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Original Research

Remediation of Acid Mine Drainage Based on a Novel Coupled Membrane-Free Microbial Fuel Cell with Permeable Reactive Barrier System

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Abstract

In this study, a coupled membrane-free microbial fuel cell (MFC) with permeable reactive barrier (PRB) was reported and its treatment performance and electricity generation for acid mine drainage (AMD) were examined. The pilot-scale continuous flow MFC-PRB was operated for five periods at a hydraulic retention time of 48.0 h, and the average sulphate removal percentages of 51.2%, 39.8%, and 33.1% were obtained in effluent of 1,000, 2,000, 3,000 mg/l, respectively. More than 99.5% of the initial concentrations of Cu^{2+}, Zn^{2+}, and Pb^{2+} were removed, resulting in concentrations of those elements of 0.01-0.05 mg/l in the effluent. The results demonstrated that the MFC-PRB holds a potential capacity for remediation of AMD.

Keywords: membrane-free microbial fuel cell, permeable reactive barrier, acid mine drainage, bio-remediation, electricity generation

Introduction

Acid mine drainage (AMD), resulting from the chemical reaction of oxygen and water (or atmospheric humidity) with sulfide minerals (e.g., pyrite), has a relation with the release of acidic, sulphate, and metal-containing (Pb, Fe, Cd, Cu, Zn, etc.) wastewater. AMD can contaminate both ground and surface waters and has been recognized as one of the more serious elements of environmental pollution in China and around the world, and is currently being studied by several researchers [1-7].

There are various techniques available for remediation of AMD, which may be divided into either chemical or biological mechanisms to remove metals from solution. A number of reported studies have shown that a bioreactor based on *n*ZVI and sulfate-reducing bacteria (SRB) media can be applied for the treatment of a real acid water system containing a mixture of sulphate, heavy metals, and low pH-value pollutants [8-10]. Furthermore, permeable reactive barriers (PRB) as an alternative option for in-situ removal of contaminated groundwater [10-12] have been used widely to provide treatment of contaminants from AMD [13-15]. In addition, we assessed the efficiency of new design structure PRBs to remove heavy metals from AMD and the potential of municipal compost as a carbon source for SRB to enhance metal sulfide precipitation in AMD bioremediation at high flow rates [16-21].

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Microbial fuel cells (MFCs) use microorganisms as catalysts to generate electricity directly from organic compounds that have been developed as a promising technology to recover energy from wastewater, sludge, etc. [22-24]. As shown here and in previous research, MFCs can be used to treat AMD or sulphate wastewater and generate electricity [25-30]. However, there has been little in literature reporting an MFC-PRB system in relation to remediation of AMD. The aim of the present study was to construct a coupled MFC with a PRB system and investigate treatment efficiency and electricity generation, thereby gaining some insights into the AMD bioremediation mechanistic understanding for the potential utilities.

Materials and Methods

Simulated AMD, Sludge, and SRB Inoculums

AMD was characterized for its pH, metals content, and sulphate concentration (see Table 1), which consisted of NH_4Cl 0.191g/l, K_2HPO_3 0.075g/l, Na_2SO_4 2.215 g/l, $MgSO_4 \cdot 7H_2O$ 3.844 g/l, $CuCl_2 \cdot 2H_2O$ 0.0797 g/l, $FeSO_4 \cdot 7H_2O$ 0.149 g/l, $Pb(NO_3)_2$ 0.0479 g/l, $ZnCl_2$ 0.0628 g/l, and $Cd(NO_3)_2 \cdot 4H_2O$ 0.0825 g/l. The contaminants were dissolved in tap water to synthesize simulative influent wastewater, and supplemented further by sulphate whenever necessary. Sewage sludge obtained from an anaerobic sludge digester of a municipal wastewater treatment plant in Wuhu, China, was used as inoculums into the anodic zone. The sludge samples were filtered using a 40-mesh sieve to remove the larger particles and stored at 4ºC before use. An appropriate amount of glucose was added to the sludge and its total suspended solids (TSS) and volatile suspended solids (VSS) were 2.45 g/l and 1.56 g/l, respectively. The presence of SRB was showed by blackening precipitates in the test tube from the fourth day of incubation at 20ºC to 30ºC.

