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Modelling metal and energy recovery from Acid Mine Drainage by means of Bioelectrochemical Technology

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Abstract This work presents a Monod-based mathematical model able to predict the performance of a bioelectrochemical system (BES) treating Acid Mine Drainage (AMD). The BES was operated as a microbial fuel cell (MFC), in order to recover not only the metals but also all the chemical energy contained. The model was based on two different microbial populations performing electrogenic and non-electrogenic metabolisms respectively. During the MFC operation the metal contained in the AMD were the electron acceptors at the cathode. Because of that, Cu^{2+} and Fe^{3+} were reduced to Cu^{0} and Fe^{2+}. The model formulation was based on a set of differential equations describing the simultaneous evolution of the main chemical components in the system. The model developed accurately predicted the concentration of the acetate and biomass at the anode, the metals at the cathode as well as the electrical current generated.

Keywords: Acid mine drainage; bioelectrochemical system; mathematical modelling

1. Introduction

Potential sources for recovering precious metals include effluents from industrial wastes. These effluents, which include acid mine drainage, electronics manufacturing wastewater, metallic etching wastewater, and leachates from industrial zones presents environmental dangers by contaminating water supplies and endangering wildlife, plants, and people.

Acid mine drainage (AMD) is a type of metal-polluted wastewater that generates important environmental and health issues. When metal sulphides in mine wastes weather, AMD is typically produced. It is created through a mixture of chemical and biological oxidation processes (Kefeni et al., 2017). AMD is a highly acidic wastewater with a pH range of 1 to 4, high concentrations of dissolved ferrous and non-ferrous metal sulphates, and variable concentrations of dissolved metals like Al, Pb, Cd, Cu, Zn, Mn, Ni, or Sn ranging from 10 to 104 mg L^{-1} (Peiravi et al., 2017). In the scientific literature, different technologies have been suggested to treat these metal-containing effluents (Khorasanipour and Esmaeilzadeh, 2020). Some of them have been employed extensively, including active technologies such as reverse osmosis, adding alkaline materials to precipitate the metal ions, as well as passive technologies such constructed wetlands or phytoremediation (Peiravi et al., 2017). Nowadays, due to their effective operation and reduced waste generation, the electrochemical and bioelectrochemical techniques are viewed as potential alternatives (Bejan and Bunce, 2015). In terms of wastewater treatment and low energy usage, bioelectrochemical systems (BES) have emerged as a very interesting technology in recent years.

In an electrochemical cell, BESs use exoelectrogenic bacteria to catalyze electrochemical processes on electrode surfaces. The transport of electrons required for oxidation or reduction reactions is facilitated by these exoelectrogenic bacteria. BESs can function as microbial electrolysis cells (MECs), which require an external power source, or as microbial fuel cells (MFCs), which produce electricity. BESs are known to use less energy to remove contaminants than traditional electrochemical methods. The bioelectrochemical reduction and the depositing of dissolved metals onto the cathode surface by using BESs is still in its early stages and requires additional research. The goals of these researches were to investigate the effectiveness of metal removal while using less energy than conventional electrochemical methods or even generating electrical energy from the chemical energy contained in the wastes.

By defining equations that reproduce system function, mathematical modeling has become a vital tool for comprehending and engineering physicochemical processes. Although BES modeling is still in its infancy, some review publications have provided an overview of the development of BES models. Most published models assume that oxygen is the final electron acceptor in the cathode chamber with non-limiting dissolved oxygen content and focus mainly on microbial processes in the anode chamber. These models integrate many equations to explain electrochemical performance and microbiological kinetics, such as Ohm's law and the Butler-Volmer equation.

In this context, the objective of this chapter was to develop a simplified mathematical model to predict the behavior of a MFC treating AMD with the aim to recover the metals and energy contained. The novelty of this work lies in its simplified model compared to previous complex models, considering phenomena in both the anode and cathode compartments, and determining the overall process rate based on controlling processes in the MFC. To the best of the authors' knowledge, no previous modeling proposals have been reported for metal removal when BESs are employed.

2. Material and Methods

The BESs used in this work consisted of two separated transparent PVC chambers, presenting each chamber a volume of 0.1 L. The separation between the chambers was obtained by using a bipolar membrane (Fumasep® FBM). A bipolar membrane was selected in order to keep the significantly different pHs values in anolyte, pH = 7.5, and catholyte, pH = 2.5. In order to enhance the mechanical properties of the BESs, as well as to avoid liquid leakages during the BESs operation silicon gaskets were used. The anode was made of Carbon felt (KFA10, SGL Carbon Group®), specific area of 3.53×105 cm^2 g^{-1} and a porosity of 0.95, being its dimensions 25 × 25 × 8 mm. carbon felt was selected as anodic material due to its ability for biofilm formation (Mateo et al., 2018). A copper cathode electrode 25 × 25 mm was selected. Once finished the MFC operation the cathode was analyzed with the aim to identify the metals bio-electrodeposited. A schematic description of the set-up used in this study is presented in Fig. 1.

