Copper extraction from low-grade chalcopyrite in a bioleaching column assisted by bioelectrochemical system

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Abstract
Low-grade ores, tailings, and solid wastes contain small amounts of valuable heavy metals. Improper disposal of these substances 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 the 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 was 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 chemical consumption of acid to improve the copper extraction efficiency need further investigation.

Keywords Bioelectrochemical system · Low-grade chalcopyrite · Microbial fuel cell · Bioleaching · Copper extraction · Electricity production

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 (CuFeS₂) 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 the bioleaching because it has the advantages of environmental friendliness, energy saving, emission reduction (such as SO2) (Dimitrijevic et al. 2009), and cost reduction when extracting copper from oxidized sulfide ores (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 and Schippers 2019). The processes have been successfully applied in countries including the USA, Chile, Australia, Canada, South Africa, and China. Twenty-five percent of the world’s copper production is obtained through bioleaching processes. However, the cycle of bioleaching is long and itself has high environmental requirements such as pH and temperature, which results in a low leaching efficiency. The copper extraction efficiency in chalcopyrite bioleaching processes is low due...
to some reasons: high lattice energy of chalcopyrite (Wang 2005; Zhang et al. 2016), easy to form passivation layers on the mineral surface in the bioleaching process. In previous studies, some measures were proposed by researchers to solve these problems, as follows: mechanical activation can increase the specific surface area of chalcopyrite and make it easier to be adsorbed by microorganisms to promote the bioleaching rate of chalcopyrite (Cao et al. 2020); regulating factors such as pH, ORP, and temperature can promote bacterial growth and slow down the formation of passivation (Khoshkhou et al. 2017; Wang et al. 2014); introducing additives such as silver ion, activated carbon, and pyrite to enhance the catalytic effect and reduce the formation of passivation layer on the surface of minerals (Yang et al. 2020; Ma et al. 2017; Koleini et al. 2011). 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, but this process has high energy consumption and cost. Therefore, the current challenge is to develop new bioleaching process to solve these defects and improve the copper extraction efficiency.

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 and Angelidakis 2015; Zheng et al. 2020). According to the direction of electron transfer and the form of energy conversion, BES 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; Nancharaih 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 has 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. 2019a). However, considerable amounts of electrical energy are required in recovering heavy metal ions with MECs (Motos et al., 2015). Compared with MECs, MFCs are 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 and Schippers 2019). The feasibility of MFCs to assist in the bioleaching of chalcopyrite concentrates has been demonstrated (Huang et al. 2019a). The bioleaching of chalcopyrite involves a series of redox reactions, and the bioleaching mechanism. In the indirect mechanism, chalcopyrite is attacked by Fe3+ (Eq. (1)) and the role of bacteria is to regenerate the oxidizing agent Fe3+ and H+ (Eqs. (2) and (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). S2−/S0 on the mineral surface loses electrons at the anaerobic anode and is reduced to higher valent sulfate ((Eqs. (5) and (6)) (Ma et al. 2018). Compared to Cu2+, Fe3+, and dissolved oxygen have a higher electrode potential and act as electron acceptors for the reduction reaction, as in Eqs. (7) and (8). Copper extraction along with electricity generation was achieved in the chalcopyrite bioleaching assisted by MFCs.

$$\text{CuFeS}_2 + 4\text{Fe}^{3+} \rightarrow 5\text{Fe}^{2+} + 2\text{S}^0 + \text{Cu}^{2+} \quad (1)$$

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \xrightarrow{\text{bacteria}} 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (2)$$

$$2\text{S}^0 + 2\text{H}_2\text{O} + 3\text{O}_2 \xrightarrow{\text{bacteria}} 2\text{SO}_4^{2−} + 4\text{H}^+ \quad (3)$$

$$\text{CuFeS}_2 + 4\text{H}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + 2\text{S}^0 + \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (4)$$

Reactions of the anode:

$$\text{S}^2− - 8\text{e}− + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2−} + 8\text{H}^+ \quad (5)$$

$$\text{S}^0 - 6\text{e}− + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2−} + 8\text{H}^+ \quad (6)$$

Reactions of the cathode:

$$\text{O}_2 + 4\text{e}− + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad (7)$$

$$\text{Fe}^{3+} + \text{e}− \rightarrow \text{Fe}^{2+} \quad (8)$$

As a high-grade ore, the chalcopyrite concentrate has been successfully bioleached with the assistance of MFCs (Huang et al. 2019a). 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. At the same, different types of waste are generated...
in mining and processing activities, such as low-grade ore, mine waste, and tailings. These wastes contain more types of heavy metals but less content, and improper disposal of these wastes can cause 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. Heap leaching is a key technology for the leaching of valuable metals from low-grade ores (Petersen 2016), and column leaching is used as an indoor simulation test of heap leaching processes to obtain some process parameters (Dhawan et al. 2012; Panda et al. 2013). In current study, the feasibility of low-grade chalcopyrite bioleaching assisted by MFCs was investigated in a column bioleaching system. Then the mechanism for the promotion of copper extraction by MFCs was discussed.