A Coupled MFC with PRB Setup

The pilot-scale continuous flow MFC-PRB system was carried out employing parallel acrylic material columns (14.5 cm i.d., 70 cm high), which were separated by a plate with a center hole (3 cm i.d.). The exterior chamber was used as PRB packed with corn cob media and inoculated by SRB, and the cathode electrode was placed at the end of an exterior chamber and covered with another end plate. The inner chamber was directly used as an anode area that filled with excess sludge. The anode and cathode electrode were a piece of 43.4 cm (1.5 cm i.d., 45 cm high) carbon rod and carbon felt (4.5 cm i.d., 50 cm high, Beijing) without any pretreatment and which were connected through a 1,000x resistor. The ceramic mixtures near the inlets as supporting material were installed at the bottom of the MFC-PRB to simulate a natural aquifer and ensure flow distribution. MFC-PRB was operated for five periods at room temperature of 25±3ºC. The influent sulphate concentration was maintained at 1000 mg/l until period 1-3, and its concentration was increased to 2,000 mg/l in period four, and then to 3,000 mg/l in the last period. The 500 ml sludge (without any pre-treatment) was added to the anode chambers to produce electricity at periods 1, 3, and 5. The MFC–PRB system was continuously fed with synthetic AMD in a downflow mode using multiport peristaltic pumps. The HRT was maintained at about 48.0 h.

Analytical Methods, Instruments, and Data Processing

Unfiltered samples were immediately measured for pH (PHB-10, Shanghai Leici). Some portion of samples (about 50 ml) were filtered with 0.45 μm membrane filters, and the filtrate was immediately analyzed for sulphate (Barium Chromate Spectrophotometry) using a TU 1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). The remaining filtrates were acidified using concentrated HNO_3 and transported to a laboratory for metal analysis.

Concentrations of pb, Cd, Cu, Fe, and Zn were measured with a flame atomic absorption spectrophotometer (WFX-100, Beijing Beifen-Ruili Analytical Instrument Co. Ltd.). The COD was determined by the standard method using chromate as the oxidant as previously described [31]. Samples were sputter-coated with a mixture of gold and palladium. Scanning electron microscopy SEM (S-4800, Hitachi, Japan) equipped with an energy dispersive spectrometer (EDS) was used to determine the elemental ratio and cathode carbon felt surface compositions. All the analyzed elements were normalized and were repeated five times.

Results and Discussion

Effluent COD and Electricity Generation Performance

The electricity generation performances and effluent COD are shown in Fig. 1. During the MFC-PRB process at period 1, the circuit voltage increased and reached 190~230 mV. The initial effluent concentration of COD was 761 mg/l, which shows electroactive bacteria that

Table 1. Characteristics of AMD used in the tests.

Parameters	pH	Pb	Cd	Cu	Zn	Total Fe	SO_4^{2-}
Value	4~6	20 mg/l	20 mg/l	20 mg/l	20 mg/l	20 mg/l	3000 mg/l

might be feasibly enriched from the initial microbial source in an anodic chamber and oxidized organic matter as carbon sources to support microbial activity. However, there was a sharp decrease of voltage at period 2, which is reduced to a minimum of 52 mV, and then a portion of superior decrease in COD was observed due to organic matter biodegradation providing for bioelectricity generation. At periods 3-5, COD value increased slightly and remained steady at around 311-536 mg/l, indicating that residual COD was very likely affecting bioavailability for bioelectricity generation, whereas the trend of COD removal in MFC-PRB was almost in parallel with the voltage profile, which is relatively stable at low levels.

