

Removal of chemical oxygen demand (COD) and heavy metals by catalytic ozonation–microbial fuel cell and *Acidithiobacillus ferrooxidans* leaching in flotation wastewater (FW)

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ABSTRACT

A catalytic ozonation–microbial fuel cell and *Acidithiobacillus ferrooxidans* leaching process was used in treating flotation wastewater to remove chemical oxygen demand (COD) and heavy metals in this study. The results indicated that when adding 1 g/L of manganese/modified activated carbon catalyst and 1.5 g/min ozone flow, the COD could be degraded from 2,043.67 mg/L to 711.4 mg/L. After that, the COD could continue decreasing down to 72.56 mg/L through an air-cathode single chamber microbial fuel cell (SCMFCs), coated with 0.4 mg/cm² platinum catalyst, after 15 days. Meanwhile, the maximum voltages and the ultimate power density of the SCMFCs reached 378.96 mV and 7,608.35 mW/m², respectively. For filter residue, when 1.2 g/L Fe³⁺, 10% (m/v) filter residue, and 10% *Acidithiobacillus ferrooxidans* were added, the copper leaching rate could reach 92.69% after 7 days if the pH values were adjusted to 1.9. Furthermore, the other heavy metals were also decreased to a level lower than the pollution control standard (Chinese standard GB3838-2002). The leaching parameters in terms of pH, redox potential, and cyclic voltammetry showed that the addition of an appropriate concentration of Fe³⁺ to the leaching systems was beneficial to copper dissolution.

Key words | *Acidithiobacillus ferrooxidans*, catalytic ozonation, flotation wastewater, microbial fuel cell, removal capacity

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INTRODUCTION

With the rapid development of the mining industry, the flotation process has become the most widely used and effective technology for ore separation and enrichment. However, the flotation process will produce wastewater which is usually discharged in the form of pulp. The main pollutants of flotation wastewater (FW) are heavy metal ions and organic and/or inorganic flotation reagents including highly toxic cyanide and cyano complexes, which will seriously damage the ecological environment and human health due to their non-degradability and toxicity (Chen *et al.* 2009; Fu & Wang 2011). Moreover, FW can change the surface hydrophilicity and electrical properties of mineral particles when directly reused in the flotation process (Liu *et al.* 2013). Therefore, it is important to develop an efficient and feasible process to carry out the degradation treatment for FW.

Currently, advanced oxidation processes (AOPs) have been given more and more interest in the advanced

treatment of FW, aimed at increasing the biodegradability of contaminants through the formation of highly active oxidizing matter for mineralization (Sevda *et al.* 2013). AOPs comprise a series of methods such as ozonation (Sánchez-Polo *et al.* 2005), microbial oxidation (Gan *et al.* 2017), microbial fuel cell (Gan *et al.* 2017), and vacuum UV (Fu *et al.* 2016). Ozone is a very powerful oxidizer and reacts very well with organic pollutants to reduce chemical oxygen demand (COD) by producing a large number of hydroxyl radicals with high oxidation potential ($\cdot\text{OH}$, standard potential $E^\circ = 2.85$ V) and hydrogen peroxide ($\cdot\text{HO}_2$, $E^\circ = 1.77$ eV), respectively (Kurniawan *et al.* 2006). In particular, the oxidation of $\cdot\text{OH}$ can non-selectively degrade a wide range of organic and inorganic pollutants quickly which is second only to fluorine. However, some substances are difficult to be oxidized through ozonation. Due to heterogeneous catalytic ozonation having a potentially higher effectiveness in removing refractory organic pollutants and

reducing the negative impact on water quality, it has become a powerful treatment method for COD removal (Ma et al. 2005). The catalyst carrier includes modified activated carbon (Ma et al. 2005), MgO (Keykavoos et al. 2013), and alumina (Moussavi & Mahmoudi 2009), which can provide larger surface area and stronger adsorption strength for the active ingredient. Those catalysts can accelerate the decomposition of ozone and enhance the generation of reactive radical species, thus achieving much higher removal of contaminants in the wastewater. In addition, the microbial fuel cell (MFC) is another novel energy conversion device that uses electrogenic microorganisms as catalyst to convert chemical energy directly into electrical energy. It has the characteristics of low operating cost, insensitive to the operation environment, and ability to efficiently treat high-concentration organics (Abourached et al. 2016; He et al. 2017). Compared with the dual chamber MFCs, the air cathode single-chamber microbial fuel cell (SCMFC) equipped with a sealed anode has higher removal efficiency and electricity-generating capacity (Martin et al. 2011). The device usually transfers electrons by the electrogenic microorganisms through an external circuit from the anode to the cathode. Oxygen is usually used as an electron acceptor at the cathode side due to its high redox potential and low cost to supply (Tatinclaux et al. 2018).

