ENERGY EFFICIENCY OF AN ELECTROCHEMICAL FUEL CELL FOR TREATMENT OF WASTEWATERS, CONTAMINATED WITH SULPHIDES AND NITRATES

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Abstract

This study is an attempt for simultaneous removal of sulphates and nitrates from municipal, agricultural and industrial wastewaters by oxidation of the sulphides to sulphates and reduction of the nitrates to nitrogen in electrochemical way. The processes are carried out in newly designed fuel cells and as a result energy is released which can be used. The aim of the work is to improve the energy efficiency of the fuel cell by minimizing internal losses by optimizing the material, design and position of the electrodes.

Key words: *fuel cell, wastewater treatment, oxidation of sulphides, reduction of nitrates*

1. INTRODUCTION

With the rise of living standards and the development of industry and technology worldwide, the quantities of wastewaters have increased on an annual basis. At the same time the requirements for treatment of the wastewaters before releasing it into the environment are increasing. On the other hand the energy consumption is constantly increasing, which makes the problem of the development of new, clean energy sources even more important.

One of the most common and at the same time highly toxic and dangerous for living organisms are wastewaters, contaminated with sulphides. Due to their high chemical reactivity, they cause corrosion of metal and concrete pipes and equipment.

The main sources of sulphide pollution are the petroleum industry, the coal gasification, the natural gas industry, the production of viscose rayon, cellulose processing by the Kraft method and others. In nature sulphides are accumulated due to natural processes in closed ponds or sewage systems through decomposition of sulphur containing organic matter by sulphate reducing bacteria in anaerobic conditions, by volcanic gases and in some natural mineral waters. Due to some geographic and tectonic features, the Black Sea is a huge natural reservoir for hydrogen sulfide, which gradually fills and constitutes a serious environmental danger in the region.

Methods for treatment of sulphides from wastewaters can be divided *on* into physical, chemical, electro-chemical and biological. Among the most common processes are adsorption and absorption. They can also be combined with oxidation processes – with air (Cotrino et al. (2007), Seredych & Bandosz (2007), Yasyerli et al. (2002), Wang (2003)), with strong oxidizing agents (Tomar & Abdullah (1994)), biological oxidation (Kodama & Watanabe (2003)) or precipitation with metals (Henze et al. (1997)). Methods for thermal and electrochemical decomposition and oxidation (Gerçe et al. (2008), Zaman & Chakma, (1995), Yourong et al. (2001)) are also developed. The most well-explored and applied method is the Claus process (Capone (1997)), which is extremely energy intensive and requires expensive catalysts.

Studies in recent years show the possibilities for the use of sulphides as an alternative fuel in fuel cells (Zhai et al. (2012), Kim & Han (2014), Dutta et al.(2008)), as well as energy source in microbiological fuel cells*(Lee et al. (2012), Cai & Zheng, (2013)).* With a view to increase energy efficiency of the fuel cell, the sulfides are converted into sulphate ions instead into elemental sulfur, like it is in most of used in purification processes. This allows the products to be released into the environment because sulphate ions are present in natural water sources and are harmless in a wide range of concentrations.

Nitrates are identified as one of the dangerous pollutants in waters. Sources of wastewaters contaminated with nitrates are animal farms, households, greenhouses, petroleum industry and others.

The removal of nitrate ions from the effluent is accomplished by two sets of processes – physicochemical and biological. Generally, conventional processes include: reverse osmosis, ion exchange, electro-dialysis and adsorption with activated carbon with pH adjustment. These methods are expensive and inefficient because they do not reach the limit values for nitrates or emit other harmful and even dangerous byproducts. These disadvantages are the reasons for their limited use.

Chemical and microbial fuel cells represent a new and modern approach to the removal and disposal of these and other pollutants produced naturally or due to human activity and generate energy at the same time (Zhai et al. (2012), Cai & Zheng (2013), Demirbas (2009), Beschkov et al. (2015)).

Our team has previous studies in which we designed sulphide driven fuel cell that operates with the sulphides from the Black Sea deep waters (Razkazova-Velkova et al. (2013a, 2013b, 2014, 2015), Martinov et al. (2013, 2014). The aim of this study is to adapt the design of the fuel cell for operation on the basis of oxidation of sulfides in the anode compartment and the reduction of the nitrates in the cathode one, as well as simultaneously gaining electrical energy and solving environmental problems all at the same time. The milestones in the process for creating such a fuel cell are the choices of optimal design of the fuel cell and effective electrodes for minimizing the internal losses.

2. RESULTS AND DISCUSION

2.1. Design of sulfide driven fuel cell

A scheme of sulphide driven fuel cell is presented on Fig. 1.

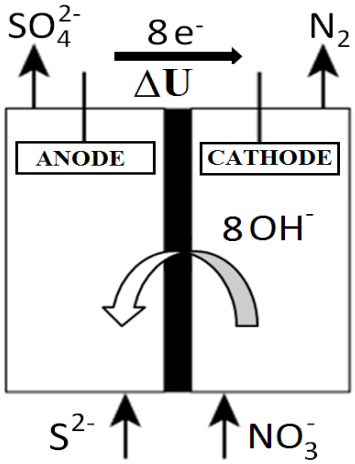


Fig.1 Scheme of the fuel cell

The desired target reactions in this case are as follows:

Anode: $S^{2-} + 6OH^- = SO_3^{2-} + 3H_2O + 6e^-$

$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$

Net anode reaction: $S^{2-} + 8OH^- = SO_4^{2-} + 4H_2O + 8e^-$

Cathode: $NO_3^- + H_2O + 3e^- = NO_2^- + 2OH^-$;

$NO_2^- + 2H_2O + 2e^- = 1/2N_2 + 4OH^-$

Net cathode reaction: $NO_3^- + 3\ H_2O + 5e^- = 1/2N_2 + 6OH^-$

The above reactions show that the 8 electrons generated in the anode compartment are more than (in excess of) the 5 required for the reactions in the cathode one. To avoid that imbalance the experiments were carried out at an approximate ratio of sulphide to nitrate ions 5:8.

