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Application of microbial fuel cell for simultaneous treatment of metallurgical and municipal wastewater – A laboratory study

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Abstract: Microbial fuel cell (MFC) is a hybrid technology that produces electricity and recovers resources from wastewater through biocatalytic and electrochemical reactions. Metallurgical facilities in Bor, Serbia, are a source of copper-rich metallurgical wastewater, and the Town of Bor is a source of municipal wastewater rich in organic matter. The aim of this paper is to investigate the possibility of application of MFC for the treatment of metallurgical and municipal wastewater that are released into the Bor River in Serbia. A prototype of MFC was constructed for this study, and 3 sets of experiments were performed using model solutions and real wastewater. Copper was successfully removed from the treated model solution with 99.42 % efficiency. Solid copper particles were obtained with a particle size of about 1 μm. Maximum chemical oxygen demand (COD) removal rate of 191.7 mg L^{-1} h^{-1} was observed in the anodic compartment. The impact of this study is significant because MFC was implemented for the simultaneous treatment of two types of wastewaters, one containing metals and the other containing organic matter, and both types of wastewater are released into the same river.

Keywords: Bor River; copper; organic matter; bacteria; electrochemical; prototype.

INTRODUCTION

Copper mine and metallurgical facilities in Bor, Serbia, are a large source of pollution. A very high concentration of contaminants poses a serious concern to scientists, experts, and citizens due to the effect on living organisms and environ-

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mental health.[1] Metal-rich metallurgical wastewater and acid mine drainage are released into the Bor River without treatment. Municipal wastewater from the Town of Bor is also released into the Bor River without treatment. This unique phenomenon, where the river water is formed solely by mixing of untreated wastewater containing a high concentration of metals and untreated wastewater containing a high concentration of organic matter, is shown in Fig. S-1 of the Supplementary material to this paper.[2] The concentration of copper in Bor River ranges from 5 to 30 mg L^{-1}, and about 500 t of copper per year is released into the Bor River through the metallurgical wastewater.[2–4] About 910 t of copper per year is transported by Bor River and Timok River to the Danube River in dissolved and particulate form, which creates transboundary pollution, affecting the Danube River in Romania and Bulgaria.[5] Various treatment methods could be used for the purification of metallurgical and municipal wastewater from Bor, however, by applying MFC, it could be possible to treat both types of wastewaters simultaneously.[6–8]

MFCs are hybrid bio-electrochemical reactors able to use concentrated organic waste streams, produce electricity, and recover resources from wastewater through biocatalytic and electrochemical reactions.[9] MFC consists of an anode and a cathode chamber which are generally separated by a proton exchange membrane (PEM) to avoid the migration of electrolytes from one chamber to the other (Fig. 1a).[10,11] There are few types of MFC systems, and this separate system is applied only to the two-chamber MFC system. In the anode compartment, bacteria are used as catalysts to break down organic matter to carbon dioxide, protons, and electrons through respiration mechanisms, but in the absence of oxygen. The resulting electrons are transferred to the anode surface which plays the role of electron acceptor. Then, they are transferred to the cathode via an external circuit, while the protons diffuse through the PEM.[12–15] The final reduction reaction is performed in the cathode compartment where protons, electrons, and usually oxygen are recombined to complete the reactor's electrochemistry. As an alternative, various metal ions can be electrochemically reduced in this reaction and eventually recovered from the solution by their conversion to elemental form. In addition to metals, free radicals can also be used as electron acceptors in the cathodic compartment.[16]

The maximum current that can be produced by an MFC depends on the actual rate of substrate biodegradation, whereas maximum theoretical cell voltage (also called electromotive force or emf) depends on Gibbs energy change of the overall reaction and can be calculated as the difference between the standard reduction potentials of the cathodic oxidant (oxygen) and the chosen anodic substrate.[17] Power output of MFC could be enhanced by modification of electrodes and PEM using polymeric nanocomposites.[18] However, the main advantages of the MFC type reactors are beyond energy production and they could be a powerful tool for wastewater treatment, as an alternative to the conventional biological processes.