Up to now, microbial oxidation has played an important role in removing heavy metals and may be the most cost-effective and environmentally friendly alternative (Latorre et al. 2016; Hao et al. 2017). *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), an aerobic acidophilic chemoautotrophic Gram-negative bacterium, is the most widely used microorganism in bioleaching (Devasia & Natarajan 2010). Most scholars agree that *A. ferrooxidans* is firstly absorbs to the mineral surface, then develops special cell structures such as cilia or slender extracellular polymeric substances (EPS), which are a complex high-molecular mixture of polymers excreted by microorganisms (Li et al. 2016). EPS mediate the contact between microorganisms and the mineral surface. Thus, an oxidizing space is formed between the EPS and the mineral surface, which contains rich Fe^{3+} ions. The energy metabolism pathway of *A. ferrooxidans* is that Fe^{2+} is oxidized to Fe^{3+} and element S is finally oxidized to high-priced sulfate via $\text{S}^{-1} \rightarrow \text{S}_n^2 \rightarrow \text{S}^0 \rightarrow \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$ (Vilcáez & Inoue 2009; Feng et al. 2017). Chalcopyrite, which is clearly influenced by a saturated covalency between S, Fe, and Cu, has the formal oxidation states of $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$. This bonding can thus be broken apace by several oxidation steps, with the attacking agent Fe^{3+} causing a break of the bonding between the metal and the sulfur moiety of the sulfide,

leading to mineralization and desulfurization. In addition, since *A. ferrooxidans* can use Fe^{3+} as an electron acceptor and chalcopyrite containing reduced sulfur as an electron donor for respiration, the presence of Fe^{3+} was more efficient in extracting electrons from a mineral lattice, then causing the cell concentration on the mineral surface and a higher solubilization effect on sulfide ore.

The objectives of this study are: (1) to assess the technical feasibility of simultaneous removal of COD and heavy metals in FW via a catalytic ozonation-SCMFCs and *A. ferrooxidans* leaching process; (2) to investigate the effects of various parameters of catalytic ozonation-SCMFCs and *A. ferrooxidans* leaching on filtrate and filter residue, respectively; (3) to propose the role of adding Fe^{3+} in *A. ferrooxidans* leaching.

MATERIALS AND METHOD

Materials

The raw FW discharged after the flotation of chalcopyrite was received from Gansu Province, China. The main chemical composition is given in Table 1. The COD and copper content reached 2,043.67 mg/L and 2.09%, respectively. Meanwhile, the other heavy metal contents (e.g., Cu, Pb, Hg, Cr, As) were very high, indicating exceedance of the surface water environmental quality standards (Chinese standard GB3838-2002). All the reagents used in the

Table 1 | Composition of the total FW aqueous solution

Element	Content ^a
COD	2,043.67 mg/L
Cu	2.09
Fe	6.12
P	0.19
Ni	0.06
Zn	0.04
As	0.17
Pb	0.21
Hg	0.07
Cr	0.15
Mn	0.09
Cl^-	5.79
Solution pH	9.10

^aAll values, except for COD and pH, are percentages.

experiments were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in the experiments.

Preparation of a homogeneous catalyst

The production process of the homogeneous catalyst, i.e., manganese/modified activated carbon (Mn/GAC) catalyst, was as follows: 10 g powdered activated carbon (the fraction with particle size distribution of 59.61% passing 0.038 mm, the surface area 1,051.34 m²/g and void volume 0.76 mL/g) was washed by deionized water, boiled in water for 2 h, and dried at 105 °C for 4 h to remove impurities. The above modified activated carbon (GAC) was sonicated at 100 W, 50 Hz for 60 min, then immersed in 100 mL of 5% manganese nitrate for 24 h in a shaker at 160 rpm. The impregnation liquid was slowly added to 45 mL of 2 mol/L NaOH and shook for 1.5 h. Finally, the catalyst underwent filtration and drying at 110 °C for 12 h, and was then roasted at 600 °C for 3.5 h. The resulting catalyst powder was cooled for future use.

