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Electricity generation from sulfide tailings using a double-chamber microbial fuel cell

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ABSTRACT Here we established a new approach to pyrrhotite tailings leaching (ferrous sulfide as model) by double-chamber microbial fuel cell technologies to generate electricity while recovering valuable metals. The cell voltage showed values of up to 690.4 mV and the iron recovery of up to 44.6%. Pyrrhotite tailings had potential to drive electricity generation accompanied by microbial leaching of valuable metal using the established double-chamber MFC reactor.

Introduction

It is estimated that iron tailings with an average iron content of 8-15 wt% were deposited into the tailing dam, in total over one billion tons, in China. The tailings have been exposed to air and rainwater, resulting in oxidation to derive low-pH (2-4) acidic wastewater and further dissolving lots of toxic heavy metal.[1] The mainly water-soluble, secondary minerals have been transported by the surface streams towards anywhere to incur the secondary pollution. With the increasing mine tailings pollution and depletion of mineral resources, the recovery of valuable metals from tailings becomes hot topics in recent years.[2] Due to the low capital, short treatment flowsheet and no secondary pollution, the microbial leaching is widely probed for treating tailings.[3,4] During microbial leaching, iron sulfide tailings are biologically oxidized, and valuable metals inlayed in minerals are dissolved in the aqueous solution to be separated and further recovered.

With pyrrhotite tailings (ferrous sulfide tailings) as an example, the mechanism of microbial leaching involves in the direct oxidization and indirect interaction.[6] The direct oxidization implies that the microorganisms have capability of directly oxidize pyrrhotite tailings, i.e. the dissolution of valuable metals is due to the direct contact of bacteria with tailings (eq 1).[7] The ferric ions abiotically leach pyrrhotite tailings into ferrous ion and the elemental sulfur during the indirect interaction.[8,9] Further, ferrous ion and the elemental sulfur are biologically oxidized to ferric ion and sulphuric acid, the leaching agents, and the overall reaction of indirect interaction follows Equation 2. More and more researchers support that the microbial leaching gives priority to the indirect interaction.[6]

$$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-} \quad (1)$$

$$FeS + 6Fe^{3+} + 0.5O_2 + 3H_2O \rightarrow 7Fe^{2+} + SO_4^{2-} + 6H^+ \quad (2)$$

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In recent years, the microbial fuel cell (MFC) technology becomes widely focused in the field of environmental biotechnology because it directly converts the chemical energy of various substrates into clean electricity.[10] Here, we speculate the microbial leaching reaction (eqs 1 and 2) can be split into two half-cell reactions, the oxidation and reduction half-reactions (eqs 3-5), that can separately occur at the anode and cathode of double-chamber MFC reactor (here named FeS-MFC), as shown in Figure 1. Then, the electricity is harvested from the microbial leaching of pyrrhotite tailings accompanied by the recovery of valuable metals. Because the protons produced during the anode oxidization of tailings are continuously delivered across the PEM to the cathode and consumed, the acid corrosion of the reactor expects to be effectively alleviated.

Anode half-reaction (Anaerobic):

$$FeS + 4H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^- \quad (3)$$

$$FeS + 6Fe^{3+} + 4H_2O \rightarrow 7Fe^{2+} + 8H^+ + SO_4^{2-} + 2e^- \quad (4)$$

Cathode half-reaction (Aerobic):

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (5)$$

However, the elemental sulfur is generally produced during the oxidization of sulfide to sulfate in the conventionally microbial leaching (eqs 6 and 7) and the further oxidization of the elemental sulfur to sulfate is postulated to be the rate-limiting step.[2] Thus, we doubt that the elemental sulfur deposit on the anode or sulfide surface of FeS-MFC reactors, and eventually passivate them, which are expected to make microbial leaching reaction as well as electricity generation restrained or even stopped. Besides, the outputted voltages of FeS-MFC reactor would be significantly cut down by 75% because only two electrons per mol sulfide were released to the anode with the elemental sulfur deposit, whereas eight electrons per mol sulfide could be transferred by the direct oxidization of sulfide to sulfate. Fortunately, by joining sulfur-oxidizing bacteria in the conventional microbial leaching, the elemental sulfur was easily oxidized to sulfate, the sulfur passivation effectively removed and the leaching process speeded up.[11] The findings of Holmes et al demonstrated that the passivation of the anode was microbiologically alleviated in benthic MFC reactors recovering electricity from marine sediments.[12-14]

