2(\text{SO}_4)_3$ solution was, for the first time ever, used as the leaching agent to leach Cu from malachite in this work. The results confirmed that malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) could be easily converted to water-soluble $\text{CuSO}_4$ through a nearly stoichiometric reaction with $\text{Fe}_2(\text{SO}_4)_3$ in the leaching solution and the leaching efficiency of Cu could reach $\approx 100\%$ under the optimum conditions (the $\text{Fe}^{3+}/\text{Cu}$ molar ratio = 0.8, the liquid-to-solid ratio = 1–10 ml/g, the stirring speed = 300 rpm, and the leaching time = 120 min). This study provides a new hydrometallurgical method for the treatment of carbonate-type Cu ores such as malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) and azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$).

KEYWORDS: Cu, malachite, leaching, $\text{Fe}_2(\text{SO}_4)_3$
pickling waste liquor (H$_2$SO$_4$ conc. 5%–10%, FeSO$_4$ conc. 17%–23% by weight) [12–14]; titanium white waste acid (H$_2$SO$_4$ conc. 10%–20%, FeSO$_4$ conc. 15%–20% by weight) and the FeSO$_4$ by-product from titanium dioxide production [15, 16]; acid mining drainage (AMD) (pH 1–3.5, TFe conc. 1.5–4.3 g/l) and pyrite from sulfide mine [17]; and various Fe-bearing wastewaters in hydrometallurgical processes (Fe$^{3+}$ conc. ~6.5 g/l) [18, 19]. FeSO$_4$ and FeS$_2$ in these wastewaters can be easily oxidized to Fe$_2$(SO$_4$)$_3$ via bio-oxidation [20–22], which can be used as an available source of Fe$_2$(SO$_4$)$_3$ leaching agent. The oxidation of Fe$^{2+}$ through bio-oxidation occurs as follows:

$$\text{FeSO}_4 + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{SO}_4 \xrightarrow{\text{Bacteria}} \text{Fe}_2(\text{SO}_4)_3 + \frac{1}{2} \text{H}_2\text{O}$$

(6)

$$\text{FeS}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{Bacteria}} \text{FeSO}_4 + \text{H}_2\text{SO}_4$$

(7)

From the perspective of developing a circular economy and protecting the ecological environment, these Fe-bearing wastes can be used to leach malachite, wherein Cu can be leached out and these Fe-bearing wastes can be further utilized. The commonly used H$_2$SO$_4$ leaching agent can be replaced with the Fe$_2$(SO$_4$)$_3$ solution to reduce acid consumption. Therefore, the proposed process is of great significance.

In this work, an agitated Fe$_2$(SO$_4$)$_3$ leaching of malachite ores was conducted to investigate the effects of the Fe$^{3+}$/Cu molar ratio, the liquid-to-solid ratio, the stirring speed, and the leaching time on the leaching efficiency of Cu. The leaching residues were characterized via X-ray diffraction (XRD) and Fourier-transform infrared spectrometry (FT-IR).

**Materials and Methods**

**Materials**

The Fe$_2$(SO$_4$)$_3$·5H$_2$O reagent used in this investigation was an analytical grade chemical purchased from Sinopharm Chemical Reagent Co., Ltd., China. The malachite sample was obtained from Daye City, Hubei Province, China.

**Preparation of malachite sample**

This malachite sample was ground. The d$_{10}$, d$_{50}$, and d$_{90}$ of the sample were 1.7, 13.7, and 151.3 µm, respectively. The X-ray diffraction (XRD) (RU-200B/D/MAX-RB, Rigaku, Japan) pattern of the sample is shown in Fig. 1. Most of the diffraction peaks can be attributed to malachite, with several very weak peaks corresponding to gangue minerals. The Cu content, as determined via the chemical titration method (GB/T8151.17, 2012), of the malachite sample was 54.58% (Table 1). The X-ray fluorescence (XRF) (PANalytical.B.V., Zetium, Netherlands) analyses of the sample (Table 1) show that the ore also contained a small number of other gangue minerals consisting of Si, Al, Ca, Mg, and Fe, etc.

**Operation of the leaching process**

1 g malachite sample, a defined amount of Fe$_2$(SO$_4$)$_3$·5H$_2$O according to the Fe$^{3+}$/Cu molar ratio, and a known volume of distilled water, according to the liquid-to-solid ratio, were put into a glass beaker. Then, the magnetic stirring started to run at a fixed stirring speed for a particular time. After the agitation, the slurry in the glass beaker was filtered and the residues were washed with distilled water. Finally, the leaching solution was collected for concentration measurement. The residues obtained were dried at 80 °C for 6 h for further analyses. All the experiments were conducted at room temperature.