SCMFCs reactor

A air-cathode SCMFCs reactor with a total volume of 450 mL and a working volume of 370 mL was used in this study and was made from an acrylic cylindrical chamber. The materials of anode and cathode were made of graphite felt; the surface area was 42.95 cm² and 94.99 cm², respectively. Meanwhile, the anode and cathode were connected with titanium wire and external resistance of 500 Ω which formed a circuit. The liquid-contact side of the cathode electrode was evenly coated with 38 mg platinum (Pt) catalyst, i.e., the coverage density of platinum was 0.4 mg/cm², whereas the air-contact side of the cathode electrode was coated with gas diffusion layers with 50% polydimethylsiloxane binder. The anolyte and bacterial liquid were added in a volume ratio of 3:1. The bacterial liquid was a mixture of electrogenic microorganisms extracted from deep seabed hydrothermal sulfide deposits derived from the State Key Laboratory of Biochemical Engineering, Chinese Academy of Science. The composition of anolyte was KCl 0.13 g/L, NH₄Cl 0.31 g/L, NaH₂PO₄·2H₂O 2.93 g/L, and NaCl 2.90 g/L. In the start-up phase, 20 mmol/L sodium acetate as substrate was put into the SCMFCs. When SCMFCs were running, the output voltage was automatically recorded by a data acquisition card with a sampling interval of 5 min. The wastewater dosage would occupy one half of the total volume of SCMFCs when the voltage runs for several cycles.

Microorganism and medium

A. ferrooxidans used in this experiment came from State Key Laboratory of Biochemical Engineering, Chinese Academy of Science. It was cultured and maintained in a 9K growth medium, the composition of which was (NH₄)₂SO₄ 0.15 g/L, KCl 0.05 g/L, K₂HPO₄ 0.05 g/L, MgSO₄·7H₂O 0.05 g/L, Ca(NO₃)₂ 0.01 g/L, and FeSO₄·7H₂O 44.1 g/L. For bioleaching of filter residue, an admixture without FeSO₄·7H₂O was prepared. At the same time, a solution of 30% H₂SO₄ was used to adjust the pH of the solution.

Experimental procedures

The FW was first filtered through a 0.45 μm Newstar qualitative filter paper (Special Paper Co., Ltd, Hangzhou, China) to obtain filtrate and filter residue, respectively. One hundred millilitres of the filtrate was poured into a 250 mL Erlenmeyer flask with 0.1 g Mn/GAC catalyst and shaken well. Then, O₃ was introduced into the bottom of the Erlenmeyer flask with a gas diffuser. The effect of ozone flow rate on COD removal rate in the range of 1–2.5 g/min was investigated, while the ozone exhaust was absorbed with a KI solution. After that, the catalytic ozone solution would be further removed in the air-cathode SCMFCs reactor, which was operated in batch feeding mode (Figure 1). The removal of COD by SCMFCs with or without Pt catalysts was studied. The polarization curve and power density curve were also used to characterize the internal resistance and output power of the SCMFCs by using the external resistance method.

All bioleaching tests on the filter residue were conducted at 30 °C and 120 rpm in 250 mL shaking flasks. Firstly, 90 mL of 9K growth medium (without FeSO₄·7H₂O) and 10% (m/v) filter residue were mixed, and pH adjusted to 1.9. Then, the mixed solution was added to 10 mL *A. ferrooxidans* inoculum that was propagated to the logarithmic phase. The effect of Fe³⁺ concentration was studied by varying the initial concentration (0–2.4 g/L) by providing Fe₂(SO₄)₃. At the same time, the influence of Fe³⁺ on the bioleaching system was examined by the cyclic voltammetry, and the pH value and redox potential (E_h) which were measured periodically with a pH composite electrode (PHS-2F, Yidian Co., Ltd, Shanghai, China). The loss of the solution was supplemented with equivalent 9K medium after each sampling.

