The impact of pesticides on the electrogenic activity of the sludge in microbial fuel cells

G O Zhdanova¹, M Yu Tolstoy², A B Kupchinsky³ and D I Stom¹,²,³

¹ Irkutsk State University, Irkutsk, Lenin Street, 3, Russia
² Irkutsk National Research Technical University, Irkutsk, Lermontov Street 83, Russia
³ Baikal Museum of the ISC, Listvyanka, Akademicheskaya Street, 1A, Russia

E-mail: stomd@mail.ru

Abstract. The influence of Gezagard herbicide (active ingredient – promethrin, 500 g / l) and fungicide Kolosal (active principle – tebuconazole 250 g / l) on the dynamics of electrical indicators of microbial fuel cells (MFC) with activated sludge treatment plants as a bioagent was studied. It was shown that the tested pollutants reduced the electrogenic activity of sludge in MFC when the content in wastewater was from 0.1 g / l. The studied toxicants in the indicated concentrations significantly inhibited the dehydrogenase activity of the sludge microorganisms and the total microbial number. At the same time, the Kolosal fungicide had a more pronounced negative effect on all the studied parameters than the Gezagard herbicide. There is a positive relationship between the results of evaluating the electrogenic activity of sludge and such classical methods of its analysis as dehydrogenase activity and the total microbial number. This suggests that the ability of the sludge to generate an electric current in MFC can be used as one of the parameters for assessing its physiological state. In addition, in the case of a mono-composition of pollutants, MFC with activated sludge can be used as a tool for the initial non-specific assessment of wastewater pollution by pesticides.

1. Introduction

Once in the environment, pesticides are able to persist and accumulate in the components of the ecosystem [1]. Moreover, in the case of persistent pesticides, their concentrations increase when moving along trophic chains [2]. This ability determines their high biological hazard to natural environments. Pesticides can be part of the wastewater of agricultural enterprises and settlements related to crop production. In this regard, they can have a negative impact on the processes of biological treatment of effluents. A negative role can also be played by these components when using sludge as a bioagent in biological wastewater treatment processes using MFC technology. The aim of the work was to study the influence of Gezagard and Kolosal pesticides on the electrogenic activity of microorganisms of activated sludge in MFC.

2. Materials and research methods

The activated sludge of sewage treatment facilities on the right bank of the Angara River in Irkutsk was used as a bioagent in MFC. To maintain activated sludge in a viable state under laboratory conditions, it was incubated in plastic containers at room temperature, aerating using Dezzie D-044 aerators (China). Glucose was added daily (0.5 g / l once a day). Generation of electric current by activated sludge was investigated in two-chamber MFCs. The design and methodology of assembling,
staging and fixing electrical indicators of MFCs is described in [3]. The change in the electrogenic activity of sludge was evaluated under the influence of the Kolosal fungicide (active ingredient – tebuconazole 250 g / l) and the Gezagard herbicide (active substance – promethrin, 500 g / l). Pesticides were added to the MFC anolyte at concentrations of 0.1 and 1 ml / l. MFC without the addition of pollutants was taken as a control. Peptone (0.15 g / l) served as a substrate for feeding silt microorganisms and an electron donor in the MFC anolyte. The catholyte in MFC was model wastewater. Its composition (mg / l): sodium carbonate 50.0; potassium phosphoric acid monosubstituted 25.0; ammonium phosphoric disubstituted 25.0; calcium chloride 7.5; magnesium sulfate 5.0 (GOST R 50595 - 1993). In parallel with measuring the electrical parameters of MFCs, the total microbial number of sludge microorganisms (Koch method) and their dehydrogenase activity (for the recovery of 2,3,5-triphenyltetrazole chloride) were periodically evaluated in the experiment [4, 5]. Samples of the contents of the anode space of the MFC were sampled using a sterile syringe through a special rubber plug in the side of the MFC [3]. Statistical processing of experimental data was carried out using the Microsoft Office software package. All experiments were carried out in at least 5 independent experiments with 3 parallel measurements in each. Conclusions are made when the probability of an error-free forecast is P ≥ 0.95.

3. Results and discussions

The experiments showed that the Kolosal pesticide, starting from a concentration of 0.1 g / l, reduced the sludge performance in MFC. The voltage generated in 4 days was 705 mV. While in MFC without the addition of pesticides, this indicator increased to 843 mV. An even greater negative effect was noted with an increase in the concentration of the pesticide to 1 g / l. The generated EMF was only 230 mV (Fig. 1).

Figure 1. The influence of the Kolosal pesticide on the dynamics of the voltage generated in MFC by activated sludge using peptone (electrodes – carbon cloth, substrate – peptone 0.5 g / l, pesticide concentrations – 0.1 and 1 g / l).

A similar trend was noted when measuring the current strength in the experiment (Fig. 2). Gezagard pesticide also caused a decrease in the electrogenic activity of sludge in MFC. However, the negative effect was less than in experiments with the Kolosal pesticide. The introduction of “Gezagard” in concentrations of 0.1 and 1 g / l led to a slight decrease in the generated potential. It was only 160-170 mV lower than in the control MFC. For example, in MFC with the addition of 0.1 g / l pesticide, the voltage for 4 days of incubation increased to 684 mV, 1 g / l to 681 mV. At the same time, in the control MFC without the addition of pesticides, this indicator reached 843 mV (Fig. 3).
A more pronounced negative effect was revealed when measuring the current strength in the studied MFCs. So, in a fuel cell with the addition of 0.1 g/l, the current strength for 4 days of the experiment increased to 991 μA, 1 g/l – 756 μA. This was lower than the similar indicator (1394 μA) generated by sludge without adding a pesticide, in 1.4 and 1.8 times, respectively (Fig. 4).

