

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

Kui Wang, Qiwu Zhang*, Huimin Hu, Yanchu Liu

School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070 China

*Corresponding author, e-mail: zhangqw@whut.edu.cn

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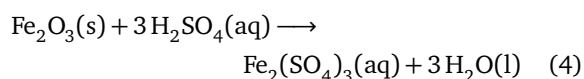
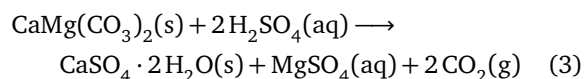
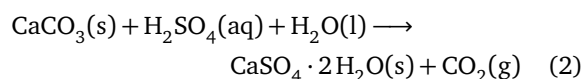
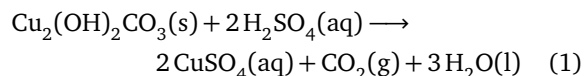
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ABSTRACT: $\text{Fe}_2(\text{SO}_4)_3$ solution was, for the first time ever, used as the leaching agent to leach Cu from malachite in this work. The results confirmed that malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) could be easily converted to water-soluble 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 ~100% under the optimum conditions (the Fe^{3+}/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, $\text{Fe}_2(\text{SO}_4)_3$

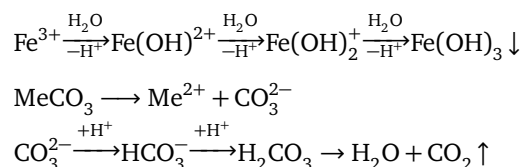
INTRODUCTION

Cu has been widely used in the electric and electronics, machinery manufacturing, alloys, construction industry, and other fields [1, 2]. Malachite is one of the most important copper oxide minerals, which is easily soluble in dilute H_2SO_4 solution according to Eq. (1) [3–5]. High acid consumption is the most significant problem encountered in the H_2SO_4 leaching process, increasing the economic cost [6, 7]. Malachite ores usually contain some gangue minerals, such as calcite, dolomite, and Fe_2O_3 , which can consume H_2SO_4 during the acid leaching process according to Eqs. (2)–(4) [8, 9]:

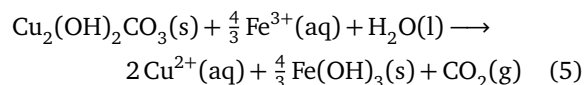


Solutions containing Fe^{3+} ions are acidic because Fe^{3+} ions have a strong hydrolyzability. When

carbonates (MeCO_3 , Me represents a certain metal element) are added to $\text{Fe}_2(\text{SO}_4)_3$ solution, the hydrolysis of Fe^{3+} ions will be enhanced with colloidal $\text{Fe}(\text{OH})_3$, of which the solubility product is as low as 2.79×10^{-39} [10] formed as follows [11]:

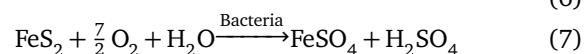
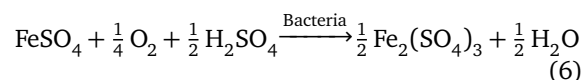


Based on the above principle, $\text{Fe}_2(\text{SO}_4)_3$ solution can be used to leach malachite. In the leaching process, the Cu in the malachite presents in the solution in the form of soluble CuSO_4 , and the Fe^{3+} ions in the form of insoluble precipitate (i.e. $\text{Fe}(\text{OH})_3$). The change in the Gibbs free energy of the $\text{Fe}_2(\text{SO}_4)_3$ leaching reaction of malachite, shown in Eq. (5), was calculated by the HSC Chemistry(V6) software. The ΔG^θ of the chemical reaction is -41.86 kJ/mol, proving that the reaction may be thermodynamically feasible at ambient temperature and pressure (298.15 K, 100 kPa).



Furthermore, a large amount of acidic Fe-bearing wastes are generated during the industrial production process. These wastes include: steel

pickling waste liquor (H_2SO_4 conc. 5%–10%, FeSO_4 conc. 17%–23% by weight) [12–14]; titanium white waste acid (H_2SO_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 wastes can be easily oxidized to $\text{Fe}_2(\text{SO}_4)_3$ via bio-oxidation [20–22], which can be used as an available source of $\text{Fe}_2(\text{SO}_4)_3$ leaching agent. The oxidation of Fe^{2+} through bio-oxidation occurs as follows:



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_2SO_4 leaching agent can be replaced with the $\text{Fe}_2(\text{SO}_4)_3$ solution to reduce acid consumption. Therefore, the proposed process is of great significance.