The effect of *A. ferrooxidans* leaching was investigated by the leaching rate of copper. Herein, the weight loss ratio (γ) and copper leaching rate (η), calculated as Equations (1) and (2), were used to evaluate the leaching

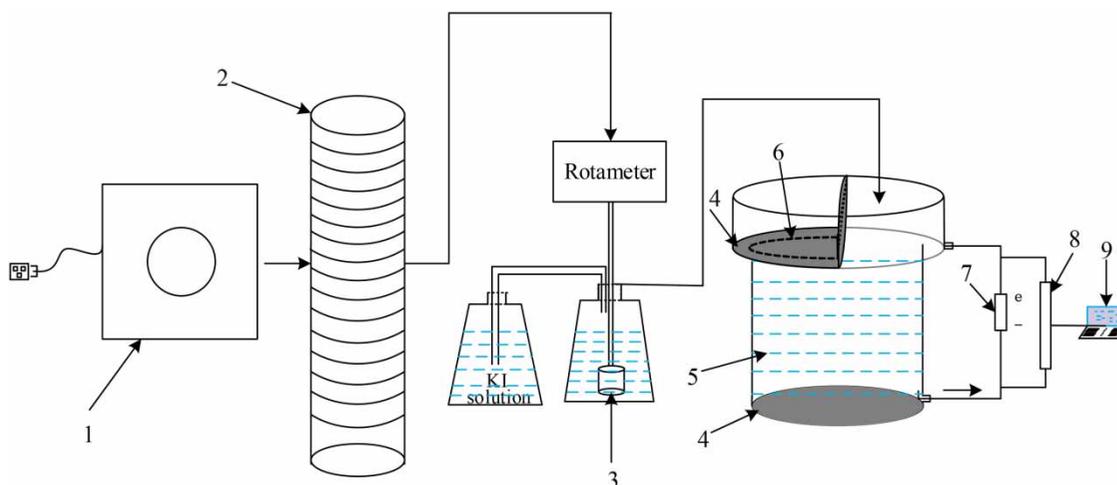


Figure 1 | Schematic diagram of catalytic ozonation-SCMFCs reactor (1 air generator; 2 ozone generator; 3 gas diffuser; 4 graphite felt; 5 SCMFCs reactor; 6 gas diffusion layer; 7 external resistance; 8 data acquisition card; 9 computer).

process, respectively.

$$\gamma = \frac{w_0 - w_1}{w_0} \quad (1)$$

$$\eta = \frac{w_0 \times \beta_0 - w_1 \times \beta_1}{w_0 \times \beta_0} \quad (2)$$

where γ and η were the weight loss ratio (%) and copper leaching rate (%), respectively, w_0 was the weight of filter residue (g), β_0 was the copper content (%) of filter residue. w_1 was the weight of *A. ferrooxidans* leaching residue (g), and β_1 was the copper content (%) of *A. ferrooxidans* leaching residue.

Analytical techniques

The laboratory ozone set-up was based on an ozone generator from O₃-high pressure discharge technology, supplied with air gas (Sankang Environmental Co., Ltd, Jinan, China). The COD value was determined by a potassium dichromate method (Chinese standard GB/T 11914-89). The copper content of *A. ferrooxidans* leaching residue was analyzed by a trichloromethane extraction copper reagent spectrophotometry method (Chinese standard GB/T 22319-89). The element content of filter residue and *A. ferrooxidans* leaching residue was determined with multiphase X-ray fluorescence (Axios, PANalytical B.V., Almelo, The Netherlands). Cyclic voltammetry was measured by an electrochemical workstation (CHI660D, CH Instruments, Inc., Austin, USA), scanning potential interval: -1.2 to 1.5 V (vs SCE), scanning speed: 2.5 mV/s, and the reference electrode was a saturated calomel electrode.

RESULTS AND DISCUSSION

COD removal efficiency of Mn/GAC, O₃, Mn/GAC catalytic ozonation

To evaluate the superiority of the Mn/GAC catalyst, the experiment investigated the COD removal efficiency in three different processes (Figure 2). During the first 30 mins, the COD removal increased in the three different action processes and finally reached the maximum removal which was 12.04%, 34.15% and 64.79%, respectively. When the Mn/GAC catalyst continued acting alone, the COD removal showed almost no change, whereas the treatment with ozonation and Mn/GAC catalytic ozonation showed a rapid decrease in COD removal after 30 mins, suggesting that the reaction of $\cdot\text{OH}$ with the organic matter was

