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Copper recovery combined with wastewater treatment in a microbial fuel cell

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A novel type of microbial fuel cell (MFC), called metallurgical MFC, is an attractive alternative for metal recovery with simultaneous wastewater purification. Valuable metals can be recovered at the cathode by using electricity generated from microbial-assisted oxidation of organic matter at the anode. In this study, the possibility for copper recovery combined with wastewater treatment in double-chamber MFC was examined. $CuSO_4$ solutions with different concentrations were used as a catholyte and synthetic wastewater inoculated with activated sludge from municipality WWTP-Blagoevgrad was applied as an anolyte. Current generation resulting in a decrease of copper ions concentration in the catholyte and deposition of copper on the cathode was documented. It was established that the use of more diluted Cu^{2+} solutions enhances the degree of copper recovery. The decreased COD in the anolyte at the end of experiments proves the concept for simultaneous copper recovery and wastewater treatment by means of MFC technology.

Keywords: Metallurgical microbial fuel cell; Copper recovery; Wastewater treatment; Electricity generation.

INTRODUCTION

As a result of the rapid industrialization and continually expanding production activities, huge quantities of waste containing various metals are generated. Without responsible waste management, metal-contaminated wastewater can cause serious environmental and health problems because most metals are toxic, non-biodegradable and accumulate in plant, animal and human organisms. On the other hand, the natural resources of metals are limited, which in the long-term perspective requires that their mining be reasonably controlled. For the storage of the metal pool and the prevention of negative ecological consequences, along with effective corrosion protection and recycling of solid metal waste, it is necessary to regenerate the metals mainly from industrial wastewaters. Various technologies based on physical, chemical and biological processes have been developed in this direction, with the greatest efforts being directed to the effective regeneration of precious metals [1]. The main problem with the application of the developed technologies is that in most wastewaters the concentration of metals is relatively low (in the range of μg/l to mg/l), which requires additional energy and raw materials to be pre-concentrated by large volumes of water.

Bioelectrochemical systems that combine the biocatalyzed anodic oxidation of biodegradable organic products with the reduction of diverse electron acceptors offer a new alternative for the recovery of metals from wastewaters without the need to pre-concentrate them. They can be particularly effective for regenerating noble and other metals that have a more positive potential than that of the bioanode. In this case, the available metal ions can be directly reduced on the microbial fuel cell cathode, with simultaneous generation of electric current.

Despite the obvious thermodynamic possibility of implementing such a process, the concept of the so-called metallurgical microbial fuel cell (MMFC) was demonstrated a few years ago [2, 3]. After proof of principle, the number of publications related to the recovery of different metals in MMFC continuously grows. Along with studies, in which a high degree of recovery of metal ions as Ag (I), Au (III), Cu (II) and Hg (II) has been achieved [4-10], simultaneous reduction of several metals in MMFC has been also reported [11].

Copper is one of the four structural metals whose high electrical and thermal conductivity, corrosion resistance, ductility and extensibility define a very wide range of applications in various industries. The biggest sources of copper pollution are mining, metallurgical and semiconductor industries, as well as various galvanic industries. Although it is an essential microelement, at higher concentrations copper is toxic to living organisms, which imposes strict measures to remove it from industrial wastewaters before discharging into natural water bodies. The applied technologies for copper removal from industrial wastewaters are mainly based on

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methods such as precipitation, adsorption and chemical reduction. An attractive alternative to the methods used, based on the positive Cu^{2+}/Cu standard redox potential (+0.34 V *vs.* SHE), is the spontaneous electrochemical reduction of Cu^{2+} ions to elemental copper on the microbial fuel cell cathode. Depending on the type and concentration of the substrate used, which determine the value of the anode potential, the theoretical electromotive force of MFCs, combining Cu^{2+} cathode reduction and bio-catalyzed anode oxidation of acetate or glucose as an electron donor, reaches 0.49 to 0.69 V [12].