In this work, an agitated $\text{Fe}_2(\text{SO}_4)_3$ 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 $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ 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 d10, d50, and d90 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

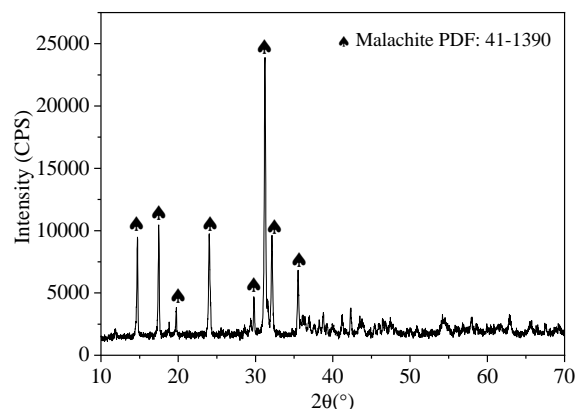


Fig. 1 X-ray diffraction pattern of the malachite.

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 $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ 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.

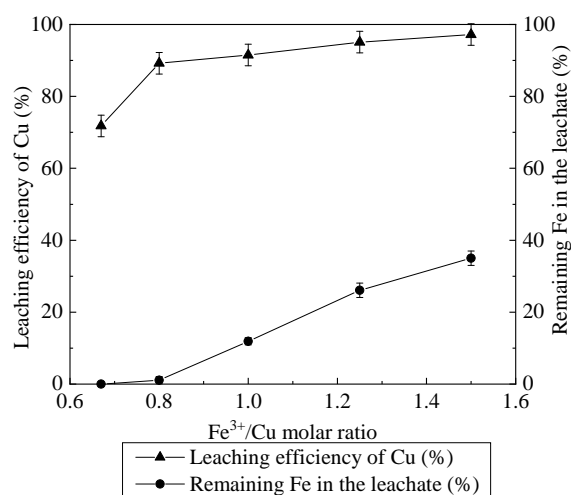
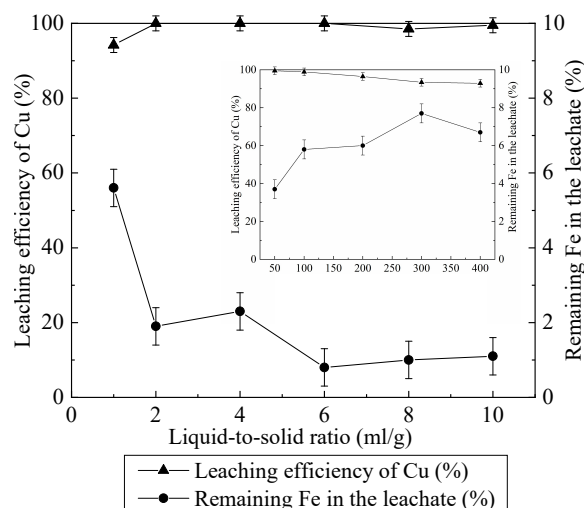
Analytical methods

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 ^a
Content (wt %)	54.58	2.29	0.37	0.06	0.98	0.50	1.23	0.08	25.95

^a Loss on ignition.

**Fig. 2** Effect of the Fe³⁺/Cu molar ratio on the leaching efficiency of Cu.**Fig. 3** Effect of the liquid-to-solid ratio on the leaching efficiency of Cu.

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

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

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

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 Fe₂(SO₄)₃ · 5 H₂O (g).

RESULTS AND DISCUSSION

Effect of the Fe³⁺/Cu molar ratio

Fig. 2 shows the effect of the Fe³⁺/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 Fe³⁺/Cu molar ratio increased. When the Fe³⁺/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 Fe³⁺/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 Fe₂(SO₄)₃ was left in the leaching solution. The Fe³⁺ ions were an impurity in the leachate containing CuSO₄, 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 Fe³⁺/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, while the Fe³⁺/Cu molar ratio, the stirring speed, and the leaching time were kept constant at 0.8, 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%.

