MICROBIAL ELECTROLYSIS CELLS - A NEW APPROACH TO WASTEWATER TREATMENT WITH HIGH SULPHATE CONTENT

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ABSTRACT
An experimental installation of a microbial electrolytic cell for desalination of wastewater with high sulfate and heavy metals content was designed and implemented. The potential of the investigated method for treatment of high sulphate mining wastewater in laboratory conditions was established, investigating two variants of the bioelectrochemical system operation - in microbial fuel cell (MFC) mode and in microbial electrolysis cells (MEC) mode. Prospective results have been obtained for further technology-optimized reduction of the copper ion concentration in the cathode area, where the MEC - variants reaches better results (for Cu - 37,1% and 35,2% for SO_4), compared with MFC-options reaches (for Cu - 4,6% and 32.2% for SO_4) for the 10 day period.

Introduction

The depletion of conventional energy resources and especially the environmental problems associated with the use of carbon-based fossil fuels determine the important role of renewable energy sources for the development of modern civilization. That is why one of the biggest challenges at the beginning of the 21st century is to find alternative, environmentally friendly and competitive energy sources. Hence the growing interest in fuel elements as environmentally friendly and efficient converters of chemical energy of fuel directly into electricity. In the last 10-15 years, microbial fuel elements (MFE) have aroused considerable interest among the scientific community due to the possibility of simultaneous generation of electricity and purification of water from various pollutants (Angelov et al., 2013). In addition, in these elements, the oxidation of the substrate (fuel) is carried out with the help of microorganisms that can reproduce easily and sustainably under normal environmental conditions. The driving force of this process is the difference between the equilibrium and current oxygen concentrations in the liquid phase:

At the end of the last century, it was estimated that approximately 19,300 km of streams and rivers and approximately 72,000 hectares of lakes and reservoirs in the world were severely damaged by wastewater, although the true amount of environmental pollution caused by the discharge of such water it is difficult to determine precisely *(Johnson and Hallberg, 2005)*. This environmental problem exists in most European countries, especially in those with well-developed mining and mineral processing industries.

In systems such as microbial electrolysis and fuel cells (MECs / MFCs), the main process is carried out by electrons detached from the respective donor, and during its oxidation are transferred, instead of to the corresponding natural acceptors (oxygen, sulfates, ferroions, nitrates), to the insoluble anode of the bioelectrochemical system (BES). Various microorganisms are used to carry out the process, including mixed cultures in BES with the most diverse structure and configuration. Information on technologies associating the purification of contaminated water by microbial electrolysis cells is almost entirely limited to the use of various organic compounds dissolved in contaminated water as electron donors for microorganisms in the system *(Wang et al., 2012).*

As a result of these studies, the efficiency of this type of water treatment systems shows a steady upward trend but is still low for the start of the industrial stage. Information on water purification from inorganic contaminants is scarce and is associated with the removal of sulfate and thiosulfate by sulfate-reducing bacteria (CRB) (Lee et al., 2014; Mirjafari et al., 2015), removal of hydrogen sulfide *(Gardner et al., 2002)* and the use of Fe (III) oxides as electronic acceptors supporting the development of microorganisms immobilizing heavy metals and uranium *(Uzun et al., 2016).*

Microbial electrolysis cells (MECs) are a new and promising approach to producing hydrogen from organic matter, including wastewater and other renewable resources *(Logan, 2008 and Meda, 2015).* Energy

from MEC is an environmentally friendly, renewable and innovative technology for hydrogen production. MECs produce hydrogen mainly from waste biomass supported by exoelectrogenic bacterial *strains (Mirjafari et al., 2015).*

MECs were discovered in 2005, in which electrochemically active bacteria oxidize organic matter and generate CO_2, electrons and protons. Bacteria transfer electrons to the anode and protons are released into the solution. The electrons then pass through a wire to the cathode and combine with the free protons in the solution passed through the cation exchange membrane (CEM). However, this does not happen spontaneously. To produce hydrogen at the cathode from the combination of these protons and electrons, MEC reactors require additional external voltage (at least 0.2 V) to biologically stimulate the process at pH = 7, T = 30 ° C, P = 1 atm *(Liu, 2005).* MECs were found to require relatively low energy power (0.2-0.8 V) compared to typical aqueous electrolysis (1.23 -1.8 V). A schematic of the principle of operation of the two-chamber MEC is shown in Figure 1.