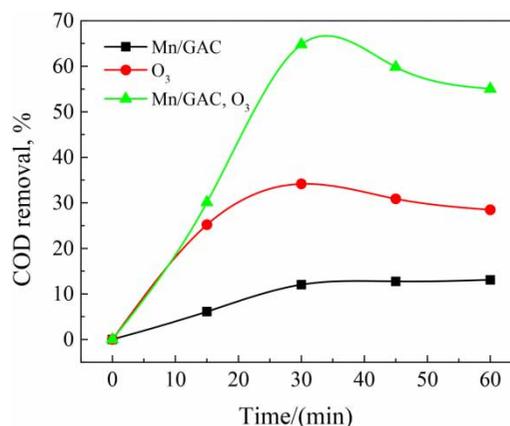


Figure 2 | COD removal in different processes with the catalyst concentration of 1 g/L, ozone flow of 1.5 g/min.

inhibited at a high concentration of O_3 . Hence, the method of Mn/GAC catalytic ozonation was used to pretreat the filtrate.

When Mn/GAC catalyst was in contact with filtrate, the organic matter was first adsorbed on the surface of this catalyst to form an affinity surface chelate, which made ozone oxidation more efficient. Furthermore, Mn/GAC catalyst could also effectively catalyze the activation of ozone molecules to produce highly oxidized active species and increase the rate of electron transfer. The reason for the low efficiency of only using Mn/GAC catalyst to degrade organic matter was that catalyst deposits on the active site prohibit degradation of organic components and only play a role in adsorption.

Effect of O_3 flow rate

The effect of O_3 flow rate under the similar experimental conditions as mentioned above was investigated with respect to the COD removal (Figure 3). The COD removal increased rapidly from 51.1% to 65.19% when the O_3 flow rate increased from 1 to 1.5 g/min, which indicated that the dissolved ozone concentration reached a maximum, thereby prompting the generation of free radicals. However, there was a slight increase in the COD removal when the O_3 flow rate further increased up to 2.5 g/min, suggesting that ozone concentration had gradually reached saturation. Obviously, when ozone was continually introduced for more than 30 min, the COD removal would drop dramatically. Therefore, 1.5 g/min ozone flow rate and 30 mins were considered optimum.

Mn/GAC catalyst particles could provide an opportunity for ozone to enter the catalyst void in the action of water and gas in-phase flow. Under the condition of 1.5 g/min O_3 flow rate, ozone molecules were catalyzed to produce the

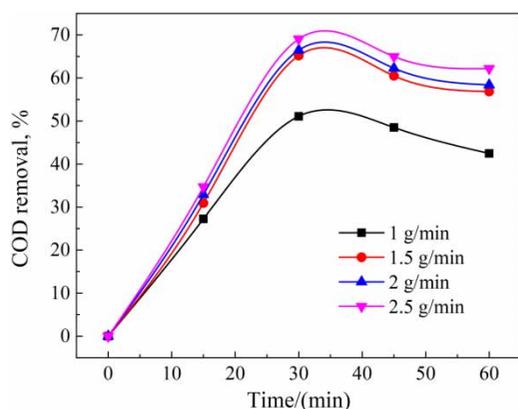


Figure 3 | COD removal in different ozone flow with the catalyst concentration of 1 g/L.

largest amount of hydroxyl radicals. Thus, the synergistic effect of ozone and Mn/GAC catalyst was more efficiently exerted to remove contaminants. The reason for the low COD removal after 30 mins was due to the fact that excess ozone would react with $\cdot OH$, and produce peroxy hydroxyl radical ($\cdot HO_2$), whose potential strength is weaker than that of $\cdot OH$ under the condition of high ozone concentration. This was mentioned in the Introduction.

Removal efficiency and electricity generation performance of SCMFCs

The removal efficiency of SCMFCs was analyzed at two different conditions, i.e., Pt-free and Pt catalyst (Figure 4(a)).