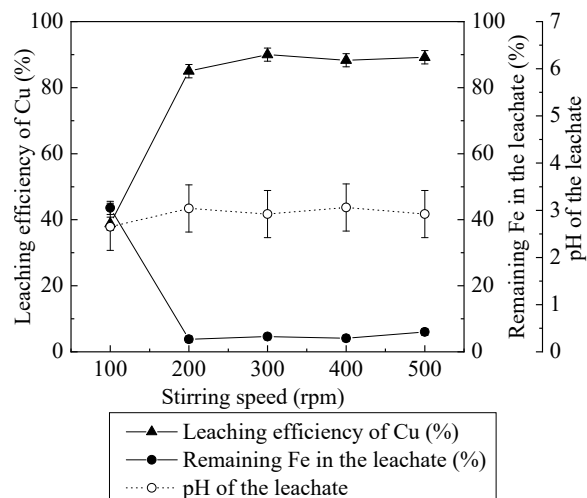


Fig. 4 Effect of the stirring speed on the leaching efficiency of Cu.

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 $\text{Fe}_2(\text{SO}_4)_3$ (Fe^{3+} conc. 38–380 g/l) could achieve a Cu leaching efficiency of ~100%. However, a low concentration of $\text{Fe}_2(\text{SO}_4)_3$ (Fe^{3+} conc. 1–8 g/l) could also achieve a relatively high leaching efficiency of Cu (> 90%). These results suggest that the $\text{Fe}_2(\text{SO}_4)_3$ 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,

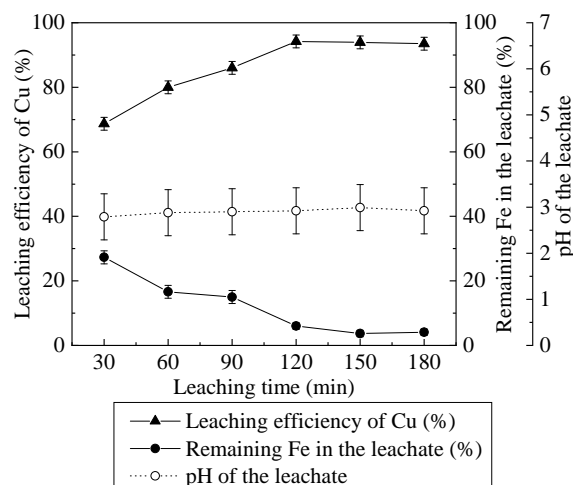


Fig. 5 Effect of the leaching time on the leaching efficiency of Cu.

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-

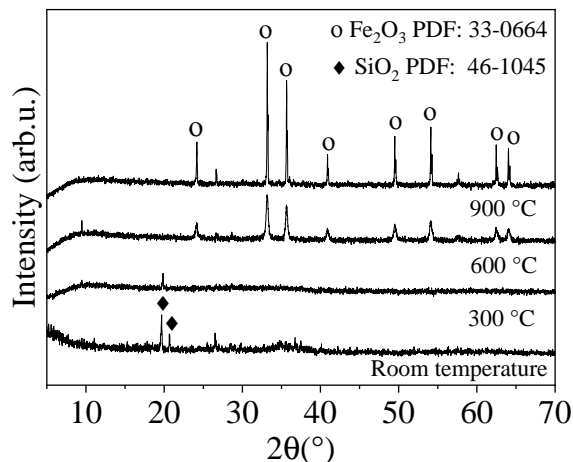


Fig. 6 X-ray diffraction patterns of the $\text{Fe}_2(\text{SO}_4)_3$ leaching residues at different temperature.

tions (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). At room temperature, the pattern exhibited no obvious diffraction peaks corresponding to a certain Fe phase, which indicated that the Fe-bearing precipitates 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 phase still existed in an amorphous state. At 600 °C, the peaks corresponding to Fe_2O_3 were observed. At 900 °C, the intensity of peaks corresponding to Fe_2O_3 was enhanced because the crystallinity of Fe_2O_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 $\text{Fe}_2(\text{SO}_4)_3$ 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 $\text{Cu}(\text{OH})_2\text{CO}_3$. The bands at 1495 cm^{-1} , 1096 cm^{-1} , 820 cm^{-1} , 776 cm^{-1} , and 749 cm^{-1} belonged to the CO_3^{2-} in $\text{Cu}(\text{OH})_2\text{CO}_3$ [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.