When compared with other two-chamber MFC studies for treating sulphate wastewater from glucose and acetate, the electricity production was similar [5, 25]. Nevertheless, Liu et al. [32] obtained 220.7 mW/m^2 using a single chamber floating-cathode MFC employing sludge as the substrate, although electricity production in the present study was lower. These differences are probably a consequence of the type and structure of MFC employed. Consequently, the results demonstrated that the treatment of AMD using excess sludge as the MFC-PRB anode substrate is effective.

Sulphate Reduction

The influent and effluent sulphate concentrations and sulphate reduction percentage are presented in Fig. 2. It was observed that the average SO_4^{2-} removal rate percentage with 1,000Ω were 51.2%, 39.8%, and 33.1% with influent concentrations of 1,000, 2,000, and 3,000 mg/L, respectively. The corresponding sulphate reduction rates were 1.2 g/d, 3.0 g/d, and 5.0 g/d at periods 3-5, respectively. Some similar results reported that the total sulphate removal efficiencies of the proposed system achieved 52.7% using a new type of UASB-MFC [33] treating molasses wastewater; otherwise Zhao et al. [34] found that sulphate (3.03 g/dm^3) represented 99% removal by use of activated carbon cloth as an anode in MFC-based single-chamber air-breathing treating organic wastewater

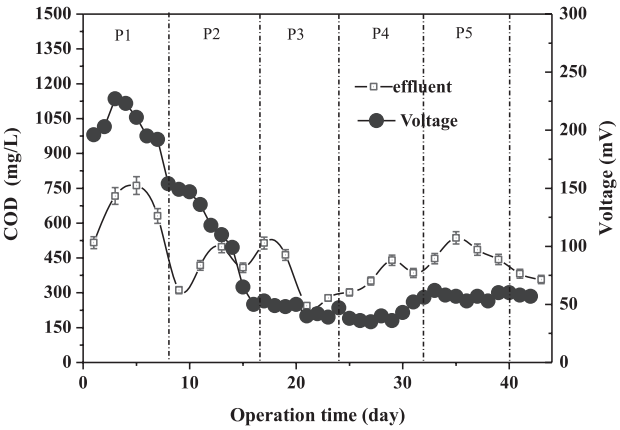

Fig. 1. Effluent of COD and voltage for the MFC-PRB reactor treating AMD.

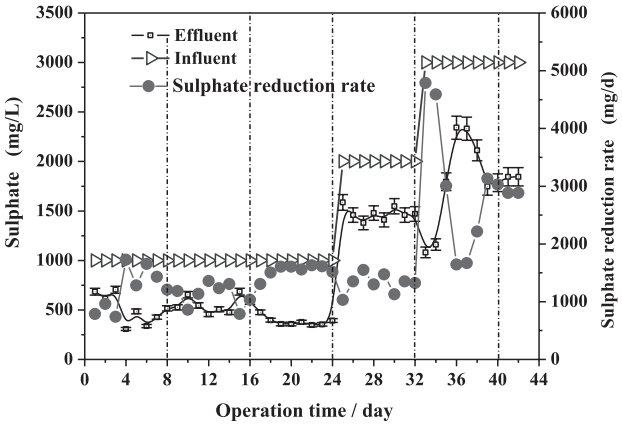

Fig. 2. Sulphate reduction for an MFC-PRB reactor treating AMD.

containing high sulphate [35]. It seems that a lower removal rate can account for the fact that the excessive concentration of sulphates are biologically toxic; thus, they may hinder the growth of microorganisms, including the SRB bacteria, electrogenic bacteria, and other bacteria [35].

