Copper Extraction from Low-Grade Chalcopyrite in a Bioleaching Column Assisted by Bioelectrochemical System

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Research Article

Abstract

Low-grade ores, tailings and solid wastes contain small amounts of valuable heavy metals. Improper disposal of these results in the waste of resources and contamination of soil or groundwater. Accordingly, the treatment and recycling of low-grade ores, tailings and solid wastes attracted much attention recently. Bioelectrochemical system, an innovative technology for the removal and recovery of heavy metals, has been further developed and applied in recent years. In current study, the low-grade chalcopyrite was bioleached with the assistance of microbial fuel cells. Copper extraction along with electricity generation from the low-grade chalcopyrite were achieved in the column bioleaching process assisted by MFCs. Results showed that after 197 days bioleaching of low-grade chalcopyrite, 423.9 mg copper was extracted from 200 g low-grade chalcopyrite and the average coulomb production reached 1.75 C/d. The introduction of MFCs into bioleaching processes promoted the copper extraction efficiency by 2.7 times (3.62% vs. 1.33%), mainly via promoting ferrous oxidation, reducing ORP and stimulating bacterial growth. This work provides a feasible method for the treatment and recycling of low-grade ores, tailings and solid wastes. But balancing energy consumption of aeration and circulation frequency and chemicals consumption of acid to improve the copper extraction efficiency need further investigation.
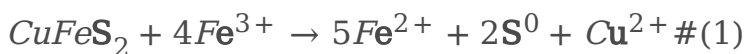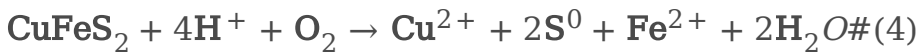
1. Introduction

Copper is one of the most common heavy metals and an essential raw material for many industries due to its inexpensive and excellent in performance. Copper is also an essential trace element for organisms, but it can be extremely toxic when ingested in excess (Yang et al., 2020). Copper is released into the environment and society through industrial activities such as mining, metallurgy and secondary processing. (Araújo et al., 2019). Chalcopyrite ($CuFeS_2$) is the main source of global copper reserves, and is the most abundant and widely distributed copper-bearing mineral in the earth's crust (Sun et al., 2021; Xu et al., 2016; Zhao et al., 2019). Traditional copper extraction technologies such as pyrometallurgy and hydrometallurgy have the disadvantages of high energy consumption and large environmental pollution. In current mining industry, attention has been given to bioleaching due to the processes of it was clean (Ma et al., 2021; Sun et al., 2021). Bioleaching applies microorganisms and their secretions (mainly extracellular polymeric substances, EPS) to recover value-metals from minerals at mild conditions (Tanne & Schippers, 2019). However, the copper extraction efficiency in chalcopyrite bioleaching process is low due to some reasons: high lattice energy of chalcopyrite (Wang, 2005; Zhang et al., 2016), and easy to form passivation layers in the bioleaching process. In previous studies, by mechanochemically activated (Cao et al., 2020), regulating factors (Khoshkhoo et al., 2017; Wang et al., 2014), and introducing additives (Yang et al., 2020; Ma et al., 2017; Koleini et al., 2011) to improve copper extraction. In addition, high ore heap bioleaching and in-situ bioleaching need to solve the problem of insufficient electron acceptors inside the mine heap through aeration, which increases energy consumption (Huang et al., 2019). Therefore, the current challenge is to develop new technologies to solve these defects.

Bioelectrochemical system (BES) is unique systems that integrate microorganisms with an electrochemical method, and it shows the process of electricity generation or achieve the redox reaction
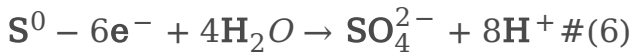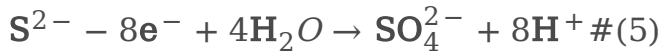
with a certain potential poised by means of electron transfer between the electron acceptors and electron donors (Zhang & Angelidaki, 2015; Zheng et al., 2020). According to the direction of electron transfer and the form of energy conversion, bioelectrochemical system main can be divided into microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) (de los Ángeles Fernandez et al., 2016). In MFCs, microorganisms or enzymes as catalysts can covert the chemical energy stored in biodegradable materials to electricity. Electrons and protons released as the product of bacterial metabolism onto the anode travel towards the cathode through two paths, and electrons are finally captured and utilized by the terminal electron acceptor (TEA) of cathode (Almatouq et al., 2020; Nancharaiah et al., 2015; Pant et al., 2012; Wilberforce et al., 2021). MECs also use microorganisms or enzymes as catalysts, but the form of energy conversion and the direction of electron transfer of MECs are opposite to those of the MFCs. Recently, bioelectrochemical system as an innovative technology for the removal and recovery of heavy metal ions from wastewater have become research hotspots (Yazdi et al., 2015). In MFCs, the crude metal was deposited and recovered through reduction of heavy metal ions in the cathode chamber while organics were used as the electron donor in the anode chamber (Huang et al,.2019). However, considerable amounts of electrical energy are required in recovering heavy metal ions with MECs (Motos et al., 2015). Compared with MECs, MFCs is an environmentally friendly and sustainable way to recover heavy metal.

Bioleaching as an intersection of multiple disciplines is well suited to implement electrochemical approaches for the optimization of metal leaching and recovery (Kaksonen et al., 2020; Tanne & Schippers, 2019). The feasibility of MFCs to assist in the bioleaching of chalcopyrite concentrates has been demonstrated (Huang et al., 2019). The bioleaching of chalcopyrite involves a series of redox reactions, and the bioleaching mechanism. In the indirect mechanism, chalcopyrite is attacked by Fe^{3+} (Eq. (1)) and the role of bacteria is to regenerate the oxidizing agent Fe^{3+} and H^+ (Eq. (2) and Eq. (3)) (Ma et al., 2018; Mahmoud et al., 2017; Pattanaik et al., 2020). Under acidic conditions, abiotic oxidative dissolution of chalcopyrite occurs (Eq. (4)) (Zhao et al., 2019). The direct contact mechanism was microorganisms attached to the mineral surface directly erode and oxidize metallic minerals by biological means, without any involvement of iron ions and other substances (Dong et al., 2013; Ma et al., 2018). S^{2-}/S^0 on the mineral surface loses electrons at the anaerobic anode and is reduced to higher valent sulfate ((Eq. (5) and Eq. (6)) (Ma et al., 2018). Compared to Cu^{2+}, Fe^{3+} and dissolved oxygen have a higher electrode potential and act as electron acceptors for the reduction reaction, as in Eq. (7) and Eq. (8). Copper extraction along with electricity generation were achieved in the chalcopyrite bioleaching assisted by MFCs.
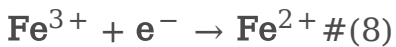
$$CuFeS_2 + 4Fe^{3+} \rightarrow 5Fe^{2+} + 2S^0 + Cu^{2+} \#(1)$$

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{bacteria} 4Fe^{3+} + 2H_2O \#(2)$$

$$2S^0 + 2H_2O + 3O_2 \xrightarrow{bacteria} 2SO_4^{2-} + 4H^+ \#(3)$$

$$CuFeS_2 + 4H^+ + O_2 \rightarrow Cu^{2+} + 2S^0 + Fe^{2+} + 2H_2O \#(4)$$

Reactions of the anode:

$$S^{2-} - 8e^- + 4H_2O \rightarrow SO_4^{2-} + 8H^+ \#(5)$$

$$S^0 - 6e^- + 4H_2O \rightarrow SO_4^{2-} + 8H^+ \#(6)$$

Reactions of the cathode:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \#(7)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \#(8)$$

As a high-grade ore, the chalcopyrite concentrate has been successfully bioleached with the assistance of MFCs (Huang et al., 2019). However, high-grade chalcopyrite ores in the world are becoming more and more scarce due to the consumption of copper resources and development of mine industry. In addition, low-grade ores, tailings and solid wastes contain some valuable metals, and improper disposal of these results in the waste of resources and the risk of contaminating soil or groundwater. Accordingly, the treatment and recycling of low-grade ores, tailings and solid wastes attracted much attention recently. In current study, the feasibility of low-grade chalcopyrite bioleaching assisted by MFCs was investigated. Then the mechanism for the promotion of copper extraction by MFCs was discussed.