**Analytical methods**

The pH of each solution was measured using a pH meter (FE20-FiveEasy™, METTLER TOLEDO, Switzerland). FT-IR spectra of the samples were recorded using a Fourier transform infrared spectrometer (Nicolet6700, Thermo electron scientific instruments, USA). The concentration of Cu and Fe in the leaching solution was determined via AAS (AA-6880, SHIMADZU, Japan). The leaching efficiency of Cu (η) and the percentage of the Fe remaining in the leaching solution (λ) were calculated.
Table 1 Chemical compositions of the malachite.

| Component | Cu | SiO$_2$ | Al$_2$O$_3$ | CaO | MgO | Fe$_2$O$_3$ | P$_2$O$_5$ | SO$_3$ | LOI$^*$ |
|-----------|----|---------|-------------|-----|-----|-------------|-----------|--------|--------|
| Content (wt %) | 54.58 | 2.29 | 0.37 | 0.06 | 0.98 | 1.23 | 0.08 | 25.95 |

$^*$ Loss on ignition.

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as Eq. (8) and Eq. (9), respectively:

$$\eta = \frac{C \times V}{M} \times 100\%,$$  \hspace{1cm} (8)

$$\lambda = \frac{C_1 \times V}{M_1} \times 100\%,$$  \hspace{1cm} (9)

where $C$ is the concentration of Cu in the leaching solution (g/l), $C_1$ is the concentration of Fe in the leaching solution (g/l), $V$ is the volume of the leaching solution (l), $M$ is the weight of Cu in 1 g mineral malachite (g), $M_1$ is the weight of Fe in the added Fe$_2$(SO$_4$)$_3$·5H$_2$O (g).

**RESULTS AND DISCUSSION**

**Effect of the Fe$^{3+}$/Cu molar ratio**

Fig. 2 shows the effect of the Fe$^{3+}$/Cu molar ratio on the leaching efficiency of Cu. The experiments were performed under the following conditions where the liquid-to-solid ratio, the stirring speed, and the leaching time were kept constant at 10 ml/g, 500 rpm, and 60 min, respectively. The leaching efficiency of Cu and the percentage of the Fe remaining in the leachate increased as the Fe$^{3+}$/Cu molar ratio increased. When the Fe$^{3+}$/Cu molar ratio was 0.8, the leaching efficiency of Cu was 89.2%, and the percentage of the Fe remaining in the leachate was 1.1%. When the Fe$^{3+}$/Cu molar ratio was increased to 1.5, the leaching efficiency of Cu increased to 97.2%, and the percentage of the Fe remaining in the leachate was 35.0%. This was because the excess amount of Fe$_2$(SO$_4$)$_3$·5H$_2$O was left in the leaching solution. The Fe$^{3+}$ ions were an impurity in the leachate containing CuSO$_4$, of which the content should be reduced to favor the future purification of the leachate [23]. For a high leaching efficiency of Cu, while controlling the content of Fe impurity in the leaching solution, the optimum Fe$^{3+}$/Cu molar ratio was set to 0.8 in the subsequent experiments. At this condition, the percentage of the Fe remaining in the leachate was 1.1% which will not burden the purification of the leaching solution.

**Effect of the liquid-to-solid ratio**

Fig. 3 shows the effect of the liquid-to-solid ratio on the leaching efficiency of Cu. The experiments were performed under the following conditions where the liquid-to-solid ratio, the stirring speed, and the leaching time were kept constant at 10 ml/g, 500 rpm, and 120 min, respectively. When the liquid-to-solid ratio increased from 1.0 to 10 ml/g, the leaching efficiency of Cu increased from 94.2% to ~100%, and the percentage of the Fe remaining in the leachate was < 5%.
When the liquid-to-solid ratio increased from 50 to 400 ml/g, the leaching efficiency of Cu decreased from 99.5% to 92.9%, and the percentage of the Fe remaining in the leachate was ∼6%. The results indicated that a high concentration of Fe$_2$(SO$_4$)$_3$ (Fe$^{3+}$ conc. 38–380 g/l) could achieve a Cu leaching efficiency of ∼100%. However, a low concentration of Fe$_2$(SO$_4$)$_3$ (Fe$^{3+}$ conc. 1–8 g/l) could also achieve a relatively high leaching efficiency of Cu (> 90%). These results suggest that the Fe$_2$(SO$_4$)$_3$ solution, with Fe$^{3+}$ concentration ranging from 1.0 to 380 g/l, can efficiently leach Cu from malachite. When the liquid-to-solid ratio was 200 ml/g, the leaching efficiency of Cu could still reach 96.5%, and the percentage of the Fe remaining in the leachate was ∼6%. At this time, the concentration of Fe$^{3+}$ in the leaching agent was approximately 1.9 g/l.