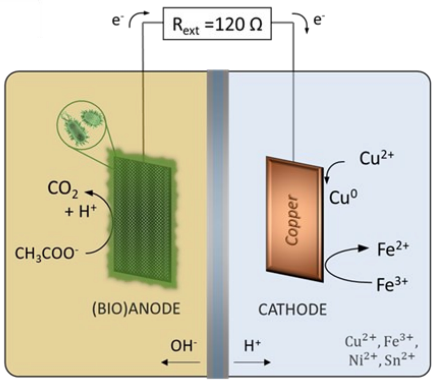

Figure 1. Set-up used in this study.

Three BESs were operated in this research, two of them were used for the experimental bioelectrodeposition tests and the third one was used as reference tests. In the reference test, an abiotic anode was used with the aim to isolate the electrochemical processes taking place in the metal recovery. The three BESs were operated as MFCs with the aim to take advantage of the energy generation due to the spontaneous reactions taking place at the anode and cathode. The experiments were carried out at 25°C and the electrodes were connected by using an external resistor of 120 Ω. The potential of the cathode was measured using a reference electrode (RE) Ag/AgCl.

The inoculation of the BESs was carried out by using activated sludge from the aerobic reactor of a domestic wastewater treatment plant (WWTP), more information about this facility can be found elsewhere (Rodríguez Mayor et al., 2004). The inoculation procedure consisted of an initial stage in which the anodic chamber was filled with activated sludge and batch operated during 3 d. Along this stage, daily cycles, in which the 80% of the anodic chamber volume was daily purged and replaced by fresh microbial growth medium, were carried out. During the inoculation stage, in order to facilitate the electron transference of anodic electrogenic microorganisms, the cathodic reaction carried out was the oxygen reduction to water. This reaction has been widely used due to its easiness and high cathodic potential. Working in this way, it was facilitated the anodic biofilm development and, therefore, the steady state operation. Once developed the electrogenic biofilm the cathodic oxygen reduction reaction was changed to a metal reduction reaction. To do that the cathodic medium was substituted by real AMD. During the BES operation daily cycles were performed by feeding raw anolyte to the anodic chamber in order to avoid substrate limitations. In order to avoid the negative effects of the oxygen in the anodic and cathodic chambers, a nitrogen purge was carried out when feeding or when the cathode was changed.

The composition of the anolyte was as follows: 1 g L^{-1} of CH_3COONa, 0.8 g L^{-1} of $(NH_4)_2SO_4$, 0.2 g L^{-1} of $MgCl_2 \cdot 6H_2O$, 0.05 g L^{-1} of $CaCl_2$ and 0.04 g L^{-1} of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$. In order to ensure the pH stability of the anodic medium around the neutrality, it contained a phosphate buffer made of 2.5 g L^{-1} of Na_2HPO_4, 0.5 g L^{-1} of NaH_2PO_4.The anodic fresh medium had a pH around 7.5 and conductivity of 5.54 mS cm^{-1}. The composition of the real AMD used in this work contained 500 mg L^{-1} of Cu^{2+} and Fe^{3+} and 50 mg L^{-1} of Sn^{2+} and Ni^{2+}, from its sulphate salts, $CuSO_4 \cdot 5H_2O$, $Fe_2(SO_4)_3 \cdot H_2O$, $SnSO_4$ and $NiSO_4 \cdot 6H_2O$. An aqueous solution of Na_2SO_4 was used as a supporting electrolyte (4000 mg L^{-1}). The pH of the real AMD was 2.5 and its conductivity was 7.24 mS cm^{-1}. The anolyte was a microbial growth medium combining sodium acetate, as the sole carbon source, and trace minerals.

In order to characterize the anodic and cathodic chambers daily samples were taken from both compartments. The metal concentrations were determined by means of an inductively coupled plasma atomic emission spectroscopy ICP-AES (Varian Liberty, EEUU). The different iron species concentration were determined by means of 5-sulfosalicylic acid colorimetric method. This chemical reacts producing a red-violet complex with Fe^{3+}. The colored samples were measured by using an UV-spectrophotometer at a wavelength of 505 nm (Paipa et al., 2005). The concentration of Fe^{2+} was determined from the mass balance by taking into account the total iron concentration, determined by means of ICP, and the Fe^{3+} determined by means of the 5-sulfosalicylic acid colorimetric method. Sodium acetate concentration was analysed by using high-performance liquid chromatograph (HPLC). The Conductivity and pH were determined by means of a Crison Cm 35 and a GLP22 Crison equipments respectively. The chemical oxygen demand (COD) was determined according to standard methods (Eaton et al., 2005).

All the processes taking place at the MFC were described by means of a simplified mathematical model that described the performance of the system for sequentially recovering dissolved metals and electrical energy. The model developed to describe the processes taking place at the MFC is presented in Table 1.

Table 1. Petersen matrix, of the main processes taking place in the MFC.