2. Materials And Methods
2.1 Mineral and inoculum

Low-grade chalcopyrite was purchased from Daye, Hubei Province, China. X-ray fluorescence spectrometer (XRF, Zetium, PANalytical B.V., The Netherlands) analysis showed that the mineral elements were Cu, 5.86%; S, 5.90%; Fe, 11.92%; Si, 24.60%; Ca, 18.37%; Mg, 13.61%; Al, 6.93%; other elements, 0.89%. X-ray diffraction (XRD, Empyrean sharp shadow, PANalytical. B.V., The Netherlands) analysis showed that the main mineral of samples was chalcopyrite. All samples were sieved to obtain 1 - 2 mm 44.04%, 2 - 2.5 mm 17.29%, and > 2.5 mm 38.68% for leaching experiments.

The inoculum was obtained from a previous bioleaching column of chalcopyrite concentrate, which has been running stably for more than one year and used a mixture of mesophilic acidophilic strains composed mainly of sulfur-oxidizing microorganisms (SOMs) and iron-oxidizing microorganisms (IOMs) as the bioleaching culture.

2.2 Reactors

Two columns (1# and 2#) (Fig. 1) were made of plexiglass (height 300 mm, inner diameter 50 mm). A perforated plate was set at 25 mm above the bottom of each column, and quartz sand with 25 mm

thickness was laid on the upper part as the supporting layer 200 g low-grade chalcopyrite was loaded in columns 1# and 2#. A solution storage tank above each column for pre-precipitation, leachate entered the column through the overflow. MFCs was introduced into column 1#, where two carbon fiber brushes (3 cm diameter × 6 cm length) were inserted into the bottom and middle of the ore heap (6 cm and 11 cm above the supporting layer, respectively) as the anode, while two pieces of carbon paper (2 cm × 3 cm) coated with 0.5 mg/cm^2 Pt catalyst were vertically placed in the upper solution as the cathode. The anode and cathode in each column were connected by a 500 Ω resistor. Two columns were placed in an incubator at 30 ± 1 ℃.

2.3 Bioleaching experiment

Prior to the bioleaching experiment, a pre-acidification step was carried out to reduce the negative effect of alkaline gangue on minerals bioleaching. The pH of leachate was daily adjusted to 2.0 ± 0.1 with 10 mol/L sulfuric acid solution. After 71 days' pre-acidification, the bioleaching experiment was performed at the initial cell density of $0.18 × 10^7$ cell/L and the total leachate of 120 mL. The bottom anode in column 1# was connected to the external circuit at the beginning of the bioleaching experiment and the middle anode was connected to the external circuit on day 133. The leachate in each column was intermittently circulated from the bottom into the upper solution storage tank, then dropped into the column for aeration. The circulation was performed at a flow rate of 0.54 mL/min and a frequency of one day every 3 days using a peristaltic pump (BT101L, Baoding Lead Fluid Technology Co., Ltd., China). The low-grade chalcopyrite contained high content of alkaline gangue, which consumed acid and led to the increase of pH. To alleviate the adverse effect of high pH on chalcopyrite bioleaching (Wang et al., 2018a), the pH was daily adjusted to 2.0 ± 0.1 before day 112 and then the adjustment frequency was changed to once every 3 days. The bioleaching experiment lasted 197 days, among which the circulation was suspended from day 136 to day 155. Besides, the leachate in column 1# leaked by half before day 155 and was replenished with the same volume sulfuric acid solution (pH=2.0) on day 156. During the bioleaching experiment, leachate was periodically sampled for chemical analysis and cell counting. The loss of leachate due to evaporation and sampling was daily supplemented with the deionized water (Liu et al., 2017).

2.4 Analysis methods

Samples of leachate (2 mL) were regularly (six days) withdrawn for measurement of pH, ORP, cell density and concentrations of copper and iron. The copper ion concentration was determined by BCO spectrophotometry (Yang et al., 2020), and the accumulative copper ion was calculated to accurately obtain the copper extraction efficiency. The concentrations of both ferrous ion and total iron (TFe), the pH and the ORP of leachate were measured using the method as described previously (Huang et al., 2019). The cell voltage (U) across the resistor was recorded every 4 min with a digital multimeter (UT71D, Uni-Trend Technology Co. Ltd, China). The daily coulomb (C) was calculated by integrating over time as follows: C = Σ240×U / R. Where 240 was the time interval (s) and R was the external resistance (500 Ω).

At the end of the experiment, bioleaching residues at the bottom carbon brush of each column were sampled and washed three times in turn with dilute sulfuric acid and dilute hydrochloric acid whose pH values were equal to the leachate, finally divided into two sub-samples. One residue sub-sample was observed with a scanning electron microscopy (SEM, JEM-7500F, Japan) to detect the corrosion degree of mineral surface and the morphology of attached microorganisms. Another residue sub-sample, as well as the original minerals, were freeze-vacuum dried, finely ground and sieved through a 200-mesh sieve and stored in nitrogen-filled sealed bags at -20°C for further testing (Liu et al., 2017). XRD was used to analyze the mineralogical compositions. All chemicals used in this study were of analytic grade.

3. Results And Discussion

3.1 Variation of copper ion during the chalcopyrite bioleaching

According to the variation of copper ion concentration in the leachate of columns 1# and 2# (Fig. 2), the bioleaching process was divided into three stages: stage I (day 1-31), stage II (day 31-136) and stage III (day 156-197). In stage I, the concentrations of copper ion in both columns showed a simultaneous and slow increase, suggesting that the inoculum gradually adhered to the mineral surface and adapted to the bioleaching circumstance (Li et al., 2013; Ma et al., 2021). On day 31, the copper ion concentrations in column 1# and 2# were 37.1 mg/L and 37.7 mg/L, respectively. In stage II, the copper ion concentrations of both columns increased faster than that in stage I. Moreover, the copper ion concentration in column 1# increased faster than that in column 2#. On day 136, the copper ion concentration in column 1# was 2481.2 mg/L, twofold higher than that in column 2# (813.3 mg/L). During the stop of circulation (from day 136 to day 155), the copper ion concentration in column 2# increased slowly due to the insufficiency of oxygen supply, but the copper ion concentration in column 1# sharply decreased due to the leakage of leachate. After supplementing the dilute sulfuric acid solution of pH 2.0 into column 1#, the copper ion concentration rapidly increased from 1385.7 mg/L on day 157 to 2130.1 mg/L on day 197. The possible reasons were as follows: 1) the bioelectrochemical action can greatly promote the bioleaching reaction (Khoshkhoo et al., 2017) and the connection of the middle anode to the external circuit further enhanced the bioelectrochemical action; 2) the leakage can effectively alleviate the inhibition of metals on the proliferation and activity of bacteria (Wang et al., 2018a). On day 197, the copper ion accumulation of column 1# reached 423.9 mg, 1.7 times higher than that from column 2# (155.7 mg).

