

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

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Received: 13 October 2015

Accepted: 4 December 2015

## 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  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  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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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<sup>2</sup> 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<sub>4</sub><sup>2-</sup> 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<sup>3</sup>) represented 99% removal by use of activated carbon cloth as an anode in MFC-based single-chamber air-breathing treating organic wastewater

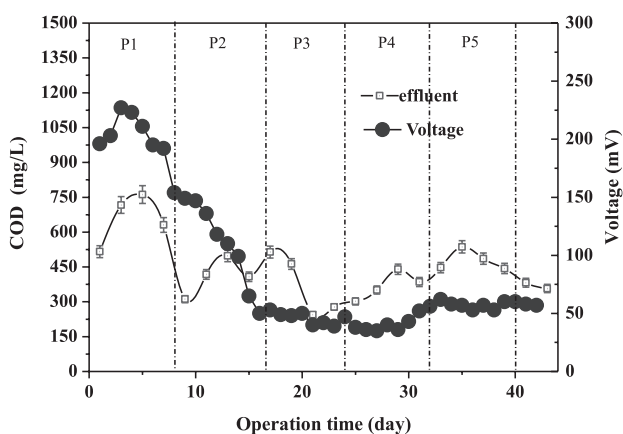


Fig. 1. Effluent of COD and voltage for the MFC-PRB reactor treating AMD.

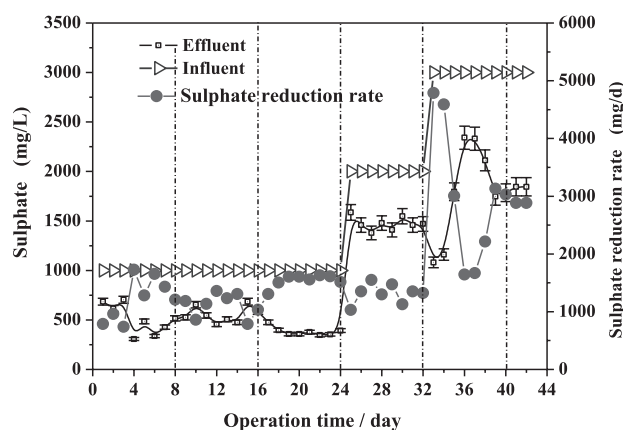


Fig. 2. Sulphate reduction for an MFC-PRB reactor treating AMD.

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<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> 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<sup>2+</sup> concentrations decreased to <0.02 mg/l. By contrast, the effluent concentration of Cd<sup>2+</sup> 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<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> was established due to the low-solubility products of zinc sulfide ( $K_{sp} = 1.3 \times 10^{-24}$ ), lead sulfide ( $8 \times 10^{-28}$ ), and copper sulfide ( $K_{sp} = 1.3 \times 10^{-36}$ ), independent of initial concentrations of sulphate. Compared with the previous studies, 99% of Cu<sup>2+</sup> was removed with the effluent concentration at 0.2 mg/l, and Fe<sup>2+</sup> was decreased from 545 mg/l to 75 mg/l in effluent when the AMD was treated by SRB and Fe<sup>0</sup> [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

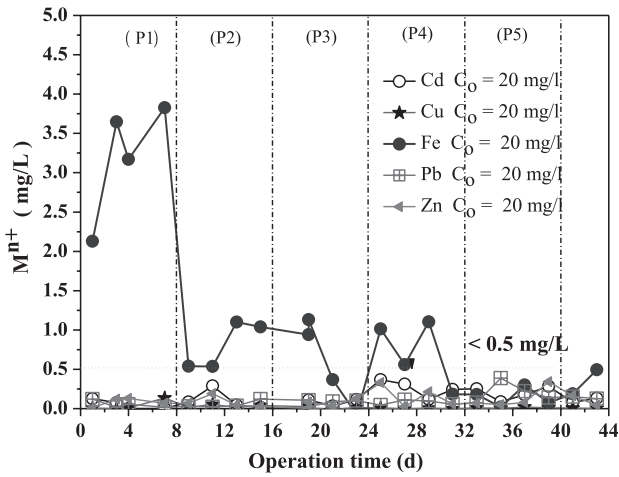
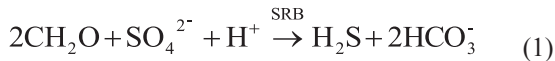


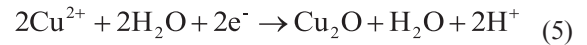
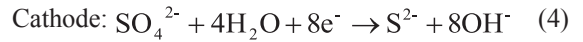
Fig. 3. Effluent of heavy metals concentrations for MFC-PRB reactor treating AMD.