In one of the first studies on copper recovery by MFC, Ter Heijne *et al*. [10] use a two-chamber fuel cell with flat graphite electrodes, a bipolar membrane separating the cathode and anode compartments, and acetate as an electron donor. At continuous mode of MFC operation, almost complete removal of Cu^{2+} ions (1 g/l) in the catholyte to levels below the allowable drinking water standards (<1.3 mg/l) and deposition of elemental copper on the cathode was achieved within 7 days. In addition, it has been found that the process proceeds with equal efficiency both at anaerobic and aerobic conditions in the cathode chamber. High efficiency with respect to copper regeneration under different experimental conditions in MFC is also reported by other authors. Tao *et al.* [6] investigated the copper regeneration of $CuSO_4$ solutions with different concentrations in two-chamber MFCs and achieved almost complete copper removal (> 99%) from a solution of 196 mg/l Cu (II). The same research team has achieved 97% copper recovery using an ash leachate extract from the incineration of municipal solid waste as a catholyte in MFC [13].

The aim of this paper is to prove the principal possibility for development of MFC technology for simultaneous electricity generation, copper recovery and wastewater treatment by using activated sludge from a municipal wastewater treatment plant (WWTP) as a biocatalyst.

EXPERIMENTAL

The experiments were carried out in two-chamber MFCs with a working volume of 0.1 L of each chamber. Carbon felt (SPC-7011, 30 g/m^2, Weißgerber GmbH & Co. KG) with a geometric area of 4.5 cm^2 was used as an anode and electrolytic copper foil of the same size as a cathode. Synthetic wastewater with a composition 5.00 g/l glucose, 1.00 g/l NaCl, 3.00 g/l $NaHCO_3$, 0.40 g/l NH_4Cl, 0.33 g/l $MgCl_2.7H_2O$, 0.28 g/l $CaCl_2$ mixed in a volume ratio 9:1 with activated sludge from the municipal WWTP – Blagoevgrad was used as an anolyte. $CuSO_4$ solutions with different initial concentrations (0.1M, 0.01M, 0.005M) were used as a catholyte. In each individual experiment, two MFCs (K1 and K2) operating under identical conditions and one abiotic (K3) without activated sludge in the anolyte as a control were examined. After an open circuit acclimation period, the fuel cells were tested at a constant load (1 kΩ) with different concentrations of copper in the catholyte for 6 to 9 days. The cell voltage across the load resistor, as well as the anodic potential (*vs*. Ag/AgCl, 3M KCl) were recorded in 5 min intervals by using a multichannel digital multimeter Keithley DMM 2700. The generated current at each measured point was calculated by using Ohm's law.

The efficiency of copper recovery was evaluated by the degree of copper regeneration, η_{Cu}, calculated as the mass ratio of copper deposited on the cathode, $m_{deposit}$, to the mass of copper in the stock solution, $m_{initial}$:

$$\eta_{Cu}\,(\%) = (m_{deposit}/\, m_{initial}).100, \qquad (1)$$

while the percent reduction of COD in the anolyte, determined by the standardized permanganate Kübel's method, served as a wastewater treatment measure:

$$\eta_{COD}\,(\%) = (COD_{initial} - COD_{final}).100 \,/\, COD_{initial} \qquad (2)$$

RESULTS AND DISCUSSION

After the start-up of MFCs, when a load resistor was connected in the external electric circuit, the anode potential maintained relatively high values, but after a certain period it began steeply shifting in a negative direction, reaching stationary values over 500 mV more negative than the initial ones in most cases (Fig. 1). It was found that the observed anode potential shift starts faster with the increase of copper ions concentration in the catholyte.

During the different periods of MFC operation, using mixed cultures as a biocatalyst, the most adaptive types of microorganisms to the certain conditions of the biofuel cell are developed [14]. Positive anode potential at startup of fuel cells favors the development of facultative anaerobic and aerobic microorganisms. As the process progresses, a biofilm is gradually formed on the anode surface, as a result of which the anode potential begins to shift in a negative direction.

The positioning of the potential at steady-state negative values testifies to the formation of a mature biofilm with optimal thickness (Fig. 2), providing access for the entire microbial community to the available substrate [15].

In the presence of exoelectrogenic bacteria in the consortium, the formed anode biofilm is

electroactive and when the circuit is closed, the system generates electrical current. Direct proof of the formation of an electroactive biofilm and its key role in the overall behavior of the system is the change of the generated current over time, which in all experiments carried out strictly follows the changes of the anode potential (Fig. 3). In the absence of a biocatalyst, respectively anode biofilm, the electric current generated by the abiotic fuel cell (K3) is negligible and does not change over time.