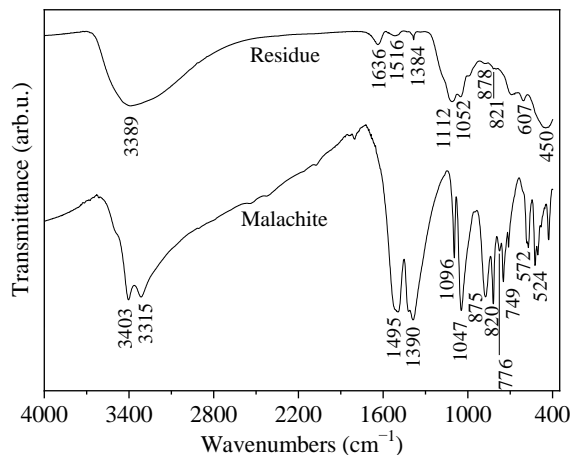


Fig. 7 FT-IR spectra of the malachite and the $\text{Fe}_2(\text{SO}_4)_3$ leaching residue.

The leaching of Cu from malachite was confirmed to be possible by a simple agitation leaching process with the $\text{Fe}_2(\text{SO}_4)_3$ 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, $\text{Fe}_2(\text{SO}_4)_3$ 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 = 1–10 ml/g, the stirring speed = 300 rpm, and the leaching time = 120 min) were identified for the $\text{Fe}_2(\text{SO}_4)_3$ 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. $\text{Fe}_2(\text{SO}_4)_3$ solutions with Fe^{3+} concentration ranging from 1.0 to 380 g/l could efficiently leach Cu from malachite.

REFERENCES

1. Wang YJ, Zhang ZF, Kuang ST, Wu GL, Li YL, Li YH, Liao WP (2018) Selective extraction and recovery of copper from chloride solution using Cextrant 230. *Hydrometallurgy* **181**, 16–20.
2. Arzutug ME, Kocakerim MM, Copur M (2004) Leaching of malachite ore in NH_3 -saturated water. *Ind Eng Chem Res* **43**, 4118–4123.