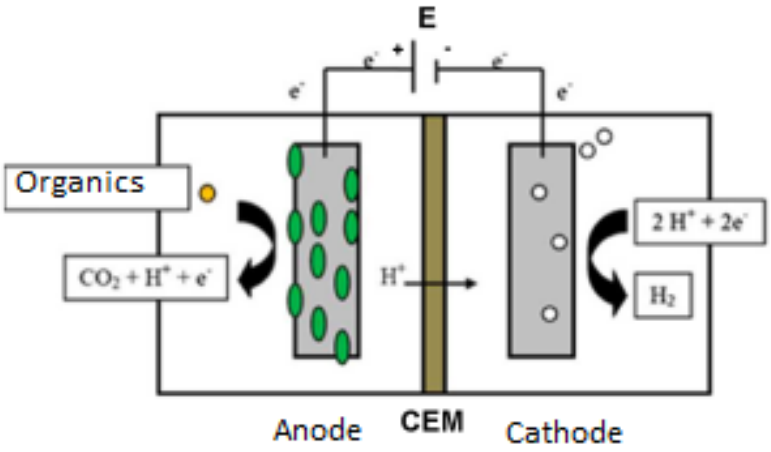

FIG. 1. *Principle of operation of the microbial electrolysis cell (MEC*)

Microbial fuel / electrolysis cells based on the process of dissimilative microbial sulfate reduction, provide the opportunity to simultaneously production of electricity and sulfates removal from the incoming water. For this type of biological fuel elements, it is known that it is not necessary to add additional mediators, and the role of mediator is performed by microbially produced hydrogen sulfide. In this process, oxidation of the surface of the anode of hydrogen sulfide to elemental sulfur takes place. Other final products are possible in this process depending on the composition of the anolyte and the environmental conditions - thiosulfates, polysulfides or dithionates.

In most cases, during continuous operation of the biological fuel cell on the surface of the anode or in the space around it, elemental sulfur accumulates, which degrades the electrochemical characteristics of the element. On the other hand, the typical design (sandwich type) of microbial fuel cells is such that optimal conditions are not created for the development of the respective microorganisms, as in the case of bioreactors with immobilized biomass.

The main goal of the present study is to test new constructions of two-chamber and three-chamber microbial fuel / electrolysis cells based on the process of dissimilative microbial sulfate reduction and to prove - technological possibility for removal of the elemental sulfur formed in the fuel element and removal of sulphates and heavy metals from the treated water**.**

Materials and methods

To achieve this goal, the experiments were conducted in 2 different laboratory installations, respectively laboratory installation - variant 1 and variant 2 (Fig.2 and 3). The main difference between the two installations

is the construction of the bioelectrochemical system (BES). Both constructions are "sandwich" type, but while in variant 1 a cylindrical bioelectrochemical cell is used, in variant 2 the construction is in the form of a rectangular parallelepiped. Both variants use graphite electrodes and anion exchange membrane type - AMI7001. In variant 2 the area of the electrodes is optimized and about one order of magnitude larger than the area of the electrodes in variant 1 (respectively - 0.02 m^2 and 0.002 m^2), another significant difference is in terms of areas of anion exchange membranes - in variant 1 - 0.007 m^2 and 0.01 m^2 in variant 2. The same sulfidogenic bioreactors were used in both laboratory installations in which approximately half the volume of 0.7 dm^3 was filled with 0.3 kg of modified zeolite. The reactors are connected in series with the anode sections of the cells, and the inserted modified zeolite acts as a carrier of the biofilm of CRB and other metabolically related groups of microorganisms.