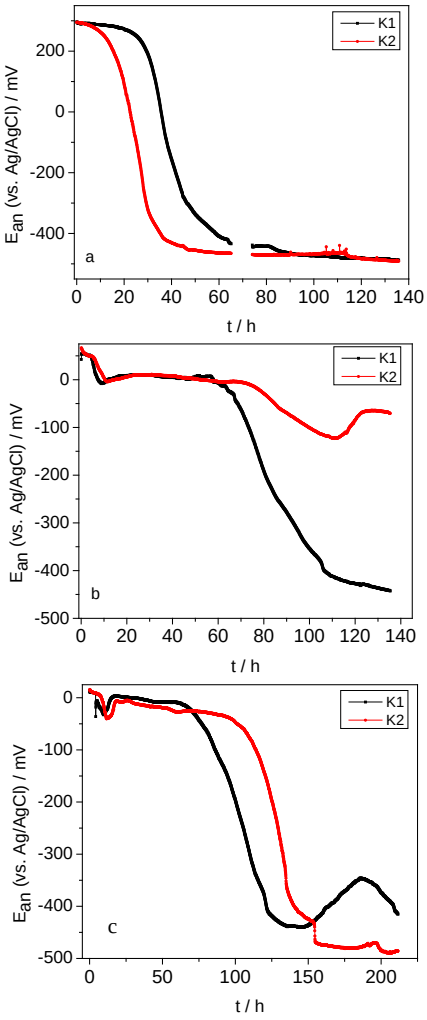

Fig. 1. Changes of the anode potential of microbial fuel cells over time with the use of: a) 0.1 M $CuSO_4$; b) 0.01 M $CuSO_4$; c) 0.005 M $CuSO_4$ as a catholyte.

Fig. 2. Anodic biofilm formed during prolonged operation of MFC (K1) under load (1 kΩ).

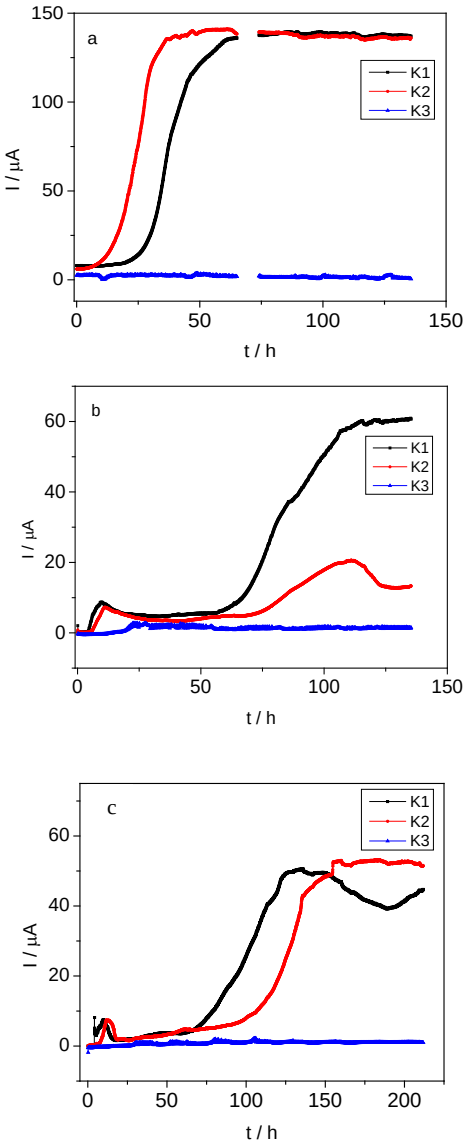

Fig. 3. Generation of electric current from microbial fuel cells over time using: a) 0.1 M $CuSO_4$; b) 0.01 M $CuSO_4$; c) 0.005 M $CuSO_4$ as a catholyte.

As a result of the generated electric current, copper is deposited on the cathodes of the investigated fuel cells (Fig. 4), the amount of which is determined by weight analysis after each experiment (Table 1).

Fig. 4. Deposition of copper on cathodes after operation of microbial fuel cells at constant load (1 kΩ).