3. Liu ZX, Yin ZL, Hu HP, Chen QY (2012) Dissolution kinetics of malachite in ammonia/ammonium sulphate solution. *J Cent South Univ* **19**, 903–910.
4. Deng JS, Wen SM, Yin Q, Wu DD, Sun QW (2017) Leaching of malachite using 5-sulfosalicylic acid. *J Taiwan Inst Chem E* **71**, 20–27.
5. Nicol MJ (2018) The kinetics of the dissolution of malachite in acid solutions. *Hydrometallurgy* **177**, 214–217.
6. Wu DD, Wen SM, Yang J, Deng JS, Jiang L (2013) Dissolution kinetics of malachite as an alternative copper source with an organic leach reagent. *J Chem Eng Jpn* **46**, 667–682.
7. Zheng QQ, Zhang YM, Bao SX, Huang J, Zhang GB (2019) Effects of different alkalis on the behaviour of vanadium loss in the pretreatment of vanadium-bearing acid leaching solution. *ScienceAsia* **45**, 43–49.
8. Bingöl D, Canbazoglu, M (2004) Dissolution kinetics of malachite in sulphuric acid. *Hydrometallurgy* **72**, 159–165.
9. Ata ON, Çolak S, Ekinçi Z, Çopur M (2001) Determination of the optimum conditions for leaching of malachite ore in H_2SO_4 solutions. *Chem Eng Technol* **24**, 409–413.
10. Lide DR (2001) *CRC Handbook of Chemistry and Physics*, 82nd Edn, CRC Press, Boca Raton, USA.
11. Lupeiko TG, Gorbunova MO, Bayan EM (2004) Deep purification of aqueous solutions to remove iron(III) with carbonate-containing industrial waste. *Russ J Appl Chem* **77**, 79–82.
12. Agrawal A, Kumari S, Ray BC, Sahu KK, (2007) Extraction of acid and iron values from sulphate waste pickle liquor of a steel industry by solvent extraction route. *Hydrometallurgy* **88**, 58–66.
13. Agrawal A, Kumari S, Sahu KK (2009) Iron and copper recovery/removal from industrial wastes: a review. *Ind Eng Chem Res* **48**, 6145–6161.
14. Stamenov L, Stefanova V, Petkov K, Iliev P (2016) Treatment of ferric sulfate waste solutions for the production of ammonium ferric sulfate dodecahydrate. *Russ J Appl Chem* **89**, 1341–1346.
15. Xu TW, Yang WH (2001) Sulfuric acid recovery from titanium white (pigment) waste liquor using diffusion dialysis with a new series of anion exchange membranes-static runs. *J Membrane Sci* **183**, 193–200.
16. Liu SL, Zheng YJ, Zhang SC (2017) Recovery of sulfuric acid from titanium white waste acid by diffusion dialysis. *Technol Water Treat* **43**, 67–70+84.
17. Chen KL (2009) Design of process for the treatment of acid waste water from pyrite mines, *Industr Min Process* **38**, 28–31.
18. Liu M, Zhou YM (2005) Removal of Fe(III) from sulphate solutions by synergistic extraction using N235-TBP mixed solvent systems. *Chin J Nonferrous Metals* **15**, 1648–1654.
19. Zhang KF, Liu ZQ, Cao HY, Qiu XY (2015) Removal of Fe^{3+} from iron rich and high acidity sulfuric acid leaching liquid by extraction of N235. *Chin J Nonferrous Metals* **25**, 1370–91377.
20. Kahrizi E, Alemzadeh I, Vossoughi M (2009) Bio-oxidation of ferrous ions by acidithiobacillus ferroxidans in a monolithic bioreactor. *J Chem Technol Biot* **84**, 504–510.
21. Meng YS, Xu XJ, Wang JK (2002) Research on bacteria leaching of low-grade manganese ore. *Hydrometallurgy Chin* **21**, 184–187.
22. Santos SMC, Machado RM, Correia MJN, Reis MTA, Ismael MRC, Carvalho JMR (2010) Ferric sulphate/chloride leaching of zinc and minor elements from a sphalerite concentrate. *Miner Eng* **23**, 606–615.
23. Kokes H, Morcali MH, Acma E (2014) Dissolution of copper and iron from malachite ore and precipitation of copper sulfate pentahydrate by chemical process. *Eng Sci Technol* **17**, 39–44.
24. Wang K, Zhang QW, Hu HM, Liu YC (2019) Efficient removal of iron(II) from manganese sulfate solution by using mechanically activated $CaCO_3$. *Hydrometallurgy* **188**, 169–173.
25. Zhang WS, Cheng CY (2007) Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide. *Hydrometallurgy* **89**, 137–159.
26. Hu HM, Zhang QW, Li XW, Wu L, Liu YC (2020) Efficient heterogeneous precipitation and separation of iron in copper-containing solution using dolomite. *Sep Purif Technol* **248**, ID 117021.
27. Meng Z, Jia ZB, Wei Y (2004) Preparation and FTIR spectra of amorphous δ -FeOOH. *Chin J Process Eng* **4**, 146–149.
28. Isahak WNRW, Ramli ZAC, Ismail MW, Ismail K, Yusop RM, Hisham MWM, Yarmo MA (2013) Adsorption-desorption of CO_2 on different type of copper oxides surfaces: Physical and chemical attractions studies. *J CO₂ Util* **2**, 8–15.
29. Li Z, Chen M, Li XW, Lei ZW, Qu J, Huang PW, Zhang QW, Saito F (2017) Surface modification of basic copper carbonate by mechanochemical processing with sulfur and ammonium sulfate. *Adv Powder Technol* **28**, 1877–1881.
30. Wen L, Liang WX, Zhang ZG, Huang JC (1988) *The Infrared Spectroscopy of Minerals*, Chongqing University Press, Chongqing, China.