$$FeS + 2H^+ + 0.5O_2 \rightarrow Fe^{2+} + S^0 + H_2O \quad (6)$$

$$FeS + 2Fe^{3+} \rightarrow 3Fe^{2+} + S^0 \quad (7)$$

Here, with ferrous sulfide power (model of pyrrhotite tailings) as substrate in the anode and oxygen as electron acceptors in the cathode, we established the double-chamber MFC reactor and the mixed inocula with the sulfur-oxidizing microorganisms were seeded. We demonstrated that the outputted voltage of the established FeS-MFC reactor showed values of up to 690.4 mV and the iron recovery of up to 44.6%. Further, the mole ratio of elemental iron to sulfur in the anolyte suggested that the direct oxidization mechanism dominated the leaching of ferrous sulfide and the inoculated microorganisms

played role in oxidizing sulfur to sulfate in the examined FeS-MFC reactor. To the best of our knowledge, this is the first report of MFC able to simultaneously generate electricity from sulfide tailings and recover valuable metal.

Results and discussion

Voltage generation and iron recovery

We first examined if the cell voltage could be generated in the established MFC reactor with ferrous sulfide as the anode substrate, as expected. Within the first 624 h, the voltages of the inoculated FeS-MFC reactor were in low level fluctuation and struggling to increase (Figure 2), due to the lagged microbial adaptation shifting from shaking serum bottle to MFC system. In the next four reaction cycles, the reactor steadily and sustainably outputted cell voltages by oxidizing ferrous sulfide in the anode. Over the last four reaction cycles, the peak cell voltage was kept at a level of 690.4±6.2 mV with the peak power density of 1343±18 mW m^{-2}. The electricity generation from the chemical oxidization of ferrous sulfide alone, and the biological oxidization of sulfide mediated by microorganisms was compared. Monitoring of voltage level in the sterile control did not reveal significant increment in generation of cell voltage over about 1200 h. The final peak voltage was 168.2±3.2 mV over the last four reaction cycles, accordingly the peak power density was 80±9 mW m^{-2}. Compared to 166.8 mV in the first reaction cycle, the cell voltage presented no significant difference over 624 h, based on the chemical oxidization of ferrous sulfide. In the last four reaction cycles, the cell voltage in average increased by 310.5% from 168.2 mV in the sterile control to 690.4 mV in the inoculated FeS-MFC reactor, representing that the presence of microorganisms in the anode chamber significantly promoted the electron release from ferrous sulfide.

At the end of the operation, the anodes of the sterile control and inoculated FeS-MFC reactor were scanned using CV method at a scan rate of 1 mV s^{-1} (Figure 3). No redox peak appeared in the CV curve of the sterile anode, indicating that the anode surface of the sterile control was in absence of electrochemical substances. In the CV curve of the inoculated FeS-MFC anode, two evident oxidative peaks (P_1 and P_2) revealed. The peak P_1 visualized the maximum current of 7.6 mA (forward scan; +0.29 V *vs*. SCE) and 2.8 mA (reverse scan; −0.06 V *vs*. SCE), and the peak P_2 presented the redox couple with −0.43 V (oxidative peal) and −0.64 V (reductive peak). The similar potentials expressed by the biofilms cultured at +0.29 V and −0.43 V were in line with those reported [20-23].

The cell voltages in the inoculated FeS-MFC reactor kept at a high level for the last four reaction cycles, accompanied by the microbial leaching of ferrous sulfide in the anode chamber. The concentration of total iron and ferrous ions were monitored at the end of each last four reaction cycles and the averages were given in Table 1. As revealed as cell voltage production, the concentrations of total iron in the sterile control and inoculated FeS-MFC reactor, with the base concentration excluded from the integrated total iron, were accordingly in steady state over the last four reaction cycles. The total iron increased to 90.4±1.4