Heavy Metals Removal

The heavy metals removal results are depicted in Fig. 3. We found that the removal of Cu^{2+}, Pb^{2+}, and Zn^{2+} were very effective and stable with average effluent between 0.01-0.05 mg/l for all concentrations from the AMD throughout the process, and removal efficiency reached 99.9%, 99.5%, and 99.6%. Moreover, average Cu^{2+} concentrations decreased to <0.02 mg/l. By contrast, the effluent concentration of Cd^{2+} weakly fluctuated throughout the process – especially total Fe effluent concentration in AMD, which suddenly increased to a peak value of 3.84 mg/l on day 7 followed by a gradual decrease on day 9 until day 29, then was reduced to below 0.5 mg/l on day 31. Removal efficiency was maintained at 80.9% to 99.1%.

It was inferred that a high-level removal of Zn^{2+}, Pb^{2+}, and Cu^{2+} was established due to the low-solubility products of zinc sulfide ($K_{sp} = 1.3\times10^{-24}$), lead sulfide ($8\times10^{-28}$), and copper sulfide ($K_{sp} = 1.3\times10^{-36}$), independent of initial concentrations of sulphate. Compared with the previous studies, 99% of Cu^{2+} was removed with the effluent concentration at 0.2 mg/l , and Fe^{2+} was decreased from 545 mg/l to 75 mg/l in effluent when the AMD was treated by SRB and Fe^0 [9]. It could be concluded that MFC-PRB enhanced the removal of heavy metals in comparison to controls with SRB biological treatment.

The heavy sulfide precipitated in cathode obtained from carbon felt were confirmed and studied using SEM and EDS. The conversions of sulfur compounds and heavy metals are presented in Fig. 4. SEM/EDS spectra were found to contain high Cd, Fe, Pb, Zn, and Cu concentrations, suggesting that heavy metals precipitation crystals may have formed on the cathode

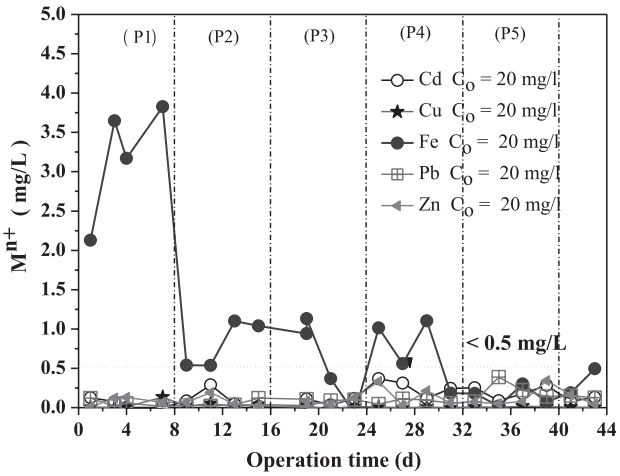

Fig. 3. Effluent of heavy metals concentrations for MFC-PRB reactor treating AMD.

surface accumulated in carbon felt. Previous studies have demonstrated that SRB converted sulphate into sulphide using the organic substrates as electron donors, then that generated heavy metals from the AMD as metal sulphides. SRB and other microbes play an essential role in the removal efficiency of heavy metals [36] (Eqs.1-2).

$$2CH_2O + SO_4^{2-} + H^+ \xrightarrow{SRB} H_2S + 2HCO_3^- \quad (1)$$

$$Me^{2+} + H_2S \rightarrow MeS\downarrow \; -2H^+ \quad (2)$$

According to other studies on MFCs, excess sludge was not only a potential carbon source for use as electron donors for biological sulphate reduction, but also sulphate radicals can be served as electron acceptors in the MFC cathode, which was converted to hydrogen sulfide or sulfur ions in the biological cathode (Eqs. 3-4) [37, 38]. Moreover, the positive charge of heavy metal ions (for example Cu^{2+}) in an MFC cathode solution is most likely to move to the cathode surface, here Cu^{2+} would get two electrons that can be reduced to elemental copper or Cu_2O and copper (Eqs. 5-6).

$$\text{Anode}: \; Sludge \rightarrow CO_2 + H_2O + e^- \quad (3)$$

$$\text{Cathode}: \; SO_4^{2-} + 4H_2O + 8e^- \rightarrow S^{2-} + 8OH^- \quad (4)$$

$$2Cu^{2+} + 2H_2O + 2e^- \rightarrow Cu_2O + H_2O + 2H^+ \quad (5)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (6)$$