After the microbial adaption in stage I, the copper ion accumulation in column 1# was always higher and showed a faster increase as compared to that in column 2#. This indicated that the introduction of MFCs into chalcopyrite bioleaching promoted copper extraction. Khoshkhoo et al. (2017) also found that the electrochemical action promoted the bioleaching of chalcopyrite. The copper extraction efficiencies in columns 1# and 2# were 3.62% and 1.33%, respectively, which were much lower than those in the aerobic bioleaching columns (Wang et al., 2018b; Zou et al., 2015) due to the cancellation of aeration. In previous work, the chalcopyrite concentrate and the mixed ore have been bioleached with the assistance of MFCs,

respectively achieving the copper extraction efficiencies of 0.19% and 0.15% (Huang et al., 2019). By comparison, a much higher copper extraction efficiency (3.62%) was obtained in the current study. It would be attributed to two reasons: 1) proper particle size ratio favoring the diffusion of leachate in the mineral heap (Lotfalian et al., 2015); 2) the cancellation of aeration, the reduction of circulation frequency and the pH adjustment alleviating ferric precipitation. It should be noted that the cancellation of aeration and the reduction of circulation frequency would reduce the energy consumption but the pH adjustment would increase the chemicals consumption. Thus, balancing energy consumption and chemicals consumption to improve the copper extraction efficiency need further investigation in future work.

3.2 Variation of iron ion and ORP during the chalcopyrite bioleaching

As shown in Fig. 3a, the concentrations of ferrous iron and total iron (TFe) in column 1# kept rising except when the leachate leaked on day 155. In column 2#, the TFe concentration increased continually, but the ferrous iron concentration maintained at a low level (below 288 mg/L) except in the initial phase of stage III. During the stop of circulation (from day 136 to day 155), the ferrous iron concentration in column 1# decreased due to the leakage of leachate, while that in columns 2# increased due to insufficient oxygen supply hindering the oxidation of ferrous iron to ferric iron (Panda et al., 2015a). By comparison, the TFe concentration in column 1# was always higher than that in column 2# before the leachate of column 1# leaked (before day 155). This implied that the dissolution of chalcopyrite in column 1# was faster than column 2#, further confirming that the introduction of MFCs promoted the bioleaching of chalcopyrite.

The ORP was mainly determined by the ratio of ferric to ferrous, which could be explained by the Nernst equation (Khoshkhoo et al., 2017; Peng et al., 2021). Therefore, the ratio of ferric to TFe appeared a variation trend similar to the ORP in each column (Fig. 3b). The ORP in both columns fluctuated greatly before day 61. After that, the ORP in column 2# maintained beyond 450 mV, while that in column 1# decreased quickly in 30 days and maintained below 450 mV after day 91. It was reported that low ORP can alleviate the formation of passivation layer such as jarosite and facilitate the bioleaching of chalcopyrite (Johnson, 2014; Yang et al., 2019). As a result, the copper ion accumulation of column 1# increased much faster than that of column 2# (Fig. 2).

3.3 Variation of pH and cell density during the chalcopyrite bioleaching

As shown in Fig. 4a, the pH in both columns appeared an increase after each pH adjustment, which was attributed to the acid consumption for the dissolution of alkaline gangue and chalcopyrite (Panda et al., 2015b). It should be noted that the pH increment after each pH adjustment gradually narrowed with time, and the pH in both columns maintained below 2.5 from day 71 to day 136. These phenomena ensured a gradual increase of copper ion accumulation (Fig. 2) because low pH was beneficial to copper extraction (Muddanna & Baral, 2021; Wang et al., 2018c). By comparison, the pH of column 1# (coupled with MFCs) was comparable to and even higher than that of column 2#. The introduction of MFCs affected the pH

through two ways. On one hand, the introduction of MFCs facilitated anodic sulfide/sulfur oxidation (Eq. (5) and Eq. (6)), enhancing the acid production (Huang et al., 2019). On the other hand, the electrical field favored the proliferation of iron-oxidizing microorganisms and the oxidation of ferrous iron (Eq. (2)), promoting the acid consumption (Wei et al., 2020). Therefore, the promotion of ferrous oxidation by MFCs seemed stronger than the promotion of sulfide/sulfur oxidation.

The cell densities in columns 1# and 2# (Fig. 4b) showed a slow rise (from 0.18×10^7 cell/L to 1.55×10^7 cell/L and 1.8×10^7 cell/L, respectively) before day 118. This slow rise was attributed to the fact that bioleaching microorganisms gradually adapted to the bioleaching circumstance and the substrate supply (sulfide/sulfur and ferrous iron) in low-grade chalcopyrite was insufficient. During the stop of circulation (from day 136 to day 155), the cell density in column 2# increased slightly due to the insufficiency of oxygen supply, but the cell density in column 1# increased sharply due to the external circuit of MFCs providing electron donors for microbial proliferation (Huang et al., 2019). By comparison, the cell density in column 1# was comparable to and even lower than that in column 2# before day 118. After that, a much higher cell density was found in column 1# as compared to column 2#. These phenomena stemmed from two effects of MFCs on bioleaching bacteria of column 1#: 1) improving microbial activity and growth by the electrical field (Wei et al., 2020); 2) enhancing microbial adsorption onto minerals by the charge imbalance around the anode (Castro & Donati, 2016). The enhancement of microbial activity and adsorption by MFCs can enhance the tolerance of microorganisms to metal inhibition and facilitate the bioleaching of chalcopyrite. As a result, higher copper ion concentration was obtained in column 1# as compared to column 2# during stages II and III (Fig. 2).

3.4 Electricity generation during the MFCs-assisted bioleaching of chalcopyrite

When low-grade chalcopyrite was bioleached under the assistance of MFCs, the daily coulomb production fluctuated due to the intermittent circulation (Fig. 5). Leachate circulation facilitated the diffusion of oxygen to the anode, thereby reducing electricity generation of MFCs (Huang et al., 2019; Liu & Logan, 2004). Within each circulation cycle of 3 d, the coulomb production when the circulation was running was lower than that when the circulation was stopped. To compare the electricity generation capacity, the average coulomb production in different stages or phases was calculated.

The average coulomb production of column 1# in stage I was 1.4 C/d. In stage II, the variation trend of daily coulomb production showed a first increase and a subsequent decrease. The first increase was attributed to the gradual adaption of electroactive microbes to the bioleaching circumstance and the gradual increase of electron donors (sulfide/sulfur) dissolved from minerals. The subsequent decrease was attributed to the inhibition of electroactive microbes by high concentrations of metals. Between day 88 and 136, the coulomb production reached a plateau and the average level was 1.55 C/d. In stage III (day 156-197), the average coulomb production was 1.75 C/d, slightly higher than the former (1.55 C/d) due to the middle anode being connected to the external circuit on day 133. The coulomb production in the current study was much lower than that (4.4 C/d) obtained in the bioleaching of chalcopyrite

concentrate (Huang et al., 2019). The reason lies: the low-grade chalcopyrite contained the lower level of sulfur content than the chalcopyrite concentrate, providing less available electron donors through bioleaching reactions for electricity generation.

3.5 Analysis of surface morphology and composition

After 197 days' bioleaching experiment, corrosion and gullies were found on mineral residues of both columns (Fig. 6). As compared to column 2#, the corrosion of residues in column 1# was more severe, indicating the occurrence of more intensive bioleaching reaction. This was consistent with that more copper ion was extracted in column 1# as compared to column 2# (Fig. 2). When an MFCs was introduced into column 1#, the enhancement of acid production via the electrochemical sulfide/sulfur oxidation around the anode (Zhang et al., 2018) and the enhancement of ferric production by the electrical field (Wei et al., 2020) both contributed to this intensification of corrosion. No cell was observed on residues of both columns, which probably resulted from the bioleaching microorganisms being covered in precipitates that formed during the bioleaching process (Castro & Donati, 2016; Huang et al., 2019).