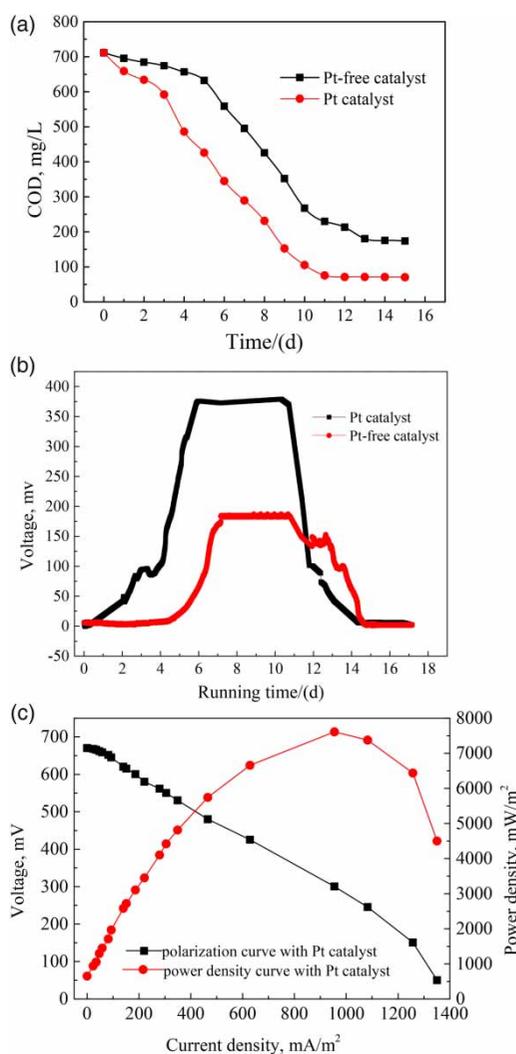


Figure 4 | (a) COD removal with Pt and Pt-free catalyst, (b) the output voltage by SCMFCs with Pt and Pt-free catalyst, (c) polarization curve and power density curve with Pt catalyst after catalytic ozonation, i.e., the catalyst concentration of 1 g/L, ozone flow of 1.5 g/min.

Treatment with Pt catalyst showed significantly higher removal of the COD than SCMFCs with Pt-free catalyst. After 15 days of treatment, the COD value from wastewater treated with coated Pt and Pt-free catalyst was 70.37 mg/L and 173.98 mg/L, respectively. The maximum voltages of Pt catalyst and Pt-free catalyst across the SCMFCs were 378.96 and 187.23 mV, respectively (Figure 4(b)). Hence, the SCMFCs with cathode-coated Pt catalyst had higher removal efficiency and larger voltage than the SCMFCs with cathode-coated Pt-free catalytic layers. The coupling of the COD removal and power generation was realized.

The open circuit voltage of the SCMFCs was 670.24 mV (Figure 4(c)). From the overall polarization curve, the voltage was linearly related to the current density within a certain range. However, the voltage decreased at the end of the period and deviated from the linear fit line, which may be due to the internal mass transfer of the reactor and an insufficient enrichment of the anode biofilm (Watson & Logan 2011). In the middle of linear scanning, the SCMFCs had reached their ultimate power density of 7,608.35 mW/m², indicating that the final polarization curve shift did not cause the power density curve to fold back.

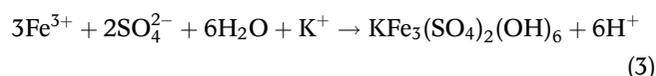
Role of manganese catalyst and application analysis

Considering that the formation of Mn⁴⁺ and Mn/GAC significantly improved the O₃ conversion as shown in Figure 2, we proposed the mechanism of the adsorbed-electron hole caused by deposited Mn/GAC catalyst. Adsorption of organic matter on Mn/GAC catalyst was an important step and would have direct influence on the effectiveness of catalytic oxidation. Meanwhile, Mn⁴⁺ acted as a highly electrophilic electron trapping center, promoting ozone to form more ·OH and ·HO₂ on the surface of activated carbon. Thus, the catalytic activity of Mn/GAC for ozone was remarkably enhanced and the organic pollutants might be further decomposed on the surface of the catalyst.

The higher concentration of flotation reagents remained at the liquid interface, and then the surrounding ozone rapidly oxidized and decomposed it under the action of Mn/GAC catalyst, which still had a good catalytic activity after repeated use. However, owing to the strong selectivity of ozone oxidation, it was difficult to thoroughly degrade the stubborn organic matter, and only oxidized macromolecular organic matter was degraded into small molecular organic matter, increasing the structural saturation of organic components. Therefore, the combination of catalytic ozonation and SCMFCs technology could completely degrade FW by converting chemical energy into electrical energy.