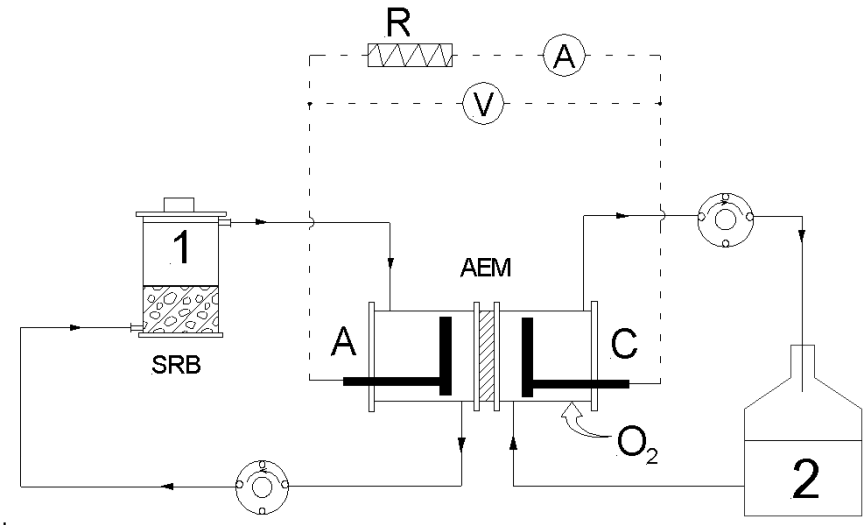

FIG. 2 *Technological scheme of the laboratory installation under Variant 1*
1- bioreactor for sulfate-reducing bacteria, 2- Buffer tank - solution of $CuSO_4$

A modified Postgate medium with a volume of 1.1 dm^3 was added to fill the volume of the anode zone of the cell and the sulfidogenic bioreactor. Inoculation of microbial cells (for both variants) was performed with 50 ml of a mixed culture of sulfate-reducing bacteria. After the formation of an active biofilm from CRB, the feeding medium began in a mode of continuous cultivation of bacteria. The nutrient medium from the tank (1) enters the fuel cell with regulated flow through the peristaltic pump. The homogenization in the microbial electrolysis cell is realized through a recirculation pump.

The chemical composition of the catholyte in both variants was identical - 1 g/l $MgSO_4$, pH=6,5-7,0 и 2-solution of $CuSO_4$- (Cu^{2+}- 1018 mg/l, SO_4 – 2,03g/l, H_2SO_4- 0,5g/l).

A pH electrode model VWR pH meter HANNA HI-9021 was used to measure the pH. The redox potential (ORP) was measured with Sen Tix ORP (WTW) electrodes. Electrical conductivity was measured using a device - WTW LF90. The parameters pH, TDS and Eh were measured at certain points of the laboratory installation. At the same test points, the concentrations of sulphates were determined spectrophotometrically by $BaCl_2$ reagent at a wavelength of 420 nm and hydrogen sulfide by using test 1-88 / 05.09 of "Nanocolor" at a wavelength of 620 nm.

The electrical parameters of the fuel cell were measured with a digital multimeter type - Keithley 175, and a precision potentiometer with a maximum value of 11 kΩ was used for the load resistance (consumer). The maximum value of power P_{max} was measured by plotting polarization curves for each of the averaged variants. Using a controller type NI SensorDAQ^R (DAQ Board) and software based on the virtual tools of LabView^R, the parameters were monitored - pH, T, Electrical conductivity, OCV and P_{max}. To provide an external voltage source, a stabilized adjustable rectifier model PS-3005D was used when operating the BES in microbial electrolysis cell (MEC) mode.