XRD showed that the major mineral phase of raw ore was chalcopyrite, accompanying by alkaline gangues such as calcite, phlogopite, annite, talc and nontronite. After 197 days of bioleaching, the adsorption peak of chalcopyrite in the residues of both columns weakened greatly. At the same time, the peaks corresponding to calcite, annite and nontronite disappeared, but brushite, gypsum and stewartite were formed. By comparison, the peak corresponding to chalcopyrite in the residue of column 1# was less intensive than that of column 2#. Besides, the peaks corresponding to phlogopite and formed phases (brushite and gypsum) in the residue of column 1# were also less intensive than those of column 2#. These indicated that the introduced MFCs in columns 1# can not only promote the dissolution of chalcopyrite but also promote the dissolution of alkaline gangues. In addition, no jarosite was detected in both columns, probably due to the continuous acid addition that was conducive to reducing the formation of the passivation layer (van Hille et al., 2010).

3.6 Mechanism for the promotion of copper extraction by MFCs

Although the coulomb production in the current study was much lower than other reports (Liu & Yin, 2017; Wu et al., 2018), the promotion of copper extraction by MFCs in the bioleaching of low-grade chalcopyrite was confirmed. The possible mechanism for the promotion of copper extraction by MFCs was speculated as follows. The bioleaching of chalcopyrite mainly depended on microbial metabolism (Liu et al., 2017). Thus the enhancement of microbial growth and adsorption, respectively driven by the electrical field (Wei et al., 2020) and charge imbalance around the anode (Castro & Donati, 2016), might be a reason for this promotion of copper extraction. The phenomenon, the ORP in column 1# (coupled with MFCs) maintaining lower than column 2# after day 61 (Fig. 3b), was accompanied by another phenomenon that the difference between columns 1# and 2# in copper ion accumulation became larger (Fig. 2). Thus, the decrease of ORP driven by MFCs might be another reason for the promotion of copper extraction. As the

main attackers for the dissolution of chalcopyrite, the regeneration of H^+ and Fe^{3+} plays a key role in the copper extraction (Liu et al., 2017). The introduction of MFCs can promote H^+ production via anodic sulfide/sulfur oxidation (Huang et al., 2019) and enhance the biological oxidation of ferrous ion to ferric (Wei et al., 2020). As stated in section 3.3, the pH in column 1# (coupled with MFCs) was comparable and even higher than column 2#, and the promotion of ferrous oxidation by MFCs seemed stronger than the promotion of sulfide/sulfur oxidation. It implied that the enhancement of ferrous oxidation by MFCs contributed much to the promotion of copper extraction.

4. Conclusions

Copper extraction along with electricity generation from the low-grade chalcopyrite were achieved in the bioleaching process assisted by MFCs. After 197 days bioleaching, 423.9 mg copper was extracted from 200 g ore and the average coulomb production reached 1.75 C/d. Bioleaching assisted by MFCs promoted the copper extraction efficiency by 2.7 times, mainly via promoting ferrous oxidation, reducing ORP and stimulating bacterial growth. Providing a feasible method for the utilization of low-grade ores, tailings and solid wastes. But balancing energy consumption of aeration and circulation frequency and chemicals consumption of acid to improve the copper extraction efficiency need further investigation.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

Material preparation, data collection, and analysis were performed by Xueming Zhang and Tao Huang. The first draft of the manuscript was written by Xueming Zhang. Zhixin Jin helped review the writing of the draft manuscript. Shaohui Zhang made a critical editing and reviewing of the whole manuscript. All authors read and approved the final manuscript.

References

1. Almatouq, A., Babatunde, A.O., Khajah, M., Webster, G., Alfodari, M. 2020. Microbial community structure of anode electrodes in microbial fuel cells and microbial electrolysis cells. *J. Water. Process.* Eng. 34.

2. Araújo, D.F., Ponzevera, E., Briant, N., Knoery, J., Sireau, T., Mojtahid, M., Metzger, E., Brach-Papa, C., 2019. Assessment of the metal contamination evolution in the Loire estuary using Cu and Zn stable isotopes and geochemical data in sediments. *Mar. Pollut. Bull.* 143, 12–23.

3. Cao, T., Zheng, F., Nie, Y., Zhou, H., Liu, C., Chen, H., Yang, Y., Xia, L. 2020. Mechanical Activation on Bioleaching of Chalcopyrite: A New Insight. *Minerals*. 10(9).

4. Castro, C., Donati, E. 2016. Effects of different energy sources on cell adhesion and bioleaching of a chalcopyrite concentrate by extremophilic archaeon Acidianus copahuensis. *Hydrometallurgy* 162, 49-56.

5. de los Ángeles Fernandez, M., de los Ángeles Sanromán, M., Marks, S., Makinia, J., Gonzalez del Campo, A., Rodrigo, M., Fernandez, F.J. 2016. A grey box model of glucose fermentation and syntrophic oxidation in microbial fuel cells. *Bioresour. Technol.* 396-404.

6. Dong, Y, Lin, H., Xu, X., Zhou, S. 2013. Bioleaching of different copper sulfides by Acidithiobacillus ferrooxidans and its adsorption on minerals. *Hydrometallurgy* 140, 42-47.

7. Huang, T., Wei, X., Zhang, S. 2019. Bioleaching of copper sulfide minerals assisted by microbial fuel cells. *Bioresour. Technol.* 288, 121561.

8. Johnson, D.B. 2014. Biomining-biotechnologies for extracting and recovering metals from ores and waste materials. *Curr. Opin. Biotechnol.* 30, 24-31.

9. Kaksonen, A.H., Deng, X., Bohu, T., Zea, L., Khaleque, H.N., Gumulya, Y., Boxall, N.J., Morris, C., Cheng, K.Y. 2020. Prospective directions for biohydrometallurgy. *Hydrometallurgy* 195, 105376.

10. Khoshkhoo, M., Dopson, M., Engström, F., Sandström, Å. 2017. New insights into the influence of redox potential on chalcopyrite leaching behaviour. *Miner. Eng.* 100, 9-16.

11. Koleini, S.M.J., Aghazadeh, V., Sandstrom, A. 2011. Acidic sulphate leaching of chalcopyrite concentrates in presence of pyrite. *Miner. Eng.* 24(5), 381-386.

12. Li, L., Lv, Z., Yuan, X. 2013. Effect of l-glycine on bioleaching of collophanite by Acidithiobacillus ferrooxidans. *Int. Biodeterior. Biodegrad.* 85, 156-165.

13. Liu, H., Logan, B.E. 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* 38(14), 4040-4046.

14. Liu, H., Xia, J., Nie, Z., Liu, L., Wang, L., Ma, C., Zheng, L., Zhao, Y., Wen, W. 2017. Comparative study of S, Fe and Cu speciation transformation during chalcopyrite bioleaching by mixed mesophiles and mixed thermophiles. *Miner. Eng.* 106, 22-32.

15. Liu, W., Yin, X. 2017. Recovery of copper from copper slag using a microbial fuel cell and characterization of its electrogenesis. *Int. J. Miner. Metall. Mater.* 24(6), 621-626.

16. Lotfalian, M., Ranjbar, M., Fazaelipoor, M.H., Schaffie, M., Manafi, Z. 2015. Continuous Bioleaching of Chalcopyritic Concentrate at High Pulp Density. *Geomicrobiol. J.* 32(1), 42-49.

17. Ma, L., Wang, X., Liu, X., Wang, S., Wang, H. 2018. Intensified bioleaching of chalcopyrite by communities with enriched ferrous or sulfur oxidizers. *Bioresour. Technol.* 268, 415-423.

18. Ma, P., Yang, H., Luan, Z., Sun, Q., Ali, A., Tong, L. 2021. Leaching of Chalcopyrite under Bacteria–Mineral Contact/Noncontact Leaching Model. *Minerals.* 11(3), 230.