Figure 2. The influence of the Kolosal pesticide on the dynamics of the current generated in MFC by activated sludge using peptone (electrodes – carbon cloth, substrate – peptone 0.5 g/l, pesticide concentrations – 0.1 and 1 g/l).

Figure 3. The influence of the Gezagard pesticide on the dynamics of the voltage generated in MFC by activated sludge using peptone (electrodes – carbon cloth, substrate – peptone 0.5 g/l, pesticide concentrations – 0.1 and 1 g/l).
The influence of the Gezagard pesticide on the dynamics of the current strength generated in MFC by activated sludge (electrodes – carbon cloth, substrate – peptone 0.5 g / l, pesticide concentrations – 0.1 and 1 g / l).

Figure 4.

Determination of the total microbial number of activated sludge after 5 days of its work in MFC showed the following. In the studied concentrations (0.1 and 1.0 g / l), Kolosal had a negative effect on the growth of cells of activated sludge microorganisms. This pesticide at a concentration of 0.1 g / l reduced the number of viable cells of sludge microorganisms by 10 times (relative to the control), 1.0 g / l – 13 times (Fig. 5).

Figure 5.

Gezagard pesticide had less impact than Kolosal. At a concentration of 0.1 g / l, it did not reduce the viability of microorganisms of activated sludge after 5 days of incubation in MFC. A negative effect was noted with the addition of 1.0 g / l of this drug. The number of viable cells (1.68 ± 0.10 · 10^8 CFU / ml) was 2 times lower than the control (2.19 ± 0.34 · 10^8 CFU / ml) (see Fig. 5).

In parallel, the dehydrogenase activity of sludge was evaluated after 5 days of incubation in MFC. Both pesticides significantly reduced the studied enzymatic activity. At the same time, Kolosal was also more toxic. At a concentration of 0.1 g / l, he reduced the test parameter by 6.8 times relative to the control. And at 1.0 g / l – completely inhibited the activity of dehydrogenases. The addition of the...
Gezagard pesticide at a concentration of 0.1 g / L led to a decrease in the dehydrogenase activity of sludge by 2.5 times, 1.0 g / L – by 8.2 times (Fig. 6).

4. Conclusion
The use of activated sludge as a bioagent in MFC is a promising area of research, since it will allow combining efficient wastewater treatment with the simultaneous generation of electricity, as well as having a cheap, highly effective bioagent with a wide spectrum of substrate specificity and the ability to effectively compete with extraneous microflora.

One of the factors determining the state of activated sludge and the degree of water purification are toxic substances of wastewater. These components can also play a negative role when using sludge as a bioagent in MFC.

The tested pesticides "Kolosal" and "Gezagard" reduced the electrogenic activity of sludge in MFC when the content in wastewater was from 0.1 g / l. At the same time, the Kolosal fungicide had a more pronounced negative effect on all the studied parameters than the Gezagard herbicide. The higher toxicity of Kolosal compared to Gezagard was previously shown by us on other test objects [6]. At the indicated concentrations, the tested pesticides also significantly inhibited the dehydrogenase activity of sludge microorganisms and had a negative effect on the number of viable cells of microorganisms in it. The results obtained suggest a positive correlation between the electrogenic activity of sludge in MFC and its parameters such as the number of viable cells of microorganisms and dehydrogenase activity. The dependence of the electrical parameters of MFC with sludge on the concentration of a toxicant present in wastewater allows an express assessment of the degree of danger of wastewater entering the wastewater treatment using MFC.

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Reference
[1] Carvalho F P 2017 Pesticides, environment, and food safety Food and Energy Security 6(2) pp 48–60
[2] Brodeura J C, Sanchez M, Castro L, Rojas D E, Cristos D, Damonte M J, Poliserpi M B, D’Andrea M F and Andriulo A E 2017 Accumulation of current-use pesticides, cholinesterase
inhibition and reduced body condition in juvenile one-sided livebearer fish (Jenynsia multidentata) from the agricultural Pampa region of Argentina *Chemosphere* **185** pp 36–46

[3] Stom D I, Zhdanova G O and Kashevskii A V 2017 New designs of biofuel cells and testing of their work *IOP Conference Series: Materials Science and Engineering* **262** 012219

[4] Miksch K 1985 Selection of the optimum methodology to determine the activity of activated sludge with the help of TTC tests (Auswahl einer optimalen Methodik für die Aktivitätsbestimmung des Belebtschlammes mit Hilfe des TTC-Tests) *VomWasser* **64** pp 187–198.

[5] Guidelines for the determination of dehydrogenase activity during technological monitoring of the operation of aeration tanks 1978 (Moscow: Ministry of Housing and Communal Services of the RSFSR, Academy of Public Utilities named after K.D. Pamfilova)

[6] Vyatchina O F, Zhdanova G O, Stom D I and Khamaganova E R 2015 Assessment of pesticide toxicity using Saccharomyces cerevisiae *In the World of Scientific Discoveries* **12.2 (72)** pp 397–409