**Effect of the stirring speed**

Fig. 4 shows the effect of stirring speed on the leaching efficiency of Cu, which was examined with the Fe$^{3+}$/Cu molar ratio of 0.8, the liquid-to-solid ratio of 200 ml/g, and the leaching time of 120 min. As the stirring speed increased from 100 to 500 rpm, the leaching efficiency of Cu increased from 38.8% to ∼90%, and the percentage of the Fe remaining in the leachate decreased from 43.6% to ∼5%. When the stirring speed exceeded 200 rpm, the leaching efficiency of Cu and the percentage of the Fe remaining in the leachate were stable at ∼90% and ∼5%, respectively. The increase of the stirring speed prompted the dispersion of malachite in the solution and its contact with the leaching agent, which enhanced the kinetic condition for the reaction. However, the stirring operation has a certain limit in promoting the leaching reaction. To avoid the power consumption of excessive agitation, the stirring speed was maintained at 300 rpm in the subsequent experiments.

**Effect of the leaching time**

Fig. 5 shows the effect of leaching time on the leaching efficiency of Cu with the Fe$^{3+}$/Cu molar ratio of 0.8, the liquid-to-solid ratio of 200 ml/g, and the stirring speed of 300 rpm. It was observed that the leaching efficiency of Cu increased from 68.7% to ∼94.2% and the percentage of the Fe remaining in the leachate decreased from 27.3% to 3.7% with the increase of the leaching time. A reasonable extension of the leaching time was beneficial to the complete leaching of Cu in the malachite. When the leaching time was 120 min, a high Cu leaching efficiency (94.2%) and a low remaining Fe percentage (6%) were achieved. Therefore, the most favorable leaching time was ∼120 min. As seen from Figs. 4 and 5, the pH of the leachate in each experiment was ∼3; therefore, it proved that the dissolution of malachite was performed in the weak acidic solution. Fe$^{3+}$ is typically removed by hydroxide precipitation at pH 3–4 [24, 25]. This means that the small amount of the Fe$^{3+}$ remaining in the leachate can be removed by precipitation method using sodium hydroxide or dolomite [26].

Fig. 6 shows the X-ray diffraction pattern of the residue obtained under the most favorable condi-
Intensities were amorphous. According to the literature [27], the similar Fe-bearing precipitates were always amorphous and crystallized phases could be obtained by calcination. The chemical analysis showed that the content of Fe in the residue reached 43.4%. To detect the well-crystallized Fe phase, the residue was further calcined separately for 1.0 h at 300 °C, 600 °C, and 900 °C. At 300 °C, the Fe residues were identified for the Fe-bearing precipitates as amorphous. At 600 °C, the peaks corresponding to Fe$_2$O$_3$ still existed in an amorphous state. At 900 °C, the intensity of peaks corresponding to Fe$_2$O$_3$ was enhanced because the crystallinity of Fe$_2$O$_3$ became better with the increase of the roasting temperature.

The FT-IR analysis was carried out to verify the complete decomposition of malachite in the Fe$_2$(SO$_4$)$_3$ leaching process. Fig. 7 shows the FT-IR spectra of the malachite and the leaching residue. For the malachite, the broad adsorption between 3500 cm$^{-1}$ and 3000 cm$^{-1}$ was caused by the surface moisture or the OH$^-$ in Cu(OH)$_2$CO$_3$. The bands at 1495 cm$^{-1}$, 1096 cm$^{-1}$, 820 cm$^{-1}$, 776 cm$^{-1}$, and 749 cm$^{-1}$ belonged to the CO$_2^-$ in Cu(OH)$_2$CO$_3$ [28–30]. The disappearance of the bands at 1495 cm$^{-1}$, 1096 cm$^{-1}$, 820 cm$^{-1}$, 776 cm$^{-1}$, and 749 cm$^{-1}$ indicated that malachite was almost completely decomposed.

The leaching of Cu from malachite was confirmed to be possible by a simple agitation leaching process with the Fe$_2$(SO$_4$)$_3$ solution as the leaching agent. Detailed investigations are under planning for the removal of the small amount of the remaining Fe impurity in the leaching solution to provide information for future applications. The application of this proposal opens a new approach for the utilization of carbonate-type Cu ores and the Fe-containing wastes.

**CONCLUSION**

In this work, Fe$_2$(SO$_4$)$_3$ solution was used for the first time ever to leach Cu from malachite. Optimized conditions (the Fe$^{3+}$/Cu molar ratio = 0.8, the liquid-to-solid ratio = 200 ml/g, the stirring speed = 300 rpm, the leaching time = 120 min) were identified for the Fe$_2$(SO$_4$)$_3$ leaching process. These conditions yielded a Cu leaching efficiency of ~100% and the percentage of the Fe remaining in the leachate limited to < 5%. Fe$^{3+}$ ions in the leaching solution precipitated into the leaching residue in the form of an amorphous phase. Fe$_2$(SO$_4$)$_3$ solutions with Fe$^{3+}$ concentration ranging from 1.0 to 380 g/l could efficiently leach Cu from malachite.

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