19. Ma, Y., Liu, H., Xia, J., Nie, Z., Zhu, H., Zhao, Y., Ma, C., Zheng, L., Hong, C., Wen, W. 2017. Relatedness between catalytic effect of activated carbon and passivation phenomenon during chalcopyrite bioleaching by mixed thermophilic Archaea culture at 65 °C. *Trans. Nonferrous Met. Soc. China.* 27(6), 1374-1384.

20. Mahmoud, A., Cezac, P., Hoadley, A.F.A., Contamine, F., D'Hugues, P. 2017. A review of sulfide minerals microbially assisted leaching in stirred tank reactors. *Int. Biodeterior. Biodegrad.* 119, 118-146.

21. Motos, P.R., ter Heijne, A., van der Weijden, R., Saakes, M., Buisman, C.J.N., Sleutels, T.H.J.A. 2015. High rate copper and energy recovery in microbial fuel cells. *Front. Microbiol.* 6

22. Muddanna, M.H., Baral, S.S. 2021. Bioleaching of rare earth elements from spent fluid catalytic cracking catalyst using Acidothiobacillus ferrooxidans. J. Environ. *Chem. Eng.* 9(1), 104848.

23. Nancharaiah, Y.V., Venkata Mohan, S., Lens, P.N. 2015. Metals removal and recovery in bioelectrochemical systems: A review. *Bioresour. Technol.* 195, 102-14.

24. Panda, S., Akcil, A., Pradhan, N., Deveci, H. 2015a. Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology. *Bioresour. Technol.* 196, 694-706.

25. Panda, S., Biswal, A., Mishra, S., Panda, P.K., Pradhan, N., Mohapatra, U., Sukla, L.B., Mishra, B.K., Akcil, A. 2015b. Reductive dissolution by waste newspaper for enhanced meso-acidophilic bioleaching of copper from low grade chalcopyrite: A new concept of biohydrometallurgy. *Hydrometallurgy* 153, 98-105.

26. Pant, D., Singh, A., Van Bogaert, G., Olsen, S.I., Nigam, P.S., Diels, L., Vanbroekhoven, K. 2012. Bioelectrochemical systems (BES) for sustainable energy production and product recovery from organic wastes and industrial wastewaters. *RSC Adv.* 2(4), 1248-1263.

27. Pattanaik, A., Sukla, L.B., Pradhan, D., Samal, D.P.K. 2020. Microbial mechanism of metal sulfide dissolution. *Mater. Today: Proc.* 30, 326-331.

28. Peng, T., Liao, W., Wang, J., Miao, J., Peng, Y., Gu, G., Wu, X., Qiu, G., Zeng, W. 2021. Bioleaching and Electrochemical Behavior of Chalcopyrite by a Mixed Culture at Low Temperature. *Front. Microbiol.* 12, 663757.

29. Sun, X., Yuan, W., Jin, K., Zhang, Y. 2021. Control of the Redox Potential by Microcontroller Technology: Researching the Leaching of Chalcopyrite. *Minerals.* 11(4), 382.

30. Tanne, C.K., Schippers, A. 2019. Electrochemical Applications in Metal Bioleaching. *Bioelectrosynthesis* 167, 327-359.

31. van Hille, R.P., van Zyl, A.W., Spurr, N.R.L., Harrison, S.T.L., 2010. Investigating heap bioleaching: Effect of feed iron concentration on bioleaching performance. *Miner. Eng.* 23(6), 518-525.

32. Wang, S. 2005. Copper leaching from chalcopyrite concentrates. *JOM* 57(7), 48-51.

33. Wang, X., Huang, N., Shao, J., Hu, M., Zhao, Y., Huo, M. 2018a. Coupling heavy metal resistance and oxygen flexibility for bioremoval of copper ions by newly isolated Citrobacter freundii JPG1. *J. Environ. Manage.* 226, 194-200.

34. Wang, Y., Zeng, W., Chen, Z., Su, L., Zhang, L., Wan, L., Qiu, G., Chen, X., Zhou, H., 2014. Bioleaching of chalcopyrite by a moderately thermophilic culture at different conditions and community dynamics of planktonic and attached populations. *Hydrometallurgy* 147–148, 13–19.

35. Wang, Y., Chen, X., Zhou, H. 2018b. Disentangling effects of temperature on microbial community and copper extraction in column bioleaching of low grade copper sulfide. *Bioresour. Technol.* 268, 480-487.

36. Wang, Y., Li, K., Chen, X., Zhou, H. 2018c. Responses of microbial community to pH stress in bioleaching of low grade copper sulfide. *Bioresour. Technol.* 249, 146-153.

37. Wei, X., Liu, D., Huang, W., Huang, W., Lei, Z. 2020. Simultaneously enhanced Cu bioleaching from E-wastes and recovered Cu ions by direct current electric field in a bioelectrical reactor. *Bioresour. Technol.* 298, 122566.

38. Wilberforce, T., Sayed, E.T., Abdelkareem, M.A., Elsaid, K., Olabi, A.G. 2021. Value added products from wastewater using bioelectrochemical systems: Current trends and perspectives. *J. Water. Process. Eng.* 39.

39. Wu, Y., Zhao, X., Jin, M., Li, Y., Li, S., Kong, F., Nan, J., Wang, A. 2018. Copper removal and microbial community analysis in single-chamber microbial fuel cell. *Bioresour. Technol.* 253, 372-377.

40. Xu, J., Qu, Z., Yan, N., Zhao, Y., Xu, X., Li, L., 2016. Size-dependent nanocrystal sorbent for copper removal from water. *Chem. Eng. J.* 284, 565–570.

41. Yang, B., Zhao, C., Luo, W., Liao, R., Gan, M., Wang, J., Liu, X., Qiu, G. 2020. Catalytic effect of silver on copper release from chalcopyrite mediated by Acidithiobacillus ferrooxidans. *J. Hazard. Mater.* 392, 122290.

42. Yang, Y., Liu, W., Gao, X., Chen, M. 2019. An XAS study of silver species evolution in silver-catalysed chalcopyrite bioleaching. *Hydrometallurgy* 186, 252-259.

43. Yazdi, H., Alzate-Gaviria, L., Ren, Z.J. 2015. Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production. *Bioresour. Technol*. 180, 258-263.

44. Zhang, Y., Angelidaki, I. 2015. Bioelectrochemical recovery of waste-derived volatile fatty acids and production of hydrogen and alkali. *Water Res*. 81, 188-95.

45. Zhang, R., Wei, D., Shen, Y., Liu, W., Lu, T., Han, C. 2016. Catalytic effect of polyethylene glycol on sulfur oxidation in chalcopyrite bioleaching by Acidithiobacillus ferrooxidans. *Miner. Eng*. 95, 74-78.

46. Zhang, S., Bao, R., Lu, J., Sang, W. 2018. Simultaneous sulfide removal, nitrification, denitrification and electricity generation in three-chamber microbial fuel cells. *Sep. Purif. Technol*. 195, 314-321.

47. Zhao, H., Zhang, Y., Zhang, X., Qian, L., Sun, M., Yang, Y., Zhang, Y., Wang, J., Kim, H., Qiu, G. 2019. The dissolution and passivation mechanism of chalcopyrite in bioleaching: An overview. *Miner. Eng*. 136, 140-154.

48. Zheng, T., Li, J., Ji, Y., Zhang, W., Fang, Y., Xin, F., Dong, W., Wei, P., Ma, J., Jiang, M. 2020. Progress and Prospects of Bioelectrochemical Systems: Electron Transfer and Its Applications in the Microbial Metabolism. *Front. Bioeng. Biotechnol*. 8, 10.