**Materials and methods**

**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%; and 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.

**Reactors**

Two columns (1# and 2#) (Fig. 1) were made of plexiglass (height 300 mm, inner diameter 50 mm). Column 1# was coupled with an MFC while column 2# was not coupled with MFCs. 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, and 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. 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)

![Fig. 1 Bioleaching column coupled with MFCs (1#)](image-url)
coated with 0.5 mg/cm² Pt catalyst were vertically placed in the upper solution as the cathode. MFCs were introduced into column 1# when the electrodes (anode and cathode) were connected with a 500 Ω resistor after pre-acidification operation. The electrodes also were added in column 2#, but they were not connected. Two columns were placed in an incubator at 30 ± 1 °C.

**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 × 10⁷ 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 and 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).

**Analysis methods**

Samples of leachate (2 mL) were regularly (6 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. 2019a). 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 = ∑240 × 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 and 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.

**Results and discussion**

**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 1–30), 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. 2013). In stage II, the copper ion concentration started to increase more rapidly due to the high metal content of chalcopyrite. In stage III, the copper ion concentration continued to increase but at a slower rate due to the depletion of copper in the chalcopyrite. The variation in concentration and accumulation of copper ion during the chalcopyrite bioleaching is shown in Fig. 2.
respectively, which were much lower than those in the aer-}

efficiencies in columns 1# and 2# were 3.62% and 1.33%,

the bioleaching of chalcopyrite. The copper extraction

bioleaching promoted copper extraction. Khoshkhoo et al.

indicated that the introduction of MFCs into chalcopyrite

accumulation in column 1# was always higher and showed

higher than that from column 2# (155.7 mg).

accumulation of column 1# reached 423.9 mg, 1.7 times

bacteria (Wang et al. 2018a). On day 197, the copper ion

ion concentration rapidly increased

to 332.58 mg and from 97.60 mg to 108.13 mg, respectively.

mulation of columns 1# and 2# increased from 297.74 mg

per extraction efficiency (3.62%) was obtained in the cur-

(Johnson 2014; Yang et al. 2021). On day 31, the copper ion concentrations in columns 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# (with MFCs) 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). The MFCs system has an obvious promotion effect on the low-grade chalcopyrite bioleaching, which promotes redox reactions of bioleaching system maybe through alleviating the lack of electron acceptors in the ore heap. During the stop of circulation (from day 136 to day 155), the copper ion concentration in column 2# increased slowly, and the copper ion concentration in column 1# sharply decreased due to the leakage of leachate. However, Fig. 2 shows that the copper ion accumulation of columns 1# and 2# increased from 297.74 mg to 332.58 mg and from 97.60 mg to 108.13 mg, respectively. It provided a basis for MFCs to promote the leaching of chalcopyrite through alleviating the problem of insufficient electron acceptors (mainly oxygen) in the system. 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 biocatalysts chemical action can greatly promote the bioleaching reaction (Khoshkhou et al. 2017) and the connection of the middle anode to the external circuit further enhanced the biocatalysts chemical 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. Khoshkhou 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 aerobioleaching columns (Wang et al. 2018b; Zou et al. 2015) due to the cancelation 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. 2019a). 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 cancelation of aeration, the reduction of circulation frequency, and the pH adjustment alleviating ferric precipitation. It should be noted that the cancelation 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. Additional, applying tank bioleaching (Hedrich et al. 2018; You et al. 2020), optimizing experimental parameters such as reducing particle size of the sample (Olubambi et al. 2009) and increasing temperature (using moderate or extreme thermophilic bacteria) (Huang et al. 2019b; Liang et al. 2018; You et al. 2020) could be used to improve the copper extraction efficiency in future work.

### 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 column 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. In stage III, the leachate of two columns resumed intermittent circulation. Fig. 3b showed that the ratio of ferric to TFe gradually rose and ferric dominated in TFe. The copper ion concentrations of two columns were also rising and the trend of rise in column 1# were more obvious than that in column 2#. Sufficient oxidant (ferric) was conducive to the bioleaching of chalcopyrite, and MFCs system can speed up the conversion between ferrous iron and ferric.