There are several reports on the successful application of MFC to remove copper from model solutions with efficiency up to 99.88 % and yield of electrical energy reaching 3.2 A m^{-2}.[19,20] The most promising characteristic of the process is that simultaneously in the anodic chamber domestic or other high organic content wastewater could be treated, as well. The existing studies reported chemical oxygen demand (COD) removal efficiency as high as 83 % in such a setup.[21] The optimal conditions for MFC operation were obtained using the microbial cultures isolated from freshwater sediments, such as the sediment from Danube River in Serbia and the sediment from Lake Uzungeren in Bulgaria.[22,23]

Based on the recent development in the field and taking into account the situation in the region of Bor, Serbia, this paper aimed to investigate the eventual application of MFC as an approach to manage the wastewater streams generated by the local metallurgical industry and community. The performance of a lab-scale reactor towards Cu ions and COD removal was tested using a model and real wastewater samples.

EXPERIMENTAL

The details of the sampling of the wastewaters are given in Supplementary material.

Materials and MFC operation

The MFC used in this study was assembled as a cylindrical plastic reactor consisting of two chambers separated by Nafion® 424 perfluorinated proton exchange membrane (Fig. 1). The cell segments were equipped with the respective sampling and gas/liquid transport ports. The electrodes were 30 mm in diameter and they were made of carbon cloth with stainless steel current collectors. They were connected with an external electric circuit loaded with a 1000-Ohm resistor. The volumes of cathode and anode chambers were 40 cm^3.

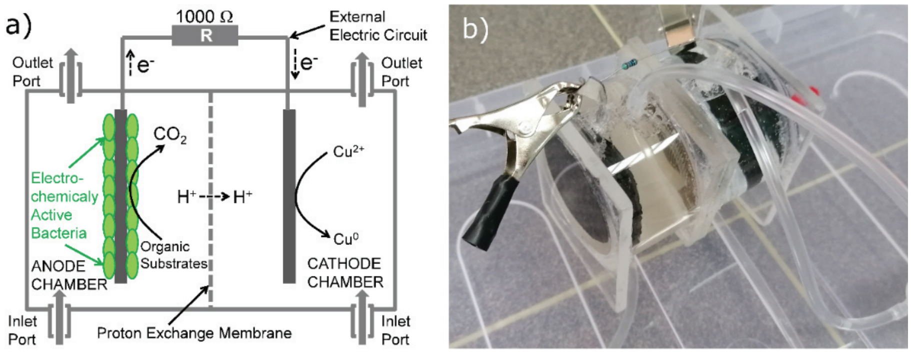

Fig. 1. Microbial fuel cell; a) schematic diagram and b) the prototype constructed for this study.

The electrochemically active microorganisms (electrogenes) were isolated from the bottom sediments of "Poda" protected site located on the outfall of Lake Uzungeren, south of

Burgas. The water of Lake Uzungeren is characterized by relatively high electrical conductivity and pH value (5230 μS/cm and 8.2, respectively), and a very low dissolved oxygen content (1.4–2.2 mg/l O_2).[23] The lake sediment had relatively high contents of organic matter (22.5 %), iron (3.05 % Fe), and manganese (935 mg/kg Mn).[23] Mersinkova and Yemendzhiev demonstrated that the mixed culture of anaerobic bacteria isolated from this lake sediment was capable of powering MFC.[23]

The enrichment of the mixed culture was performed in anaerobic conditions by inoculation of sediment samples in 20 g L^{-1} Luria–Bertani (LB) nutrient medium (10 g L^{-1} tryptone, 5 g L^{-1} yeast extract, and 5 g L^{-1} NaCl, pH 7) containing 15 g L^{-1} glucose. After 96 h of cell growth at 18 °C, the enriched culture was suspended in a fresh nutrient medium with a lower concentration of organics (5 g L^{-1} LB) and 1 g L^{-1} acetate, as a carbon source, in order to avoid fermentative metabolism. The initial microbial concentration in the anodic chamber was set to be 10^7 CFU L^{-1}. The process was conducted at 18 °C. In order to represent the biological condition specific for the municipal wastewater, glucose solution inoculated with municipal wastewater and sewage sludge from the Town of Bor were used in the Experiment 2 (Table I).

TABLE I. Compositions of solutions in anodic and cathodic compartments that were used in 3 different experiments.