Effects of Fe³⁺ on *A. ferrooxidans* leaching of filter residue

As shown in Figure 5, even the presence of a little Fe³⁺ in *A. ferrooxidans* leaching solution could promote the leaching rate of copper significantly. The copper leaching rate was significantly increased with the addition of Fe³⁺ concentration between 0 and 1.2 g/L. During 7 days, the leaching rate of copper in 1.2 g/L Fe³⁺ could reach up to 92.69%, and showed no further acceleration beyond, indicating that the charge of the solution reached equilibrium. However, when the concentration of Fe³⁺ continued to increase to 2.4 g/L, the leaching rate of copper did not increase further, which may be due to the formation of the jarosite passivation layer by excessive Fe³⁺ (Equation (3)) (Debernardi et al. 2013).



The chemical composition in Table 2 showed that the leaching residue had low content of harmful heavy elements such as Pb, Hg, Cr, and As. Therefore, there was no toxic secondary residue produced in this process.

Electrochemical analysis of bioleaching with ferric iron

The leaching parameters of the FW by *A. ferrooxidans* and sterile control assays were investigated in terms of the pH as shown in Figure 6(a). The evolution of the pH was divided into two phases except for in the sterile control. The pH first increased and then decreased with the leaching time. Compared with the medium *A. ferrooxidans* without

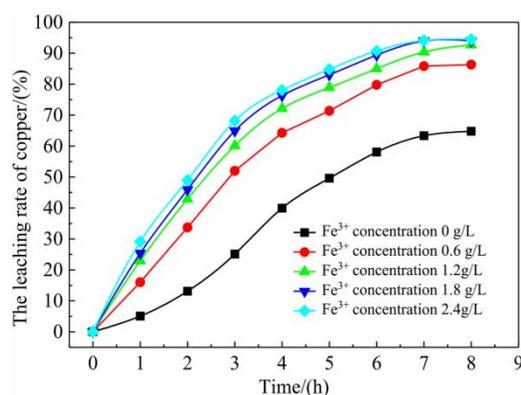
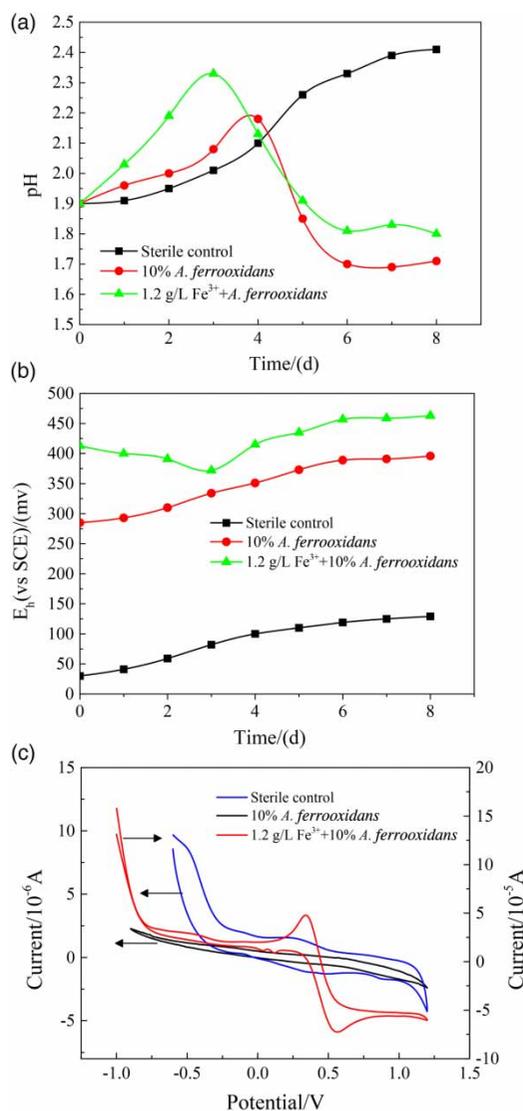


Figure 5 | Effect of Fe³⁺ concentration on leaching of residue.

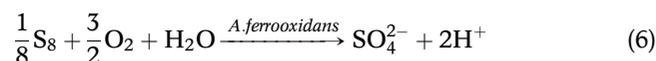
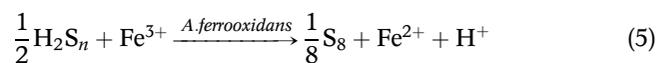
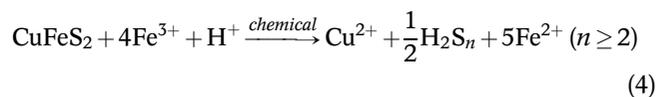
Table 2 | Chemical composition of the 1.2 g/L Fe³⁺ + 10% *A. ferrooxidans* leaching residue after 7 days

Components	Cu	Zn	As	Pb	Cr	Hg	Mn	Ni
Content (%)	0.03	0.007	0.084	0.006	0.012	0.004	0.039	–

**Figure 6** | (a) Evolution of pH, (b) redox potential (E_h) and (c) cyclic voltammetry during leaching of filter residue with sterile control, 10% *A. ferrooxidans*, and 1.2 g/L Fe³⁺ + 10% *A. ferrooxidans*.