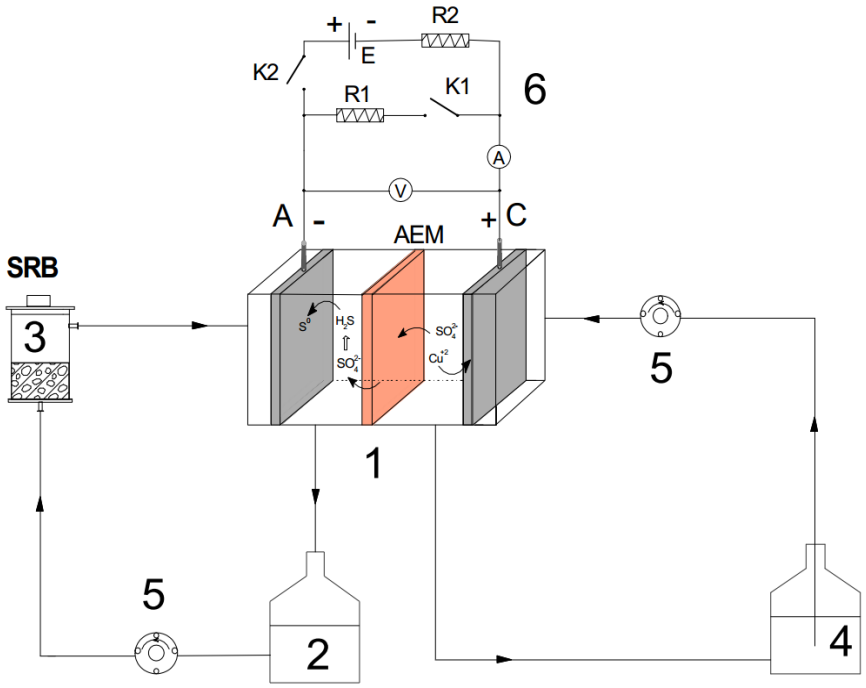

***FIG. 3**. Technological scheme of the laboratory installation under Variant 2*
1 - MEC, 2 - Buffer tank (nutrient medium for SRB), 3 - bioreactor for sulfate-reducing bacteria, 4 - Buffer tank (solution of $CuSO_4$), 5 - recirculation pumps, 6-load circuit of MEC / MFC.

Results and discussion

The expected results from variant 1 (Fig. 2) were directed to studies for desalination of model solutions in two-chamber microbial fuel cells (MFCs) based on the MSR process, with an anion exchange membrane. The studies were performed under static conditions, compensating for evaporation losses in the system at room temperature (22-24^{o}C). The volumes of the recirculation solutions in the cathode and anode chambers, together with the buffer vessels, were the same - 600 ml each. The results of 10 days of operation of the fuel element are presented in table 1 and 2.

***Table. 1.** Basic technological parameters in the anode zone of MFC in variant 1.*

Day	SO_4, mg/l	pH	EC, mS/cm	Eh, mV	H_2S, mg/l	PO, mg/l
1	1995	7,25	3,61	-375	220	521
4	468	7,49	3,47	-425	145	111
7	232	7,71	3,32	-245	61	53
10	195	7.85	3,27	-235	44	33

EC-conductivity, Eh-redox potential, PO-permanganate oxidizability.

***Table. 2**. Main technological parameters in the cathode zone of MFC in variant 1.*

Day	SO_4, mg/l	pH	EC, mS/cm	Eh, mV	Cu, mg/l
1	1995	2,38	3,19	355	1045
4	1869	2,62	3,08	340	1035
7	1492	3,04	2,20	291	1011
10	1351	3.35	2.01	277	997
%	32,2%	-	36,9%	-	4,6%

The obtained results show a decrease in the concentration of sulfates in both the anode and cathode zones of BFC for a period of 10 days, due to the ongoing process of microbial sulfate reduction in the anode zone and the transfer of sulfate ions through the anion exchange membrane (AEM) of BFC. The same trend is established with regard to the electrical conductivity of the medium in the anode and cathode zones (Tables 1 and 2), which confirms the conclusion that, in this variant of sulfide microbial fuel cell with anion exchange membrane, it is possible to treat wastewater with high sulfate concentrations. Regarding the presented values of Eh, the concentration of copper ions in the cathode zone and H_2S, permanganate oxidizability in the anode, it can be said that they are logical and support the obtained results.

In the studies performed, the concentration of sulfates in the anode zone decreased by about 90.1% (due to the MSR process), while in the cathode zone the decrease in the sulfate concentration was 32.2% (due to the mass transfer of SO_4 across the membrane) in period of 10 days. Here, a significantly higher rate of MSR in the anode zone can be noted from the process of mass transfer of sulfates from the cathode zone through the AEM membrane. The decrease in the concentration of copper ions in the cathode zone is only about 4.6%.