The ORP was mainly determined by the ratio of ferric to ferrous, which could be explained by the Nernst equation (Khoshkhou 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.
As a result, the copper ion accumulation of column 1# increased much faster than that of column 2# (Fig. 2).

**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 and gradually narrowed with time. From day 1 to day 70, the pH of the leachate of two columns changed drastically, and the concentrations of copper ion, ferrous iron, and TFe were low; the pH increment after each pH adjustment and the pH in both columns maintained below 2.5 from day 71 to day 136, it can be found the concentrations of copper ion, ferrous iron, and TFe increased. Low-grade chalcopyrite is often accompanied by a large amount of alkaline gangue, which affected the iron ions and H+ in the leachate during the dissolution process of chalcopyrite (Panda et al. 2015b; Mwase et al. 2012). Low pH of leachate was beneficial a gradual increase of copper ion accumulation (Fig. 2) (Muddanna and 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 (Eqs. (5) and (6)), enhancing the acid production (Huang et al. 2019a). 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 $0.18 \times 10^7 \text{ cell/L}$ to $1.55 \times 10^7 \text{ cell/L}$ and $1.8 \times 10^7 \text{ cell/L}$, 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. 2019a). 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#. Especially after the middle anode was connected to the external circuit on day 133, the cell density in column 1# increased obviously. 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) and (2) enhancing microbial adsorption onto minerals by the charge imbalance around the anode (Castro and 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).
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. 2019a; Liu and 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). The reasons were as follows: middle anode being connected to the external circuit on day 133 enhanced the electrochemical effect; but the dissolved oxygen content of upper ore heap was higher than that of bottom ore heap, which directly grabbed electrons and inhibited the activity of EAMs. 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. 2019a). 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.

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 and Donati 2016; Huang et al. 2019a).

XRD showed that the major mineral phase of raw ore was chalcopyrite, accompanying by alkaline gangues such as calcite, phlogopite, annite, talc, and nontronite (Fig. 7). 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 column 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).

**Mechanism for the promotion of copper extraction by MFCs**

Although the coulomb production in the current study was much lower than other reports (Liu and Yin 2017; Wu et al. 2018), the promotion of copper extraction by MFCs in the bioleaching of low-grade chalcopyrite was confirmed. The bioleaching of chalcopyrite mainly depended on microbial metabolism (Liu et al. 2017). With the assistance of MFCs system, the mechanism became complicated. The possible mechanism for the promotion of copper extraction by MFCs was speculated as follows (Fig. 8). Due to the difference in dissolved oxygen content in the system during...
the column leaching process, the leaching system in this study could be divided into three parts:

1) **Upper solution**: The dissolved oxygen content of this part was the highest among the three parts. In the conventional bioleaching, this part was the regeneration site of Fe$^{3+}$. Fe$^{2+}$ enters the upper solution through external circulation and internal free diffusion and then biological oxidized Fe$^{2+}$ to Fe$^{3+}$ by free IOMs (Eq. (2)). In the MFCs system, dissolved oxygen combines with electrons transferred from the external circuit with the catalysis of platinum on the cathode surface, and part of Fe$^{3+}$ near the cathode was reduced to Fe$^{2+}$ (Eqs. (7) and (8)).

2) **Upper ore heap**: The dissolved oxygen content of this part is lower than that of upper solution, but higher than that of bottom ore heap, so it can act as an electron acceptor to participate in the reaction. In the early stage of the bioleaching, the dissolution of low-grade chalcopyrite depended on the corrosive action of H$^+$, the attack effect of Fe$^{3+}$ and the direct contact mechanism of attached organisms (Eqs. (1) and (4)). At the same time, the intermediate products Fe$^{2+}$ and S$^{2-}$/S$^0$ were biological oxidized into Fe$^{3+}$, H$^+$, and SO2$^{-}$ by IOMs and SOMs (Eqs. (2) and (3)). Compared with the previous single anode MFCs system, the copper ion accumulation and cell density of leachate after the middle anode was connected to the external circuit increased. The dissolved oxygen directly grabed electrons near the anode and inhibited the activity of EAMs, so the rising trend of coulomb production was not obvious.