Conclusions

This study simulated AMD being treated based on a novel coupled membrane-free microbial fuel cell with a permeable reactive barrier system. The following conclusions can be drawn from the experiments:

1. The MFC-PRB could continuously generate electricity from AMD, and the average sulphate removal rates of 51.2%, 39.8%, and 33.1% were obtained in effluents of 1,000, 2,000, and 3,000 mg/l, respectively.
2. High Cu^{2+},Pb^{2+}, and Zn^{2+} removal efficiencies (99.5%) were obtained during the operation, with most of the results in the range 0.01~0.05 mg/l – far below the level required by Chinese legislation (0.5 mg/l).

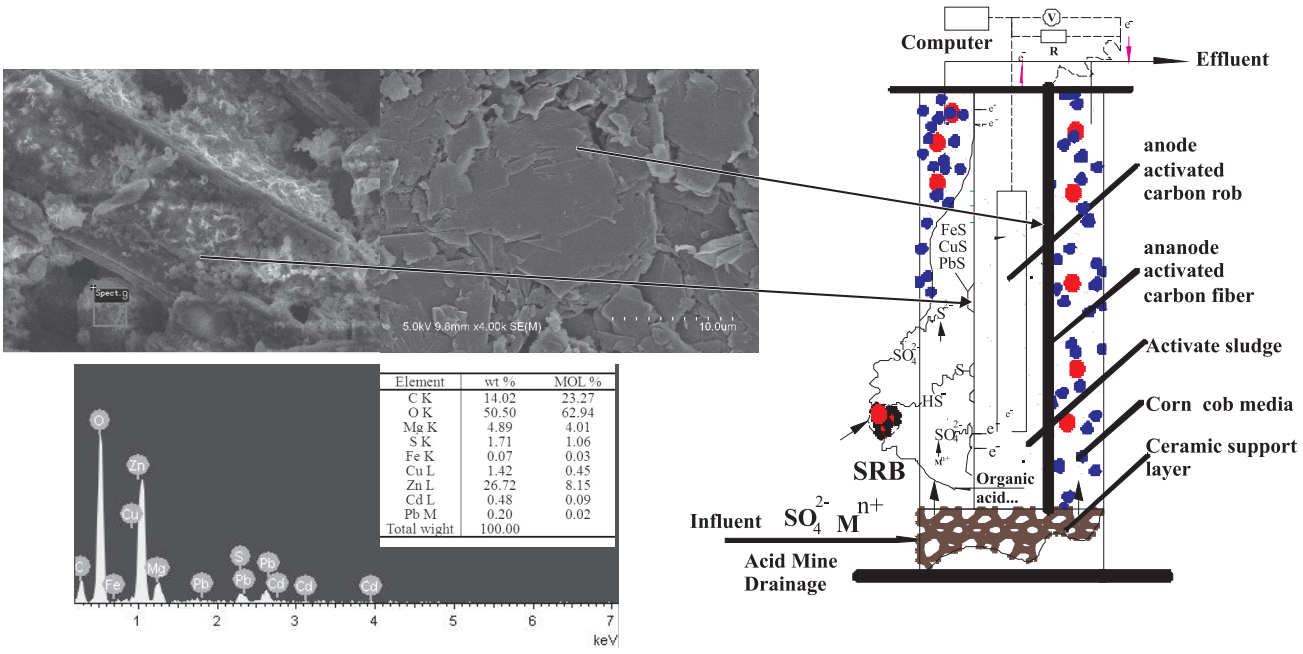

Fig. 4. MFC-PRB experimental setup and conversion of sulfur-compounds and heavy metals.

These results suggest that the MFC-PRB holds the potential for simultaneous removal of heavy metals contained in AMD.

Acknowledgements

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