mmol L^{-1} in the inoculated FeS-MFC reactor from 40.3±1.8 mmol L^{-1} in the sterile control and from 70.0±1.4 mmol L^{-1} in the conventional leaching, accordingly that the metal recovery of total iron did to 44.6% from 19.9% and from 34.5%. It illustrated that, when MFC was on-state, the leaching of ferrous sulfide could be speeded up by microorganisms. It also found that the concentrations of ferrous ions were in a higher level over the last four reaction cycles (Table 1). The average of ferrous ions increased from 27.5±0.7 mmol L^{-1} in the sterile control to 53.9±1.1 mmol L^{-1} in the conventional leaching, and to 70.0±1.1 mmol L^{-1} in the inoculated FeS-MFC reactor with the proportion of 70.0%, 78.1% and 80.0% in the total iron, demonstrating that the ratio of ferric ions in the total iron was below 20.0% and the oxidization of ferrous sulfide possibly was not associated with the indirect mechanism (eq 2). Ferrous ions cannot be abiotically oxidized to ferric ions (eq 8) because this reaction is thermodynamically unfavorable ($\Delta G°$ = +74.35 kJ mol^{-1}) under standard conditions ($[H^+]$ = 1 mol L^{-1}, pH = 0) and pH is independent.[24] It was hard for ferrous ions to further lose electrons and to be oxidized to ferric ions in the presence of microorganisms, especially in the anode of FeS-MFC reactor due to $E°$ of –0.771V. As the important leaching agent, the lower ferric ion concentration didn't have capability of initiating the reaction of sulfide leaching via the indirect interaction mechanism (eq 2) and to keep those reactions sustainable, even in reactors mediated by microorganisms.

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

Production of sulfate and energy efficiency

Formation of sulfate over the last four reaction cycles was monitored and also shown in Table 1, with the base concentration excluded from the integrated sulfate. As expected, sulfate (only 0.7 ± 0.1 mmol L^{-1}) was almost not detected in the sterile control throughout the experiment, explicating the phenomenon of no increase in the outputted cell voltage over reaction cycles (Figure 2). After addition of the microbial inocula into the anode, the sulfate concentration increased obviously, reaching 69.3±1.4 mmol L^{-1} in the conventional leaching and 89.6±1.8 mmol L^{-1} in the inoculated FeS-MFC reactor. The average sulfate amount in the anode chamber of the inoculated FeS-MFC reactor was 2.51 mmol. Sulfide was known to be oxidized to the elemental sulfur accompanied by the release of two moles of electrons per mol sulfide, and to sulfate by the release of another six moles of electrons per mol sulfide. Then, 2.51 mmol sulfate was accompanied by the release of 20.08 mmol electrons followed the direct oxidization in the anode chamber of the inoculated FeS-MFC reactor. Based on 690.4 mV voltage outputted, the current was calculated to be 1.38 mA across 500 Ω of the external loading and 784.9 C of the electrical charge was generated within 158 h. Accordingly, 8.15 mmol of the electrons were recovered, indicating that the electron (coulombic) efficiency of the inoculated FeS-MFC reactor was about 40.6%. By the same method, the coulombic efficiency of the sterile control was 73.2%. It possibly suggested that the inoculated microorganisms had the capability of simultaneously promoting

the oxidization of sulfide and unknown non-electrogenesis reactions. The higher coulombic efficiency in the established double-chamber MFC reactors implied that the passivation of anodes seldom occurred compared with that of sulfide surface.

Based on the coulombic efficiency calculated, the electricity recovery increased to 0.287 kW·h kg^{-1} in the inoculated FeS-MFC reactor from 0.004 kW·h kg^{-1} in the sterile control. Theoretically, the free enthalpy of ferrous sulfide under standard conditions was 106.94 kJ mol^{-1}, equivalent to 2.614 kW·h kg^{-1}.[24] With 81% of the maximum electricity efficiency of pyrrhotite proposed by Bockris and Drazic,[25] the maximum electricity recovered by MFC should be as high as 2.117 kW·h kg^{-1}. The further investigations on FeS-MFC reactors should be conducted in the future to enable more efficient systems for cell voltage generation and leaching of metal sulfide.