In the studies performed in a laboratory installation - variant 2 (Fig. 3), efforts were focused on comparing the performance of a two-chamber microbial fuel cell (MFC) and a microbial electrolysis cell (MEC). These studies were performed in view of the results obtained in the previous 1 variant. The used construction of the fuel element (in variant 2) was optimized in terms of area of the membrane and the electrodes, as for the cathode and anode the same graphite plates with dimensions - 100x100x6 mm and anion exchange membrane with dimensions 100x100 mm were used. The bioelectrochemical system was tested in 2 operating modes - in microbial fuel cell mode (MFC) with a load resistance of 200Ω and in microbial electrolysis cell mode (MEC), by applying a constant external voltage of 0.8V in the load circuit of the cell (figure 3). In these experiments, the possibility of On-line monitoring of temperature, pH and electrical conductivity values in both chambers of the cell was provided using Vernier^R BTA sensors and visualization and recording of data via the LabQuest^R interface.

Table. 3. *Values of the main technological parameters of the fuel cell in microbial electrolysis cell (MEC) mode in variant 2.*

Anode zone					
Day	SO_4, mg/l	pH	EC, mS/cm	Eh, mV	H_2S, mg/l
1	660	7,26	3,55	-385	330
5	277	7,55	3,47	-336	110
10	190	7.89	3,33	-244	35
%	71,2%	-	6,2%	-	-
Cathode zone					
Day	SO_4, mg/l	pH	EC, mS/cm	Eh, mV	Cu, mg/l
1	3964	4,02	6,19	364	1984
5	3012	4,25	5,55	325	1540
10	2564	4,62	4,91	281	1233
%	35,2%	-	20,7%	-	37,1%

The experiment was performed under static conditions, as the used technological solutions and nutrient medium for CRB were - respectively for the cathode zone - 4g / l SO_4 and 2g / l Cu and in the anode zone - 1g / l SO_4 (modified medium for CRB). The results obtained are presented in Table 3, measuring sulfate concentration, pH, electrical conductivity, Eh, Cu and H_2S concentrations.

The analysis of the obtained results (Table 3) shows a significant improvement in the efficiency of the bioelectrochemical system (BES), in the mode of operation as a microbial electrolysis cell (MEC) compared to the mode of operation as a microbial fuel cell (MFC). Evidence of this is the higher rates of sulphate removal in the cathode zone of up to 35.2% in MEC compared to 32.2% in the MFC options over a period of 10 days. Even more convincing are the results obtained with regard to the reduction of the concentration of copper ions in the cathode zone, where in the MEC variant (variant 2) it reaches 37.1%, compared to 4.6% in the MFC variant 1 - for a period of ten days.

On the other hand, the optimization of the design of the bioelectrochemical system, in terms of electrode area and anion exchange membrane compared to variant 1 also contributed to improving the efficiency of the system. This is more true for the removal of copper ions in the cathode zone where from 5% (in variant 1), the same increased to 37%, while for sulfates also in the cathode zone the increase is insignificant - from 32.2% (in variant 1) up to 35.1% (in variant 2). Another important result to keep in mind is the reduction of electrical conductivity in both variants - 36.9% (variant 1) and 20.7% (variant 2), respectively. These technologies can also be used to desalinate wastewater.

Conclusion

A new concept for the application of microbial fuel / electrolysis cells based on the process of dissimilative microbial sulfate reduction for the treatment of acid mine waters has been proposed. The values of the main technological parameters - pH, ORP, concentration of sulfates and Cu, H_2S, electrical conductivity, etc. are established during the operation of the fuel / electrolysis cells. The obtained results are the basis for the development of a fundamentally new technology for the treatment of wastewater from the mining industry with a high content of sulfates. For practical application of the technology it is necessary to make additional studies with real mine wastewater.

So far in the world practice there is no information about the possibility of treatment of mine wastewater through integrated MEC / MFC. In this sense the current research will make a significant contribution in this direction. The study and control of the ongoing chemical, electrochemical and biological processes in the technological schemes applied in both active and passive water treatment will lead to effective water purification from high concentrations of sulfates, as well as to the production of recoverable sludges containing various target metals and elemental sulfur.

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