Table 1. Amounts of recovered copper using $CuSO_4$ solutions of varying concentrations.

MFC	m(Cu) / g		
	0.1 M $CuSO_4$	0.01 M $CuSO_4$	0.005 M $CuSO_4$
K1	0.0198	0.0128	0.0138
K2	0.0193	0.0096	0.0096

The influence of Cu^{2+} ions as a final electron acceptor on the overall performance of the studied MFCs is more considerable when using the most concentrated catholyte (0.1 M $CuSO_4$). In addition to generating a larger quantity of electricity (Fig. 5) and a larger amount of deposited copper on the cathode, the higher current accelerates the formation of the anode biofilm, resulting in a more stable and reproducible behavior of the system over time.

Despite the higher amounts of deposited copper, however, its degree of recovery from the most concentrated catholyte (0.1M $CuSO_4$) is the lowest, whereas at 20-fold dilution of the stock solution η_{Cu} increases over 10 times - Table 2. Similar results, reported by Tao et al. [6], reveal the possibility for development of MFC-based technology for copper recovery from industrial wastewater without need of pre-concentration by applying other methods.

On the other hand, the permanganometric analysis of the anolyte showed that in most experiments the COD decreased in half (Table 3). There is no correlation between this indicator and the electrical characteristics or the Cu^{2+} concentration in the catholyte, which can be explained by the existing competition between the exoelectrogenic and the other bacteria in the consortium for the available substrates.

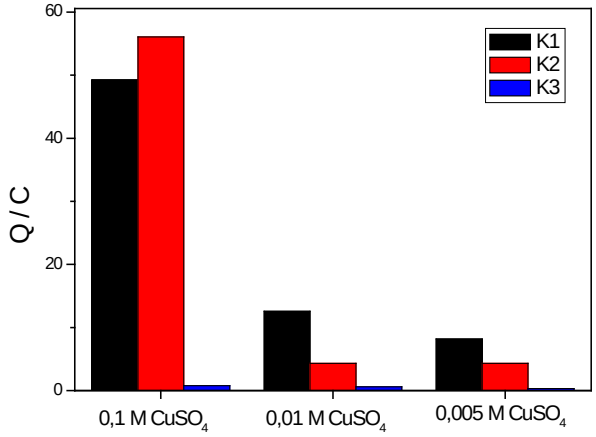

Fig. 5. Quantity of generated electricity (Q, C) of the investigated fuel cells at different concentrations of the catholyte.

Table 2. Degree of copper recovery using $CuSO_4$ solutions of varying concentrations as a catholyte in MFC.

MFC	η_{Cu} / %		
	0.1 M $CuSO_4$	0.01 M $CuSO_4$	0.005 M $CuSO_4$
K1	3.1	20.2	43.4
K2	3.0	15.1	30.2

Considering the fact that the experiments in this study were conducted in a batch system, where the available microorganisms produce and excrete various secondary metabolites in the anolyte, it could be expected that the wastewater treatment efficiency with respect to biodegradable organics will increase at operation of MFC in a flow mode.

Table 3. Percent reduction of COD in the anolyte using $CuSO_4$ solutions of varying concentrations as a catholyte in MFC.

MFC	η_{COD} / %		
	0.1 M $CuSO_4$	0.01 M $CuSO_4$	0.005 M $CuSO_4$
K1	49.5	47.7	65.5
K2	33.5	56.6	49.8

CONCLUSIONS

This study confirms the possibility for development of MFC-based technology for simultaneous copper recovery and purification of biodegradable organic products from wastewater, which additionally generates electricity. However, to achieve indicators with practical relevance further in-depth research is needed in the following directions:

- optimization of the MFC design and construction in order to reduce internal resistance and increase electrical outputs;
- optimization of conditions for formation of electrochemically active anode biofilm;
- development of a flow system providing more efficient copper recovery and treatment of the available organics in wastewater;
- investigations with real wastewater from different sources.

Future research in this area will also be directed towards regeneration of other valuable and/or toxic metals (Ag, Au, Hg, etc.) through MFC technology. A perspective approach is the combination of microbial fuel cell and microbial electrolysis cell, which would allow simultaneous regeneration of several metals present in the treated wastewater.

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