Experiment	Composition of solution in the anode chamber	Composition of solution in the cathode chamber
1	Bacteria isolated from the lake sediment and LB nutrient medium	Model solution containing 200 mg L^{-1} Cu^{2+}
2	Bacteria from municipal wastewater and glucose	Model solution containing 450 mg L^{-1} Cu^{2+}
3	Bacteria isolated from the lake sediment and LB nutrient medium	Metallurgical wastewater

2 % Potassium hexacyanoferrate solution or 1 M potassium permanganate solution was used as catholyte for preconditioning of MFC, and the model solution containing copper sulfate pentahydrate in deionized water, or real wastewater stream such as metallurgical wastewater (collected at the outlets near mining and metallurgical facilities in Bor, Serbia) were used as catholyte depending on the purpose of the experimental sets performed. Three sets of experiments that were performed using the described solutions are summarised in Table I.

Analytical methods

The pH values of underground mine wastewater, Robule Lake wastewater, and metallurgical wastewater were measured in the field using the pH meter model IM-23P.

The concentrations of elements in the wastewaters were measured using PerkinElmer ICP-MS NexION 1000. Rh was used as an internal standard for the determination of Cd, Co, Cu, Mn, Ni, Zn, As and Cr. Re was used as an internal standard for the determination of Pb. All elements were determined in Ar mode, except As which was determined in He mode. The appropriate dilutions of original samples were made to match the concentration range of the calibration curve. Certified standard solutions containing the applied elements were used for calibration and quality control. The dynamics of Cu concentration during the experiments were monitored both by ICP–MS and spectrophotometrically by HACH DR 3900 spectrophotometer with Lange LCK 329 cuvette test. COD was determined spectrophotometrically by HACH DR 3900 spectrophotometer and Lange LCK 514 cuvette test. Change of voltage was measured using a multimeter. Particle size analysis was carried out using a Microtract Nanowave II particle size analyzer.

All measurements were performed in triplicate and the results presented here are mean values.

RESULTS AND DISCUSSION

The results of the chemical characterization of the underground mine wastewater, the Robule Lake wastewater, and the metallurgical wastewater are presented in Table II. The metallurgical wastewater had higher concentrations of toxic elements such as Cd, Cu, Ni, Pb, Zn, As and Cr, when compared to the other two wastewaters. The concentration of arsenic (As) was exceptionally high in the metallurgical wastewater, reaching 28.8 ppm, which is about 3000 times higher than the limit value for drinking water (0.010 ppm). On the other hand, the concentrations of Co and Mn were the highest in the wastewater of Robule Lake (1.19 and 84.8 ppm, respectively). The metallurgical wastewater had the highest concentration of copper (215.5 ppm of Cu), so this wastewater was used as an object to test.

TABLE II. Chemical characteristics of wastewaters around Bor

Parameter	Underground mine wastewater	Robule Lake wastewater	Metallurgical wastewater	Municipal wastewater
pH	2.74	2.62	1.89	7.82
c_{Cd} / ppm	0.13	<0.10	4.38	<0.00010
c_{Co} / ppm	0.52	1.19	0.6	0.00081
c_{Cu} / ppm	130.1	41.8	215.5	<0.010
c_{Mn} / ppm	17.3	84.8	16.9	0.111
c_{Ni} / ppm	2.19	0.68	18.35	0.0033
c_{Pb} / ppm	<0.10	<0.10	3.15	0.00057
c_{Zn} / ppm	9.2	25.3	51.5	0.0140
c_{As} / ppm	0.28	<0.10	28.8	0.0037
c_{Cr} / ppm	<0.10	<0.10	0.11	<0.00050

The change of voltage during the Experiment 1 (Table I) showed that the reactor reached its optimal condition (in terms of electricity production) after 144 h of operation, which is probably a result of the growth and development of the functional anodic biofilm that accelerated the activity of the electrogenic microorganisms (Fig. 2a). On the other hand, the voltage decreased gradually during the experiment with the bacteria from municipal wastewater (the Experiment 2, Fig. 2b). Copper concentration decreased along the time in both experiments with model solution (the Experiments 1 and 2, Fig. 2d and e). However, the decrease in the concentration of copper during the Experiment 1 was more drastic compared to that in the Experiment 2. During the Experiment 1, the copper concentration decreased from 200 to 1.15 mg L^{-1} for 188 h, but the highest drop in Cu concentration occurred during the first 24 h of the experiment, from 200 to 22.6 mg L^{-1}. During the Experiment 2, the copper concentration decreased from 434 to 194 mg L^{-1} for 170 h. The efficiency of copper removal was better during the Experiment 1 (99.42 %) compared to the Experiment 2 (55.40 %).