49. Zou, G., Papirio, S., Lai, X., Wu, Z., Zou, L., Puhakka, J.A., Ruan, R. 2015. Column leaching of low-grade sulfide ore from Zijinshan copper mine. *Int. J. Miner. Process*. 139, 11-16.
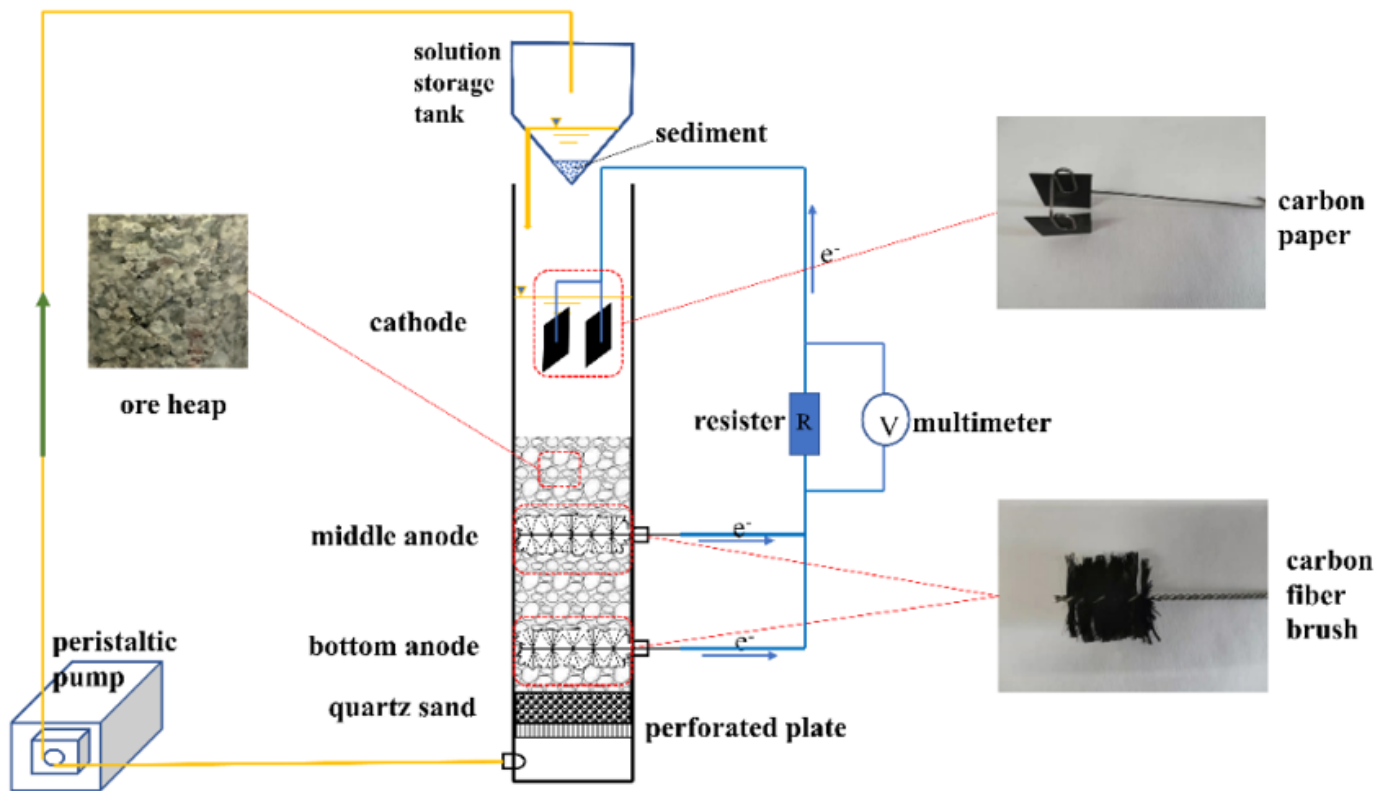
Figures

Figure 1
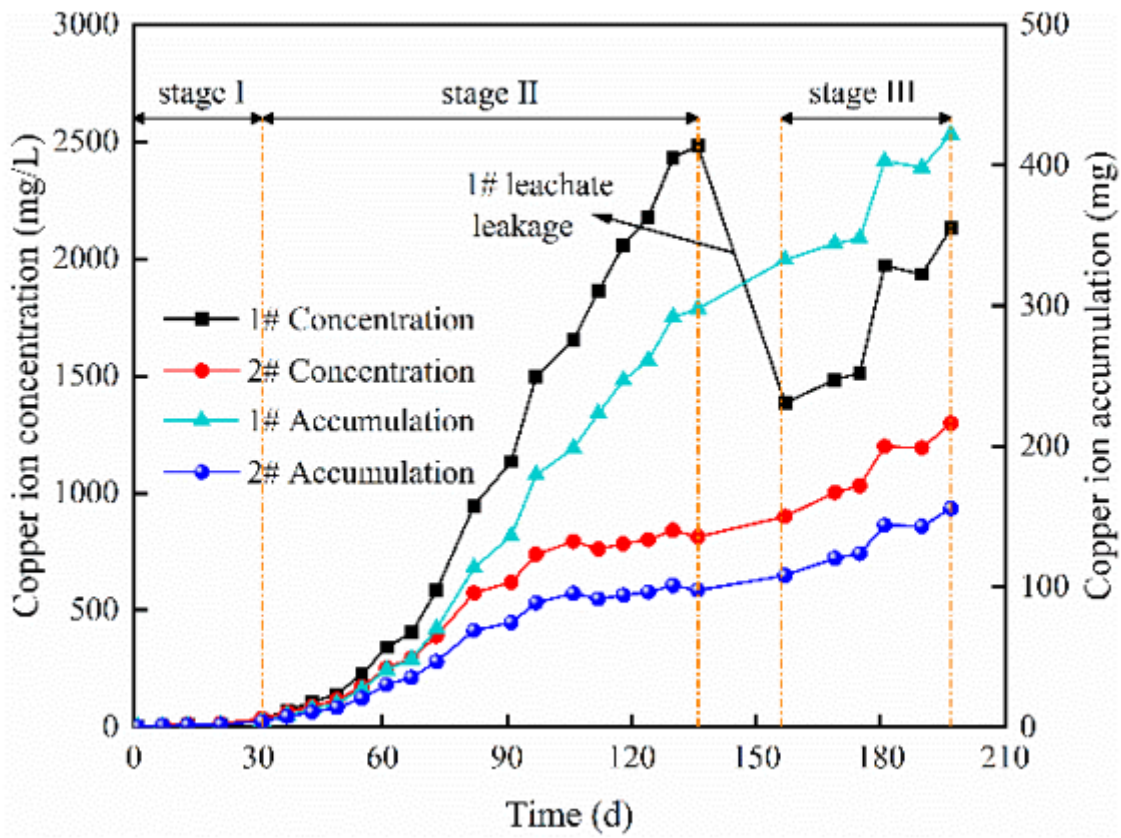
Bioleaching column coupled with MFCs.