Oxidization mechanism of ferrous sulfide

The spectra of virgin ferrous sulfide and residues after leaching was recorded using EDX (Figure 4), and the element contents were calculated and listed in Table 2. The mole ratio of elemental iron to sulfur in the virgin sample was 1:1.43 which was lower than 1:1.12 reported by Qin et al.,[26] indicating that there were vacancies of iron element in raw model sample.[27] As expected, this ratio in the sterile control presented to be 1:6.51 to confirm the deposit of the elemental sulfur on the surface of sulfide to passivate (eq 7), which was responsible for the lower cell voltage. During the conventional leaching, it increased as high as 1:0.24 with a certain amount of potassium and phosphor elements detected, suggesting that the deposits of jarosite [$KFe_3(SO_4)_2(OH)_6$] and phosphate possibly appeared (eqs 9 and 10).[28] Mediated by microorganisms, ferrous sulfide was passivated mainly by jarosite and phosphate, but not by the elemental sulfur in the conventional leaching. The mole ratio of elemental iron to sulfur decreased to 1:0.77 in the inoculated FeS-MFC reactor from 1:0.24 in the conventional leaching, still higher than that in the virgin sample, possibly due to the formation and deposit of iron phosphate. The formation of jarosite generally occurred under >0.6 V condition[28]. Therefore, compared with the conventional leaching, the established FeS-MFC reactor achieved the higher leaching efficiency mainly due to the absence of jarosite deposit. The residues after leaching as well as the virgin ferrous sulfide were imaged using SEM (Figure 5). It was obvious that the virgin ferrous sulfide presented relatively smooth and clean surface. A lot of flocs or scraps were deposited on the residue surface in the sterile control, confirming that the elemental sulfur deposited and was reluctant to be abiotically oxidized to sulfate without the microorganism mediation. The images of residues from both the conventional leaching and inoculated FeS-MFC reactor revealed heavily corroded and rough sample surface with disordered pits. Moreover, the pits were much deeper in the closed circuit (the inoculated FeS-MFC reactor) than in the open circuit (the conventional leaching).These results suggested that the microorganisms had capability of oxidizing the elemental sulfur to sulfate (eq 11 in the conventional leaching and eq 12 in the anode of FeS-MFC reactor) and efficiently prevented the sulfur passivation of ferrous sulfide surface.

$$K^+ + 3Fe^{2+} + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (9)$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \quad (10)$$

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (11)$$

$$S^0 + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 6e^- \quad (12)$$

In the sterile control, the leaching of ferrous sulfide definitely follows the indirect mechanism (eq 2) due to the absence of microorganisms. And, due to the passivation of the elemental sulfur (eq 7), a mole ratio of elemental iron (40.4 mmol L^{-1}) to sulfur (0.7 mmol L^{-1}) of 1:0.02 in the anolyte of sterile control was far away from the theoretical stoichiometry (eq 2). Further, we speculated that around 98.3% elemental sulfur in the sterile control deposited on ferrous sulfide surface, and heavily prevented the further chemical leaching although there was a certain level of ferric ions (12.8 mmol L^{-1}), the leaching agent, in the anolyte. The conversion of sulfur accompanied by electron transfer to the anode is the rate-limiting factor in the chemical leaching of ferrous sulfide in the sterile control. The mole ratio of elemental iron to sulfur in the leachate of conventional leaching was nearly 1:1, suggesting that the conventional leaching followed the direct mechanism (eq 1).

In the inoculated FeS-MFC reactor, the concentration of sulfate at the end of operation was 89.6 mmol L^{-1} and 90.4 mmol L^{-1} of the total iron was leached out, representing a mole ratio of elemental iron to sulfur in the anolyte was almost 1:1.01. This ratio is approximately in agreement with the theoretical stoichiometry based on the direct mechanism (eq 1) and closer to the measured chemical formula of ferrous sulfide (1:1.43). Also, it demonstrated that 99.1% sulfur in the inoculated FeS-MFC reactor was converted to sulfate (eq 6), suggesting that other states of sulfur (such as hydrogen sulfide) were seldom generated and there was no secondary pollution. The MFC system had potential to directly oxidize sulfide mineral to sulfate within one step. Additionally, the concentrations of the total iron and sulfate monitored in the catholyte were 2.8 mmol L^{-1} and 0.6 mmol L^{-1}, with the base concentrations excluded from the integrated values, which was so minimal as to be ignored compared to that in the anode chamber.

Experimental

Setups and media

Double-chamber MFC reactor with an internal volume of 28 mL in both anode and cathode chamber were established in this study. For each of the enumerated experimental steps, multiple identical reactors were set up and run. A magnetic stirrer (S23-2, Shanghai Sile Instrument Co. Ltd. China) set at 120 r min^{-1} was installed beneath the reactors to ensure mixing and to maintain a homogeneous electrolyte. The anode and cathode chambers were separated by a Nafion-117 membrane (DuPont Company, USA) with an effective working area of 7.1 cm^2. During operation, the anode chamber was anaerobic by simply keeping all outlets sealed, whereas the cathode chamber was aerated via magnetically stirring and the dissolved oxygen (DO)

kept ≥ 7.6 mgL^{-1}. Both electrodes were made of carbon felt with a normalized surface area of 7.1 cm^2, paralleled to each other with a distance of 4.5 cm and connected by a piece of titanium wire across an external loading of 500 Ω. The temperature was maintained at 30℃.