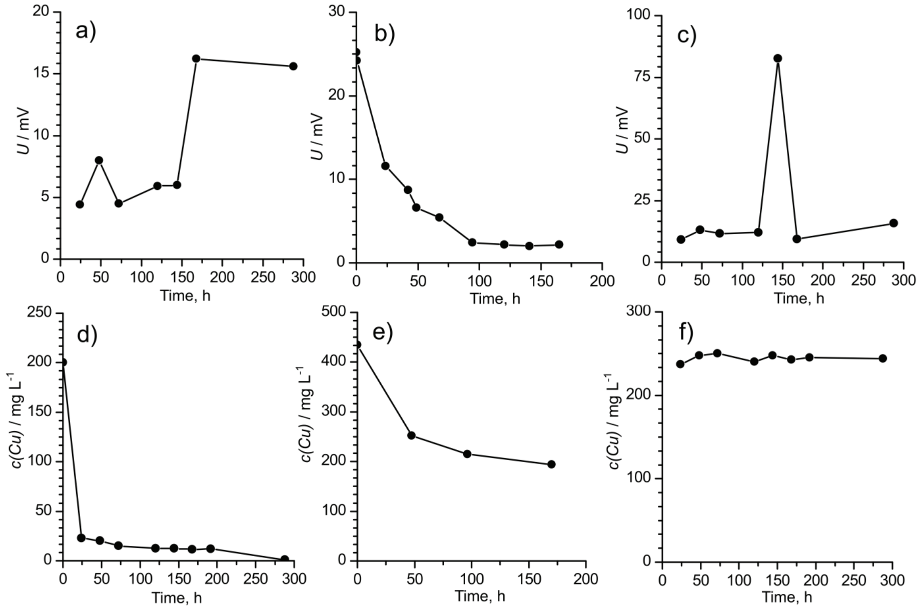

Fig. 2. Change of voltage during Experiments: a) 1, b) 2 and c) 3; change of copper concentration during Experiments: d) 1, e) 2 and f) 3.

The voltage during the Experiment 3 (Fig. 2c) increased drastically after 140 h from the beginning of the experiment. The reason for this change is unknown, and there is also a possibility of measurement error. The copper concentration did not change during the experiment with metallurgical wastewater (Fig. 2f) because of the low pH value of this water (pH 1.89), and probably the presence of other metal ions which are preferred as electron acceptors (Table II).

The effect of the cathodic reduction of the dissolved metal ions and their transformation into an elemental (unsoluble) form is also demonstrated by the data obtained from the particle size and distribution tests (Fig. 3). In the metallurgical wastewater before the start of Experiment 2, the particle size ranged from 1 to 2 nm, which is typical for smaller colloidal particles. However, larger particles were obtained in metallurgical wastewater after the treatment with a mode of about 0.9 μm, which suggests that some chemical species changed their form from dissolved or colloidal to solid during the treatment. Since the copper concentration did not change during the treatment of metallurgical wastewater (Fig. 2f), there is a possibility that chemical species other than copper were precipitated. After the treatment of model solution containing Cu ions in Experiment 1, two particle size distributions were obtained with modes around 1 μm and 2.5 μm, which suggests that two processes of solid particles formation took place. These solid particles were sedimented on the cathode chamber bottom or collected on the cathode surface.