3) **Bottom ore heap**: Dissolved oxygen content was extremely low or even negligible, and chalcopyrite dissolution relied mainly Fe$^{3+}$. The introduction of MFCs can promote H$^+$ production via anodic sulfide/sulfur oxidation (Huang et al. 2019a) and enhance the biological oxidation of Fe$^{2+}$ to Fe$^{3+}$ (Wei et al. 2020). The enhancement of microbial growth and adsorption, respectively driven by the electrical field (Wei et al. 2020) and charge imbalance around the anode (Castro and Donati 2016), might be a reason for copper extraction efficiency higher compared with conventional bioleaching. During the chalcopyrite bioleaching, elemental sulfur and jarosite were the main factors limiting the bioleaching of copper (Klauber 2008). The EAMs near the MFCs’ anode oxidized S$^{2-}$/S$^0$, reducing the deposition of elemental sulfur, meanwhile producing sulfuric acid. The formation of jarosite (Eq. (9)) was related to the temperature, pH, and ORP (ferric/ferrous) of the system (Khoshkho et al. 2017; Peng et al. 2019; Wang et al. 2014).

$$\text{M}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{HO})_6 + 6\text{H}^+$$

where M$^+$ represents H$^+$, K$^+$, Na$^+$, and NH$^+$

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. 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. SEM and XRD show the more intense erosion of the ore surface and the less sediment production such as permeable calcium phosphate in bioleaching with MFCs compared

![Fig. 8 Mechanism model of the chalcopyrite bioleaching](image-url)
conventional bioleaching system. 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). Chemical consumption of acid to improve the copper extraction efficiency need further investigation in the future work.

Conclusions

Copper extraction along with electricity generation from the low-grade chalcopyrite was 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. 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 chemical consumption of acid to improve the copper extraction efficiency need further investigation.

Author contribution Material preparation, data collection, and analysis were performed by XZ and TH. The first draft of the manuscript was written by XZ. ZJ helped review the writing of the draft manuscript. SZ made a critical editing and reviewing of the whole manuscript. All authors read and approved the final manuscript.

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Declarations

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References

Almatoouq, A., Babatunde, A.O., Khajah, M., Webster, G., Alfordari, M. 2020. Microbial community structure of anode electrodes in microbial fuel cells and microbial electrolysis cells. J. Water. Process. Eng. 34. Araújo DF, 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

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).

Castro C, Donati E (2016) Effects of different energy sources on cell adhesion and bioleaching of a chalcopyrite concentrate by extremophilic archaeon Acidithiobacillus copoheanus. Hydrometallurgy 162:49–56

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

Dhawan N, Safarzadeh MS, Miller JD, Moats MS, Rajamani RK, Lin C-L. (2012) Recent advances in the application of X-ray computed tomography in the analysis of heap leaching systems. Miner Eng 35:75–86

Dimitrijevic M, Kostov A, Tasic V, Milosevic N (2009) Influence of pyrometallurgical copper production on the environment. J Hazard Mater 164(2–3):892–899

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

Hedrich S, Joulian C, Graupner T, Schippers A, Guezenec AG (2018) Enhanced chalcopyrite dissolution in stirred tank reactors by temperature increase during bioleaching. Hydrometallurgy 179:125–131

Huang ZZ, Feng SS, Tong YJ, Yang HL (2019b) Enhanced “contact mechanism” for interaction of extracellular polymeric substances with low-grade copper-bearing sulfide ore in bioleaching by moderately thermophilic Acidithiobacillus caldus. J Environ Manage 242:11–21

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

Johnson DB (2014) Biomining-biotechnologies for extracting and recovering metals from ores and waste materials. Curr Opin Biotechnol 30:24–31

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

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

Klauber C (2008) A critical review of the surface chemistry of acidic ferric sulphate dissolution of chalcopyrite with regards to hindered dissolution. Int J Miner Process 86(1–4):1–17

Koleini SMJ, Aghazadeh V, Sandstrom A (2011) Acidic sulphate leaching of chalcopyrite concentrates in presence of pyrite. Miner Eng 24(5):381–386

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

Liang YT, Han JW, Ai CB, Qin WQ (2018) Adsorption and leaching behaviors of chalcopyrite by two extreme thermophilic archaea. T Nonferr Metal Soc 28(12):2538–2544