The anode medium consisted of 0.20 g $L^{-1}$$(NH_4)_2SO_4$, 3.93 g L^{-1} $K_2HPO_4 \cdot 3H_2O$, 0.50 g L^{-1} $MgSO_4 \cdot 7H_2O$, 0.19 g L^{-1} $CaCl_2$, and 10.00 g L^{-1} elemental sulfur.[15] The pH was adjusted to 2.5 using 5 mol L^{-1} H_2SO_4. Trace minerals consisted of 1.000 g L^{-1} $N(CH_2COOH)_3$, 1.500 g L^{-1} $MgSO_4$, 0.500 g L^{-1}NaCl, 0.050 g L^{-1} $FeSO_4 \cdot 7H_2O$,0.005 g L^{-1} potassium alum, 0.012 g L^{-1} $Na_2WO_3 \cdot 2H_2O$ and 0.050 g L^{-1} $COCl \cdot 6H_2O$.[16] Vitamins consisted of 0.020 g L^{-1} biotin, 0.020 g L^{-1} folic acid, 0.050 g L^{-1} PABA, 0.050 g L^{-1} VB_5, 0.001 g L^{-1} VB_{12}, 0.050 g L^{-1} α-lipoic acid, and 0.050 g L^{-1} riboflavin.[16] The phosphate buffer solution (PBS) medium used in the cathode chambers consisted of 11.53 g L^{-1} $Na_2HPO_4 \cdot 12H_2O$, 2.77 g L^{-1} $NaH_2PO_4 \cdot 2H_2O$, 0.31 g L^{-1} NH_4Cl, and 0.13 g L^{-1} KCl.[17] The pH was adjusted to 7.0.

10 mL effluents, from the existing well-running membrane bioreactor (MBR) treating synthetized municipal wastewater in our lab, together with 90 mL anode medium was transferred into 250 mL serum bottles, followed by addition of 0.35 mL trace minerals and 0.14 mL vitamins. The bottles were put in a shaker of 150 r min^{-1}, and cultivated for three months at 30℃. Then, the mixed inocula capable of oxidizing the elemental sulfur were obtained.

Approaches

14 mL inocula obtained above was fully mixed with 25 g L^{-1} of ferrous sulfide and added to the anode chambers of three MFC reactors, followed by addition of anode medium to 28 mL. Then, 14 mL of PBS medium above transferred to the cathode chambers and diluted to 28 mL with deionized water. One reactor (Sterile control) was kept sterile for 30 min at 121℃ before operation of each cycle. The second reactor (Conventional leaching) operated in open circuit to allow the conventionally microbial leaching to occur. The third one (Inoculated FeS-MFC) ran as double-chamber MFC treating ferrous sulfide. When the cell voltages dropped to <50 mV (around 158 h) in the last four reaction cycles, the mixture in the anode and cathode chambers was completely removed, and both chambers refilled as above. At the end of experiment, the solution in the anode chambers was monitored for total iron, ferrous ion and sulfate production, the residue was imaged by scanning electron microscopy (SEM, TM3030, HITACHI, Japan) and recorded the spectra by energy dispersive X-ray spectroscopy (EDX, S-3400N II, HITACHI, Japan), and the anodes were scanned by cyclic voltammetry (CV) using the described assays as follows.

The cell voltage (V) across the external loading (R) was automatically recorded by a computer-based data acquisition system (DAQ-2204, Taiwan ADLINK Ltd., China) at a pre-determined sampling frequency (30 min). The power output (P), normalized by the projected surface area of the anode (A), was calculated by the equation $P = V^2/(R \times A)$.

After the reactors reached stable, CV was conducted using an electrochemical workstation (CHI600D, CH Instruments Inc., China) in depleted substrate condition. Before analysis, the reactors were left in open-circuit for 1 h to reach the static state. The working and counter terminals of the electrochemical instrument were connected in-situ to the anode and cathode of the examined MFC reactor, while a saturated calomel electrode (SCE, +0.242 V *vs*. the standard hydrogen electrode [SHE], Gaoshirilian Ltd., China) as the reference electrode was placed close to the anode. Prior to use, SCE was carefully rinsed with deionized water. According to the working potential of the electrodes investigated here, CV was performed from −0.9 V to +0.9 V *vs*. SCE at a scan rate of 1 mV s^{-1}.