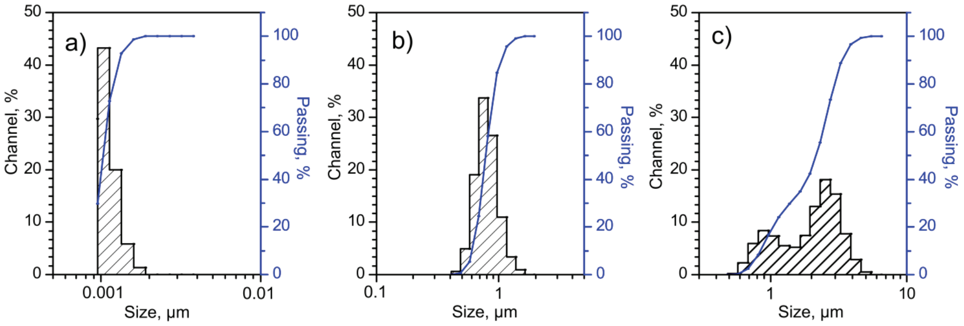

Fig. 3. Particle size distribution diagrams: a) metallurgical wastewater before the start of Experiment 3; b) metallurgical wastewater after 144 h of Experiment 3; c) model solution with copper ions after 144 h of Experiment 1.

The COD removal rate was measured in the anode chamber to estimate the organic matter degradation rate. When bacteria isolated from the lake sediment and the model solution containing copper were used (Experiment 1), the maximum COD removal rate was 191.7 mg L^{-1} h^{-1}. When the metallurgical wastewater was used as a catholyte, the maximum COD removal rate was 179.2 mg L^{-1} h^{-1} (Experiment 3).

The removal of copper from the model solution using MFC was relatively efficient in all experiments and reached 99.42 %. The removal of copper from real metallurgical wastewater using MFC did not show this positive result mostly due to the bad physicochemical conditions of the wastewater, namely low pH. Besides this, the presence of other metal ions with higher standard electrode potential could explain the low effect on copper in this set of experiments. Pretreatment (neutralization) of wastewater such as metallurgical wastewater could significantly improve the process.[6,19,24] Even after neutralization, the copper reduction and removal will start after depletion of the high potential ions available in the catholyte. The evidence that other chemical species from the metallurgical wastewater were reduced in the cathodic compartment instead of copper is the fact that a relatively high COD removal rate (179.2 mg L^{-1} h^{-1}) was observed, and larger particles were present in the anodic compartment after the Experiment 3 (Fig. 3b).

CONCLUSION

The prototype of MFC constructed for this study was efficient for the removal of copper from the model solution. Bacteria isolated from the lake sediment had a higher ability to produce electrons and reduce copper ions from the model solution than the bacteria from the municipal wastewater. Acidic pH value and the presence of reducible chemical compounds with higher redox potential than copper constrained the removal of copper from metallurgical wastewater. Additional experiments should be carried out in order to improve the efficiency of MFC for the treatment of metallurgical and municipal wastewater. The impact of this study is significant because MFC was implemented for the simultaneous treatment of two types of wastewaters, one containing metals and the other containing organic matter, and both types of wastewater are released into the same river. This is also an initial attempt to apply this technology for the purification of locally present metallurgical and municipal wastewater in the region of Bor, Serbia (Fig. S-1).

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/11261, or from the corresponding author on request.

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ИЗВОД

ПРИМЕНА МИКРОБНЕ ГОРИВЕ ЋЕЛИЈЕ ЗА ИСТОВРЕМЕНИ ТРЕТМАН МЕТАЛУРШКЕ И КОМУНАЛНЕ ОТПАДНЕ ВОДЕ – ЛАБОРАТОРИЈСКА СТУДИЈА

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Микробна горивна ћелија (MFC) представља хибридну технологију помоћу које је могуће добити електричну енергију и метале из отпадних вода путем биокаталитичких и електрохемијских реакција. Металуршки објекти у Бору извор су металуршких отпадних вода богатих бакром, а град Бор је извор комуналних отпадних вода богатих органским материјама. Циљ овог рада је да се испита могућност примене MFC за пречишћавање металуршких и комуналних отпадних вода које се испуштају у Борску реку. За ову студију конструисан је прототип MFC и изведене су 3 серије експеримената користећи припремљене растворе и стварне отпадне воде. Бакар је успешно уклоњен из припремљеног раствора са ефикасношћу од 99,42 %. Добијене су чврсте честице бакра величине од око 1 μm. Максимална брзина смањења хемијске потрошње кисеоника (COD) од 191,7 mg O_2/L на сат је измерена у анодном одељку. Значај ове студије огледа се у томе што је MFC имплементирана за истовремени третман две врсте отпадних вода, од којих једна садржи метале, а друга која садржи органске материје, а обе врсте отпадних вода испуштају се у исту реку.

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