Figure 2

Variation in concentration and accumulation of copper ion during the chalcopyrite bioleaching.
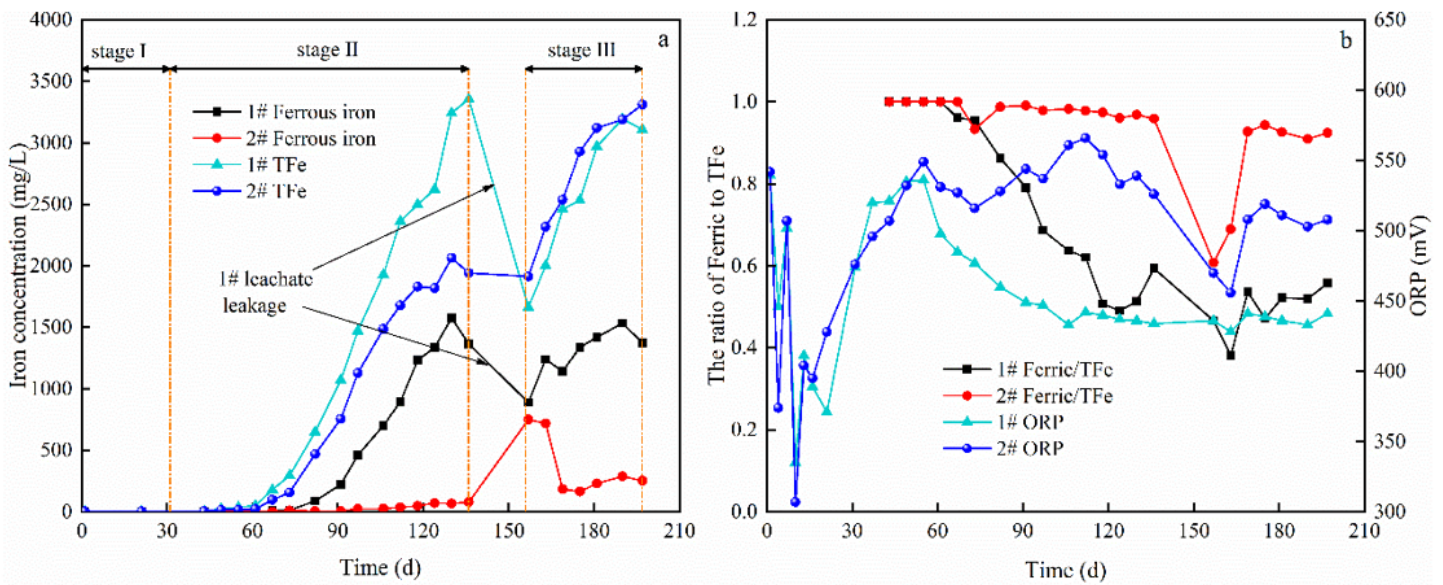

Figure 3

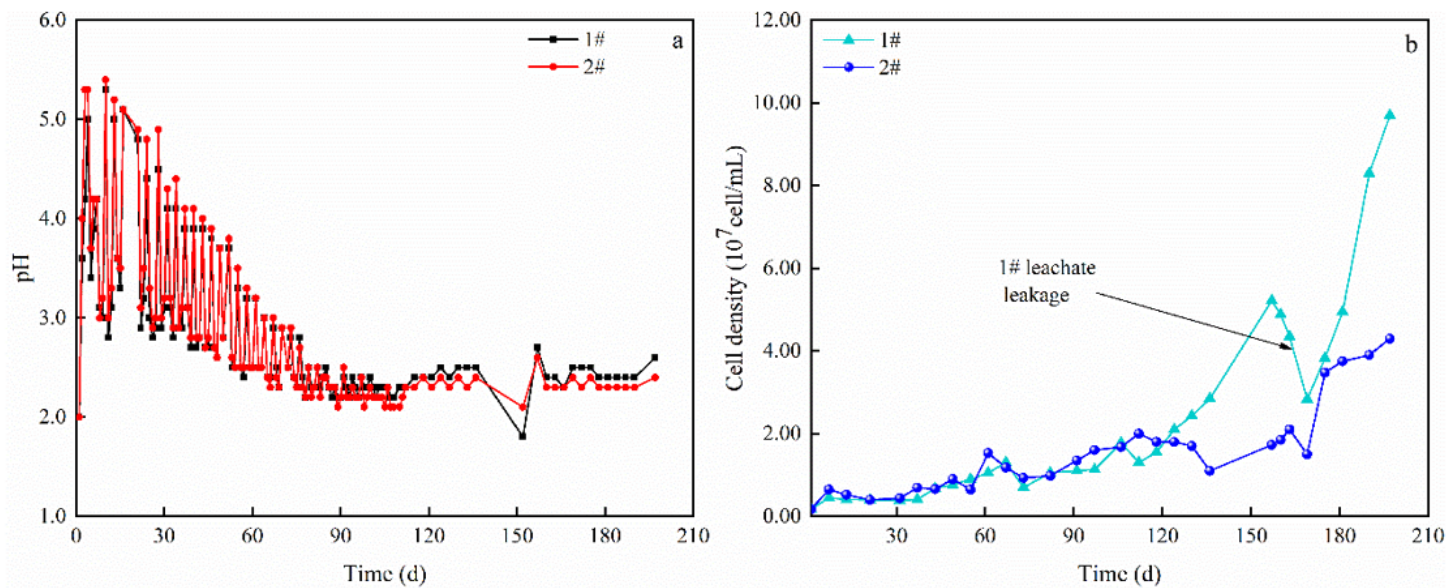Variation of the iron ion concentration, Ferric/TFe and ORP during the chalcopyrite bioleaching.

Figure 4

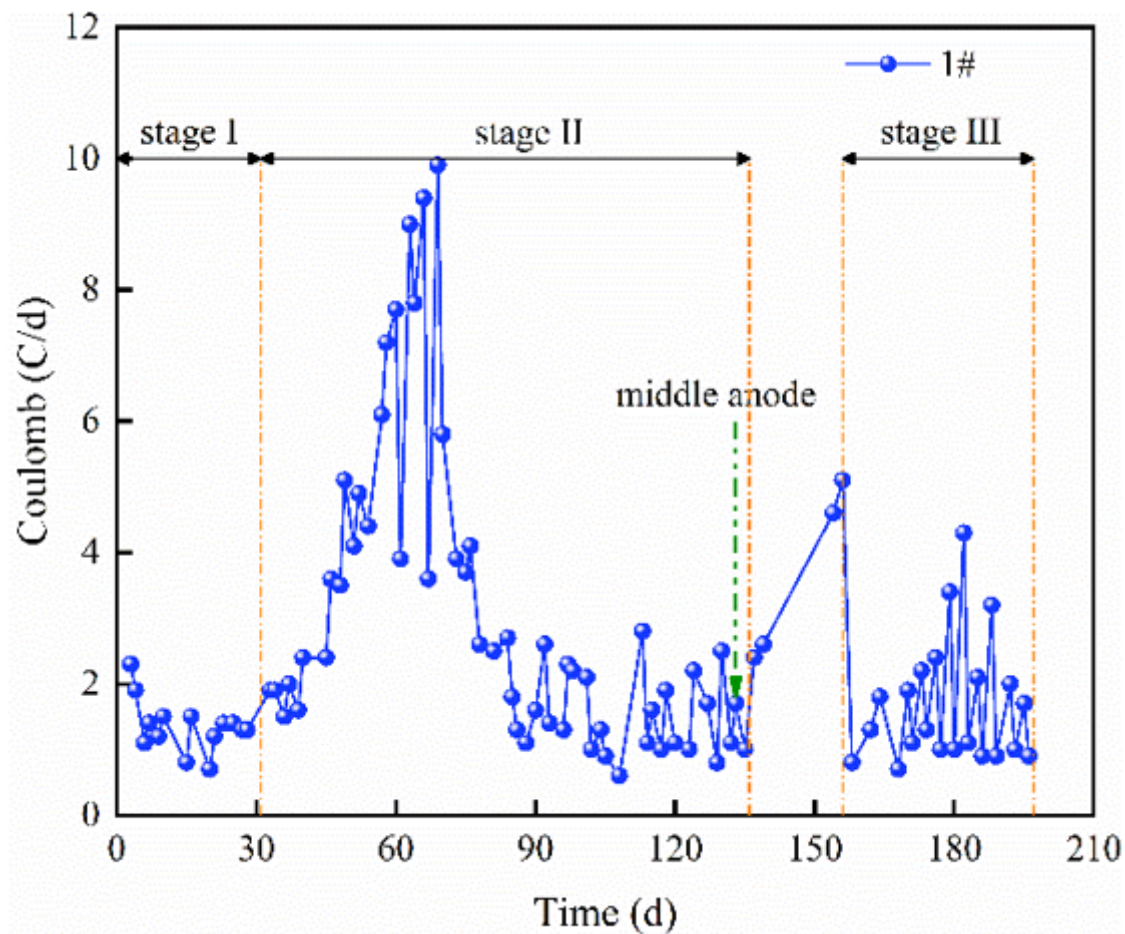Variation of pH and cell density during the chalcopyrite bioleaching.