Liu H, Logan BE (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

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

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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
Lotfalian M, Ranjbar M, Fazaelipoor MH, Schaffie M, Manafi Z (2015) Continuous bioleaching of chalcopyritic concentrate at high pulp density. Geomicrobiol J 32(1):42–49
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
Ma L, Wang X, Liu X, Wang S, Wang H (2018) Intensified bioleaching of chalcopyrite by communities with enriched ferrous or sulfur oxidizers. Bioprocess Biosyst Eng 39:415–423
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
Mahmoud A, Cezac P, Hoadley AFA, Contamine F, D’Hugues P, 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
Mottes, P.R., ter Heijne, A., van der Weijden, R., Saakes, M., Mahmoud A, Cezac P, Hoadley AFA, Contamine F, D’Hugues P, 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
Muts, P.R., ter Heijne, A., van der Weijden, R., Saakes, M., Buissman, C.J.N., Sleutels, T.H.J.A. 2015. High rate copper and energy recovery in microbial fuel cells. Front. Microbiol. 6
Muddamala, M.H., Baral, S.S. 2021. Bioleaching of rare earth elements from spent fluid catalytic cracking catalyst using Acidithiobacillus ferrooxidans. J. Environ. Chem. Eng. 9(1), 104848.
Mwase JM, Petersen J, Eksteen JJ (2012) Assessing a two-stage heap leaching process for Platreef flotation concentrate. Hydrometallurgy 129–130:74–81
Nancharat YV, Venkata Mohan S, Lens PN (2015) Metals removal and recovery in bioelectrochemical systems: a review. Bioprocess Biosyst Eng 39:105–114
Olbambani PA, Potgieter JH, Ndlovu S, Borode JO (2009) Electrochemical studies on interplay of mineralogical variation and particle size on bioleaching low grade complex sulphide ores. T Nonferr Metal Soc 19(5):1312–1325
Panda S, Pradhan N, Mohapatra U, Panda SK, Rath SS, Rao DS, Nayak BD, Sukla LB, Mishra BK (2013) Bioleaching of copper from pre and post thermally activated low grade chalcopyrite contained ball mill spillage. Front Environ Sci Eng 7(2):281–293
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. Bioprocess Biosyst Eng 196:694–706
Panda S, Biswal A, Mishra S, Panda PK, Pradhan N, Mohapatra U, Sukla LB, Mishra BK, Akcil A (2015b) Reductive dissolution by waste newspaper for enhanced meso-acidophilic bioleaching of copper from low grade chalcopyrite: a new concept of biometalurgy. Hydrometallurgy 153:98–105
Pant D, Singh A, Van Bogaert G, Olsen SI, Nigam PS, 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
Pattanaik A, Sukla LB, Pradhan D, Samal DPK (2020) Microbial mechanism of metal sulphide dissolution. Mater Today: Proc 30:326–331
Peng, T., Chen, L., Wang, J., Miao, J., Shen, L., Yu, R., Gu, G., Qiu, G., Zeng, W. 2019. Dissolution and passivation of chalcopyrite during bioleaching by Acidithiobacillus ferrooxidans at low temperature. Minerals 9(6).
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.
Petersen J (2016) Heap leaching as a key technology for recovery of values from low-grade ores – a brief overview. Hydrometallurgy 165:206–212
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
Tanne CK, Schippers A (2019) Electrochemical Applications in Metal Bioleaching. Bioelectrosynthesis 167:327–359
van Hille RF, van Zyl AW, Spurr NRL, Harrison STL (2010) Investigating heap bioleaching: effect of feed iron concentration on bioleaching performance. Miner Eng 23(6):518–525
Wang S (2005) Copper leaching from chalcopyrite concentrates. JOM 57(7):48–51
Wang Y, Zeng W, Chen Z, Su L, Zhang L, Lan W, 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
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
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. Bioprocess Technol 268:480–487
Wang Y, Li K, Chen X, Zhou H (2018c) Responses of microbial community to pH stress in bioleaching of low grade copper sulfide. Bioprocess Technol 249:146–153
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 bioelectrochemical reactor. Bioprocess Biosyst. Eng., 298, 122566.
Wilberforce, T., Sayed, E.T., Abdekareem, M.A., Elsaiad, K., Olabi, A.G. 2021. Value added products from wastewater using bioelectrochemical systems: current trends and perspectives. J. Water Process. Eng. 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. Bioprocess Technol 253:372–377
Xu J, Qu Z, Yan N, Zhao Y, Xu X, Li L (2016) Size-dependent nanocrystal sorbent for copper removal from wastewater. Chem Eng J. 284, 122566.
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
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 ferroxidans. J. Hazard. Mater. 392, 122290.
Yazidi H, Alzate-Gaviria L, Ren ZJ (2015) Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production. Bioprocess Technol 180:258–263
You, J., Solongo, S.K., Gomez-Flores, A., Choi, S., Zhao, H.B., Urik, M., Iyasa, S., Kim, H. 2020. Intensified bioleaching of chalcopyrite concentrate using adapted mesophilic culture in continuous stirred tank reactors. Bioprocess. Technol. 307.
Zhang Y, Angelidaki I (2015) Bioelectrochemical recovery of waste-derived volatile fatty acids and production of hydrogen and alkali. Water Res 81:188–195
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 ferroxidans. Miner Eng 95:74–78
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
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
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
Zou G, Papirio S, Lai X, Wu Z, Zou L, Puhakka JA, Ruan R (2015) Column leaching of low-grade sulfide ore from Zijinshan copper mine. Int J Miner Process 139:11–16

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