The concentrations of total iron were quantified at 248 nm by the flame atomic absorption spectrophotometry (AA-7000, SHIMADZU, Japan) equipped with a hollow cathode lamp (GL, SHIMADZU, Japan), and ferrous ions was by phenanthroline spectrophotometric method.[16] If not analyzed immediately, the filtered samples were kept pH < 2.5 in closed vials to prevent the oxidization of ferrous to ferric ions. Sulfate production was monitored by a barium chromate colorimetric method.[6] The virgin ferrous sulfide power and residues after treatment were imaged using SEM after softly rinsing with distilled water and drying naturally,[19] and the element contents were quantified based on the spectra of EDX.

Conclusion

These results demonstrated that pyrrhotite tailings had potential to drive electricity generation accompanied by microbial leaching of valuable metal using double-chamber MFC reactor. The cell voltage in the established FeS-MFC reactor showed values of up to 690.4 mV and the metal recovery of up to 44.6%.Normalized by ferrous sulfide mass, 0.287 kW·h kg^{-1} electricity was recovered. Mediated by sulfur-oxidizing microorganisms, the elemental sulfur was oxidized to sulfate and the passivation of ferrous sulfide surface efficiently alleviated. The mole ratio of elemental iron to sulfur in the leachate of conventional leaching and anolyte of FeS-MFC reactors indicated that ferrous sulfide was oxidized from sulfide to sulfate via the direct mechanism. Possibly due to the passivation of jarosite, the leaching efficiency in the conventional leaching was lower than that in the FeS-MFC reactor.

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1 **Table 1.** Variation in total iron, ferrous ion and sulfate at the end of operation (mmol L^{-1}).

Reactor types	Total iron ions	Ferrous ions	Sulfate
Sterile control	40.4±1.8	27.5±0.7	0.7±0.1
Conventional leaching	70.0±1.4	53.9±1.1	69.3±1.4
Inoculated FeS-MFC	90.4±1.4	70.0±1.1	89.6±1.8

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Table 2. Element contents before and after treatment based on EDX spectra.

Samples	wt(%)								Fe/S in moles
	C	O	Si	Na	P	S	K	Fe	
Virgin mineral	2.58	17.55	0.47	/	/	35.83	/	43.57	1:1.43
Residues of sterile control	39.62	15.18	2.69	/	0.80	32.90	/	8.80	1:6.51
Residues of conventional leaching	4.00	21.24	/	1.32	7.83	12.50	1.03	52.09	1:0.24
Residues of inoculated FeS-MFC	10.01	21.69	0.42	0.39	3.64	27.77	/	36.08	1:0.77

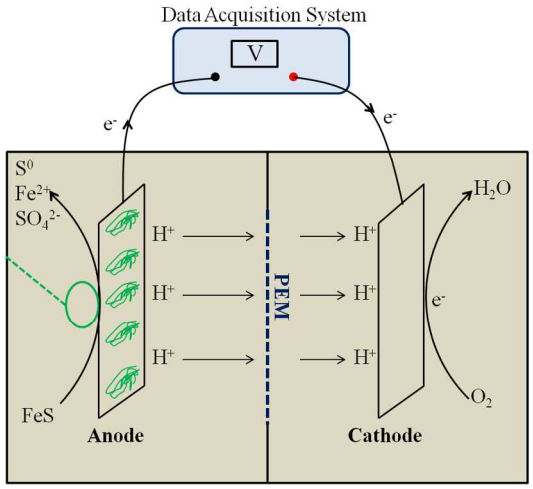

Figure 1. Schematic of the double-chamber MFC reactor for generating electricity while recovering valuable metals from pyrrhotite tailings. Tailings served as inorganic substrates in the anode and oxygen as electron acceptors in the cathode.

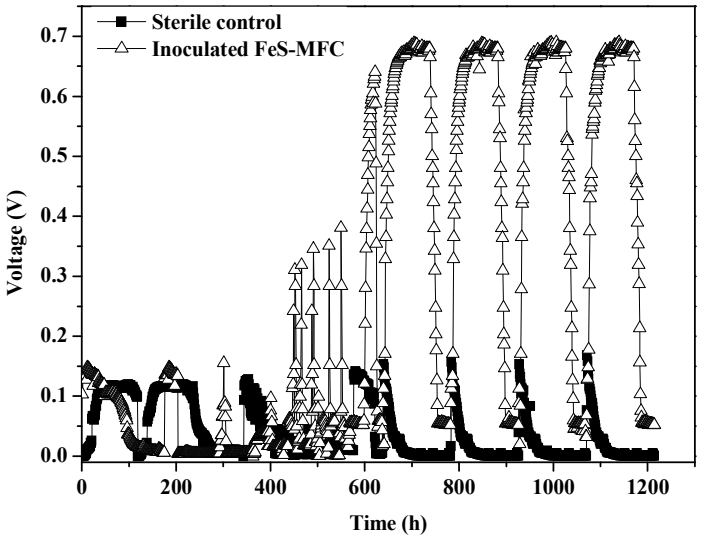

Figure 2. Cell voltages as a function of time with a 500Ω external loading. The whole operation period was 1200 h with 624 h of start-up and four stable reaction cycles.