Figure 5
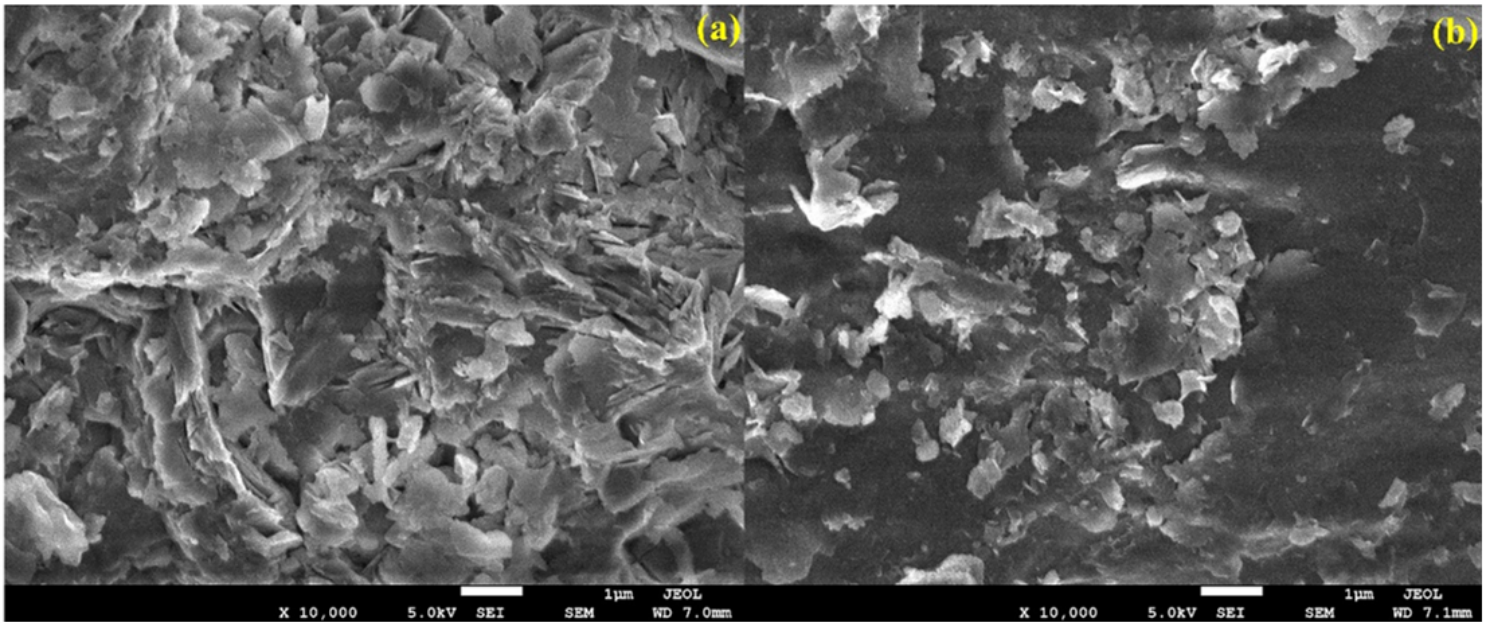
Coulomb production in column 1#.

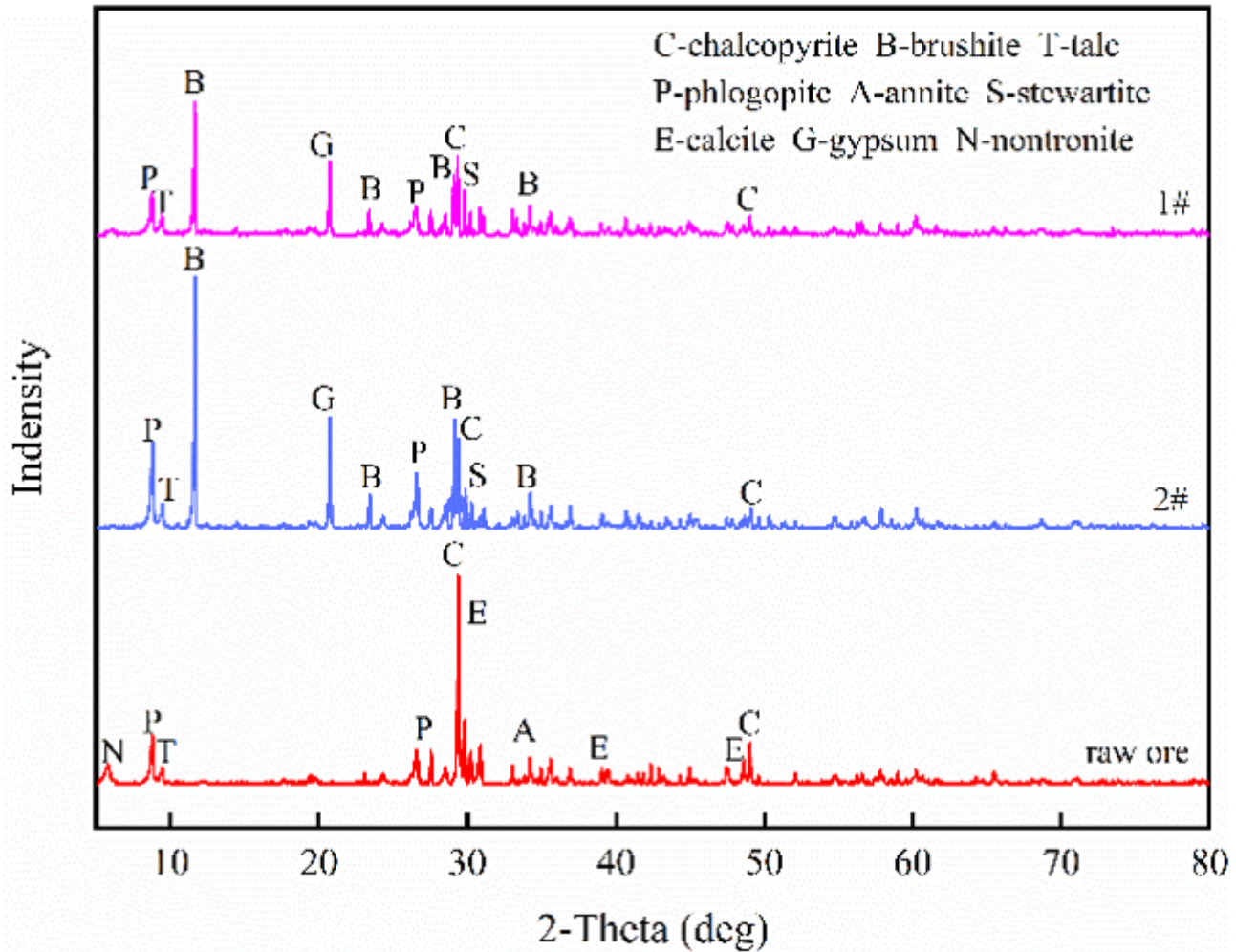**Figure 6**

SEM images (×10000) of residues in column (a) 1# and (b) 2#

Figure 7

XRD analysis of residue in different columns and raw ore