Process (j)	Components (i)	Process rate					
	X_{ne}	X_e	S	Fe^{3+}	Cu^{2+}	Electricity	
Non electrogenic metabolisms	1		$-1/Y_{S,ne}$				$r_{X,ne}$
Electrogenic metabolisms		1	$-1/Y_{S,e}$				$r_{X,e}$
Fe^{3+} Reduction		1	$-1/Y_{S,Fe}$	$-1/Y_{Fe}$		$\gamma_{e-,Fe}/ Y_{Fe}$	$r_{X,Fe}$
Cu^{2+} Reduction		1	$-1/Y_{S,Cu}$		$-1/Y_{Cu}$	$\gamma_{e-,Cu}/ Y_{Cu}$	$r_{X,Cu}$
Endogenous non-electrogenic metabolisms	-1						$r_{end,ne}$
Endogenous electrogenic metabolisms		-1					$r_{end,e}$
Cu^0 oxidation by Fe^{3+}				-1	0.5		$r_{Fe/Cu}$

3. Results

Because of the operational conditions during the metal reduction for recovery, it can be considered that both chambers were completely closed to atmospheric oxygen. Working in this way, anodic aerobic oxidation of the substrates as well as cathodic oxygen reduction reactions were avoided. The main biological reaction taking place at the anodic chamber of the BES was the acetate oxidation by means of exoelectrogenic microorganisms. However, the anodic Faradaic efficiencies obtained, less than 20%, indicating that side reactions such non-electrogenic anaerobic degradation took place. These non-electrogenic reactions does not contributed to the electricity behavior of the BES but consumed electron donors, in this case the only electron donor in the system was the acetate. Because of that, two populations were considered in this work: exoelectrogenic population (Xe) and non-exoelectrogenic population (Xne). Both microbial populations were supposed to growth by consuming acetate and by endogenous metabolisms.

Regarding to the cathodic reactions, the metal ions contained in the AMD were the cathodic electron acceptors which consumed the electron released during the anodic substrate oxidation. In this study, the Cu^{2+} and Fe^{3+} were the electron acceptors during the MFC operation due to their reduction potentials values. The correct control of pH in the catholyte avoids metal precipitation as hydroxides, and no metal adsorption on the electrode or membrane surface contributes to metal depletion. Additionally, during MFC operation, a parallel reaction in the cathode chamber was observed in the reference test: Fe^{+3} was reduced not only by bioelectrochemical mechanism but also because of oxidation of Cu^0 electrode ($Fe^{3+} + 0.5\ Cu^0 \rightarrow Fe^{2+} + 0.5\ Cu^{2+}$). This parallel reaction has been also observed in abiotic reference tests (Leon-Fernandez et al., 2021) and thus it was included in the processes considered in the MFC model.

The electricity generation along the acclimatization stage increased, reaching a steady voltage of 0.2 V after about 12 d, being the anodic potential of about −0.5 V vs Ag/AgCl, a value similar to those reported in the literature when operating with well-developed microbial electrogenic biofilms (Kato, 2017).

The model developed was fitted to the experimental dataset obtained. In Figure 2 an example of the experimental results and the fitting of the model are presented. As can be seen in Figure 2, the model accurately predicts the BES behavior. This result is very interesting since it could be used not only to predict the behavior of the systems, but also to optimize the metal recovery from waste effluents which is very useful in order to recover as much as possible the materials contained in the AMD.

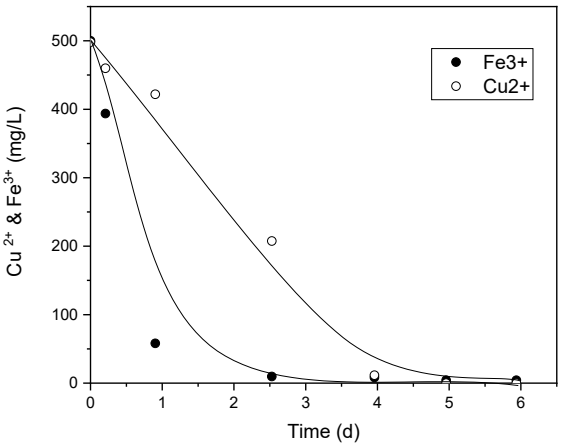

Figure 2. Experimental results and model fitting.

As can be seen in Figure 2, the proposed model predicted the evolution of Cu^{2+} and Fe^{3+} concentration while the estimation of kinetic and stoichiometric parameters agreed with previously reported values. These results offer a single grey box model proposal whose possible application is not only restricted to practical situations. Additionally, it could be easily implemented as a practical tool for quick performance testing about the removal of some dissolved metals from industrial wastewater by bioelectrochemical cathodic reduction and about the potential energy recovery from metal polluted effluents.

4. Conclusions

In this work, the modelling of the metal recovery and electricity generation from AMD by using a MFC system was studied. From the experimental results obtained it has been observed that it is possible to recover pure copper and electricity from the AMD. From the modeling works it has been observed that it is possible to accurately predict the behavior of the MFC in terms of metal and energy valorization, which is very interesting because it would facilitate the recovery of the metals as well as the chemical energy contained in these polluted effluents, which is recovered as electrical current.

Acknowledgements

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