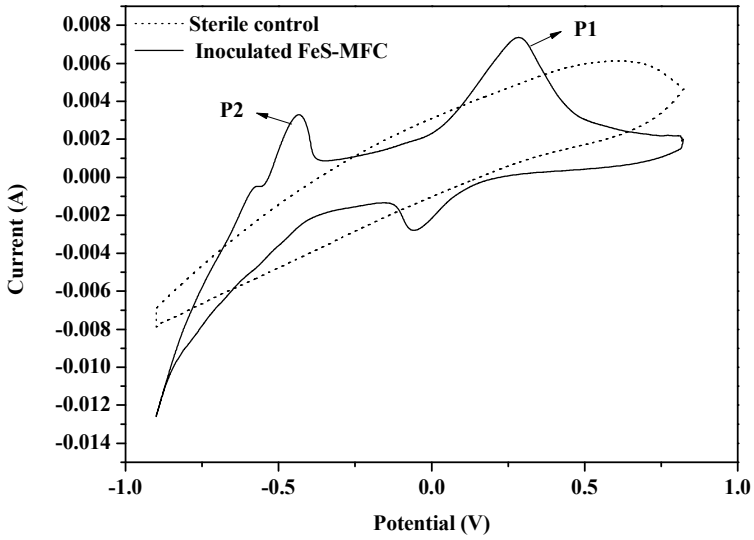

Figure 3.CV curves of the anodes performed from − 0.9 V to + 0.9 V *vs*. SCE at a scan rate of 1 mV s^{-1}.