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).



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  $\text{Cu}^{2+}$ ) in an MFC cathode solution is most likely to move to the cathode surface, here  $\text{Cu}^{2+}$  would get two electrons that can be reduced to elemental copper or  $\text{Cu}_2\text{O}$  and copper (Eqs. 5-6).



### 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  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  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).

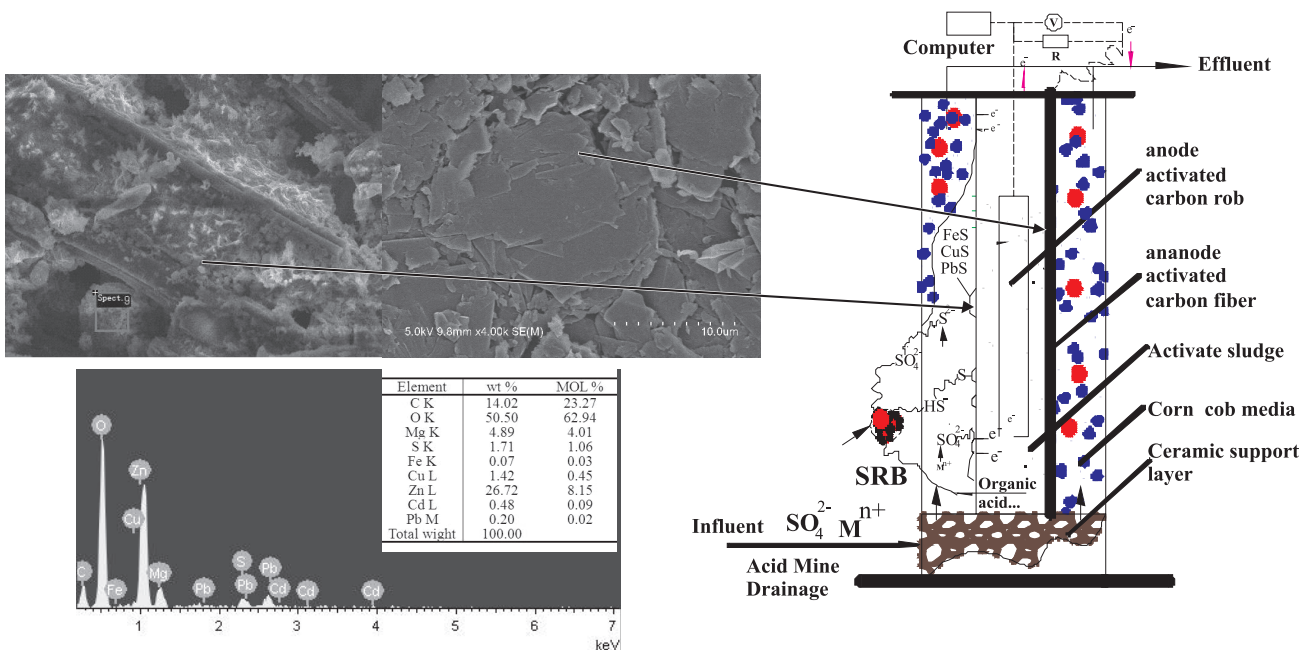


Fig. 4. MFC-PRB experimental setup and conversion of sulfur-compounds and heavy metals.

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

### Acknowledgements

The authors are grateful for the financial support of the National Nature Science Foundation of China (Project No. 51274001), Natural Science Foundation of Anhui Province (1608085ME118) and The Key Program of Youth Elite Support Plan in Universities of Anhui Province (gxyqZD2016120).

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