Fe³⁺ and the sterile control, the pH of the added Fe³⁺ medium fluctuated greatly (2.23 to 1.7), suggesting that chemical dissolution consumed parts of H⁺ in the early stage and later produced hydrophilic organic acids and inorganic acids, leading to a decrease of pH over time (e.g., H₂S, H₂SO₃ and H₂SO₄) (Liu et al. 2015).

The redox potential (E_h) during leaching of filter residue is shown in Figure 6(b). The concentration ratio of Fe³⁺/Fe²⁺ in the system was the main factor affecting the slurry potential, which compared with the decomposition of other heavy metal elements (Khoshkhoo et al. 2017). With 1.2 g/L Fe³⁺ and 10% *A. ferrooxidans* combined leaching, the E_h first reduced and then the E_h slightly rose, which was respectively due to the chemical decomposition of additional Fe³⁺ in the early stage and later the acceleration of *A. ferrooxidans* bioleaching (Equations (4)–(6)). The maximum redox potential of 1.2 g/L Fe³⁺ and 10% *A. ferrooxidans* oxide leaching could reach 463 mV. Herein, chalcopyrite could be attacked by an appropriate concentration of Fe³⁺ and get dissociated, which was conducive to a quick start-up of bioleaching of copper.



Cyclic voltammetry results are shown in Figure 6(c). A pair of redox currents appears between 0.33 and 0.56 V (vs SCE), indicating the dissolution of heavy metals in bioleaching systems. With the introduction of 1.2 g/L Fe³⁺ in iron-free solution, the intensity of current with Fe³⁺ was higher than in the sterile control and *A. ferrooxidans*, suggesting external Fe³⁺ participates in the leaching step that involved both oxidation and reduction. At the same time, the presence of Fe³⁺ could make a significant acceleration of the corrosion and electron-transfer rate.

CONCLUSIONS

A catalytic ozonation–MFC and *A. ferrooxidans* leaching process was used in treating FW to remove COD and heavy metals in this paper. The FW was first filtered to obtain filtrate and filter residue. The efficiency of COD removal by Mn/GAC catalytic ozonation was higher than

that of the Mn/GAC catalyst or O₃ acting alone. When adding 1 g/L Mn/GAC catalyst and with 1.5 g/min ozone flow, the COD could be degraded from 2,043.67 mg/L to 711.4 mg/L. After that, the COD could continue down to 72.56 mg/L in air-cathode SCMFCs after 15 days, where the liquid-contact side of the cathode was coated with 0.4 mg/cm² platinum. Meanwhile, the maximum voltage and the ultimate power density of the SCMFCs reached 378.96 mV and 7,608.35 mW/m², respectively. The proposed mechanism was the adsorbed-electron hole caused by deposited Mn/GAC catalyst. Adsorption of organic matter on Mn/GAC catalyst was an important step and would have direct influence on the effectiveness of catalytic oxidation. Meanwhile, Mn⁴⁺ acts as a highly electrophilic electron trapping center, promoting ozone to form more ·OH and ·HO₂ on the surface of activated carbon.

For the filter residue, when 1.2 g/L Fe³⁺, 10% (m/v) filter residue, and 10% *A. ferrooxidans* were mixed, the copper leaching rate could reach 92.69% after 7 days if the pH values were adjusted to 1.9. Furthermore, the other heavy metals were also decreased to a level lower than the pollution control standard (Chinese standard GB3838-2002). The leaching parameters in terms of the pH value, redox potential and cyclic voltammetry also showed that the addition of an appropriate concentration of Fe³⁺ to the leaching systems was beneficial to copper dissolution. In the leaching systems, Fe³⁺ participated in the early stage, which involved chemical decomposition that could accelerate causing a break of the bonding between the metal.

ACKNOWLEDGEMENTS

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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