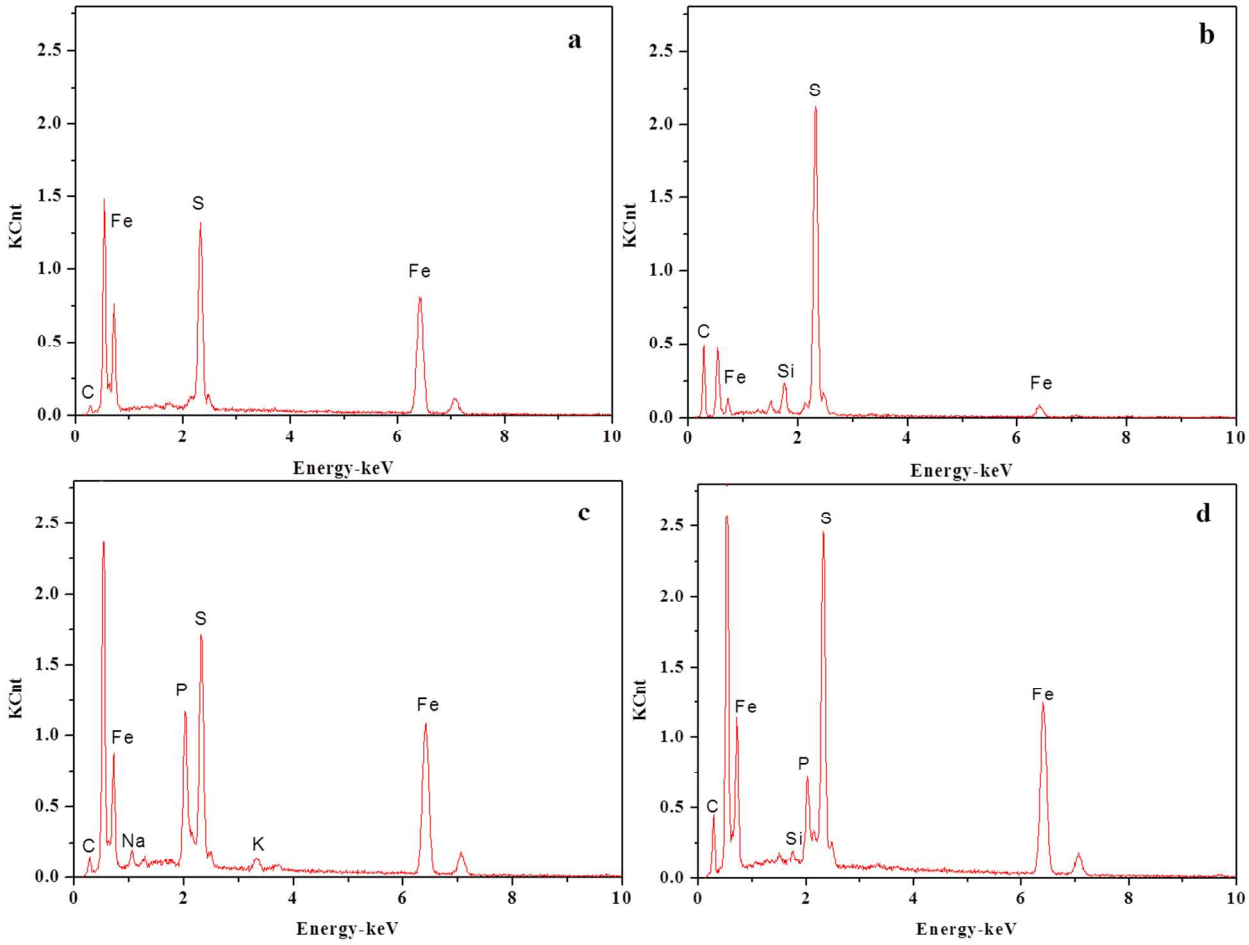

Figure 4. EDX spectra of virgin FeS (a) as well as residues from the sterile control (b), conventional leaching (c) and inoculated FeS-MFC reactor (d).

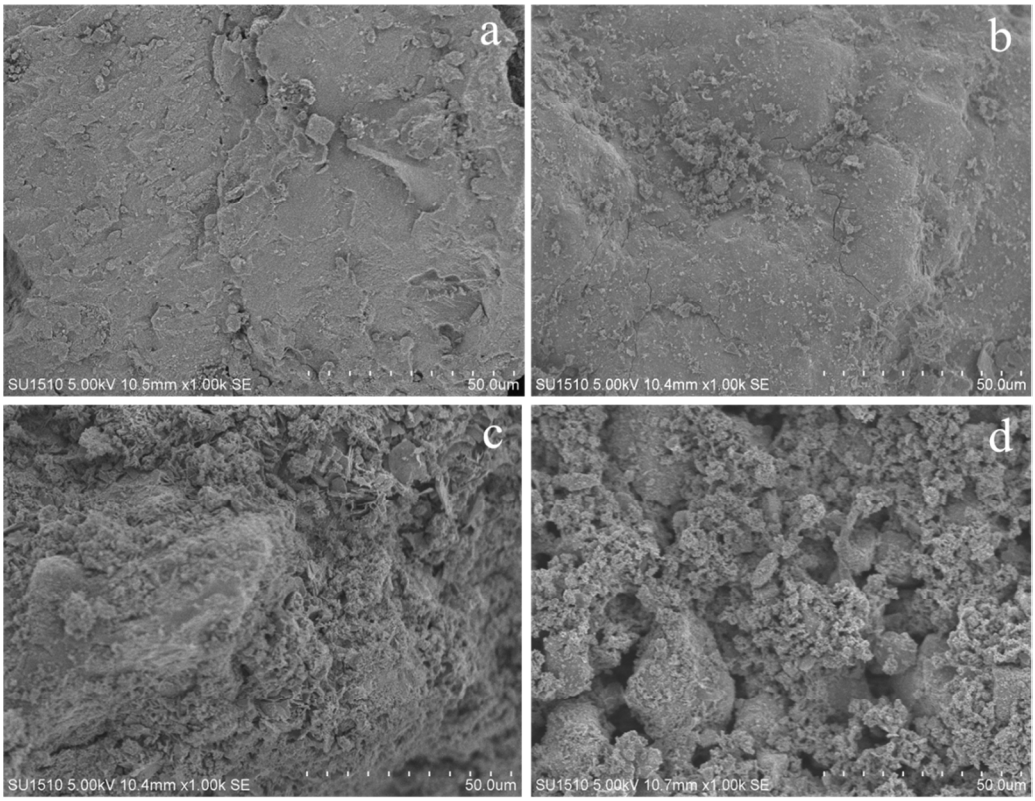

Figure 5. SEM observation of virgin FeS (a) as well as residues from the sterile control (b), conventional leaching (c) and inoculated FeS-MFC reactor (d).