The fuel cell is composed of an anode compartment (AC), wherein the sulphides are oxidized and a cathode compartment (CC), wherein the nitrates are reduced, spatially separated by ion exchanging membrane. The specific design of the fuel cell is shown in Fig. 2.

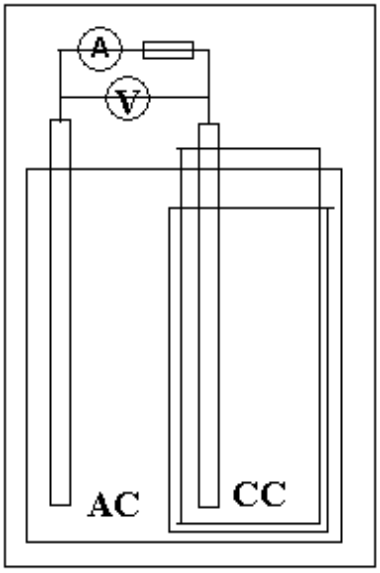


Fig. 2. Design of the fuel cell

The two compartments of the fuel cell are cylinders of different diameters (0.08 m and 0.1 m) arranged concentrically one inside the other. The membrane - Celgard 3501 (OH^- exchange membrane with a working surface of 0.02 m^2) is placed on the bottom of the cathode compartment.

In our previous work (Razkazova-Velkova et al. (2013 b)) different shapes (discs, plates, rods, bands), size and material (steel, copper, aluminum, graphite rods and pyrolyzed carbon wadding) of the electrodes were studied. Graphite rods with dimensions of 0.006/0.2 m (fig 3) and bands from carbon wadding with dimensions of 0.05x0.1 m (Fig 4) as optimal electrodes were selected. To increase the electrode surface in the CC for some of the experiments 120 g activated carbon is added (Fujikasau, Japan, 680 $m^2.g^{-1}$). Another feature of the activated carbon is its ability to catalyze the nitrate reduction (Bahri et al (2013)).



Fig.3 Graphite rods



Fig.4 Bands from carbon wadding

2.2. Electrodes in cathode compartment

Experiments are carried out with carbon wadding with working surface of 0.01 m^2 as electrode in the anode compartment and different quantities (0, 40, 80, 120 g) of activated carbon (Fujikasau, Japan, 680 $m^2.g^{-1}$.) as electrode (respectively with different working surface of the electrode) in the cathode compartment. A comparison of the levels of power and voltage as a function of current loading is shown in Fig. 5 and Fig. 6.

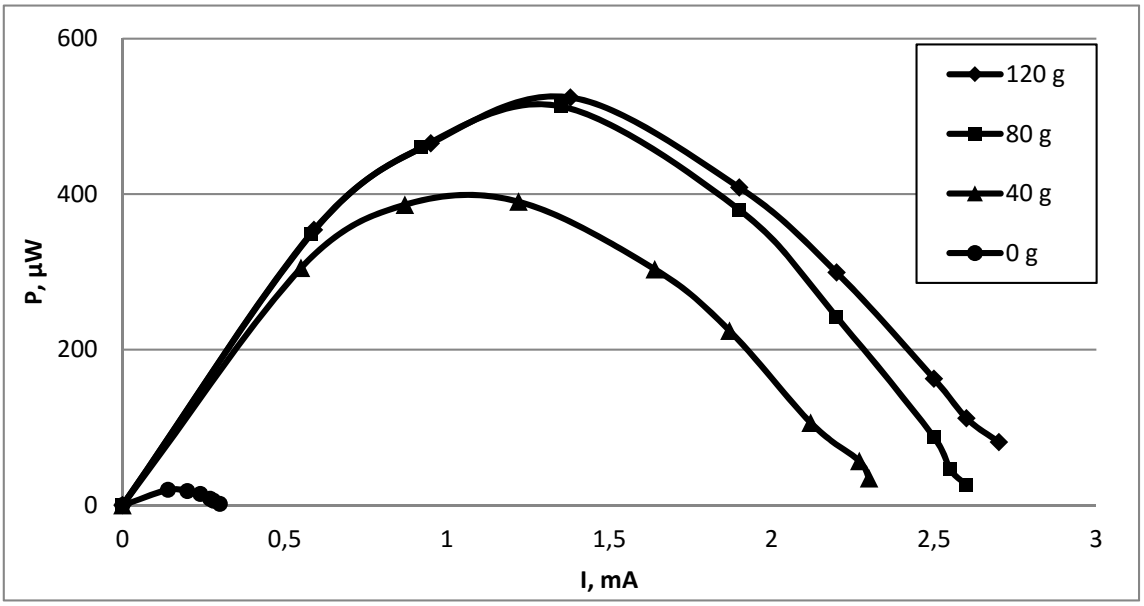


Fig. 5 Comparison of levels of power as a function of current loading of the fuel cell for different quantities of *activated* carbon

Fig. 6 shows the difference in internal resistance of the cell, which decreases (from 757 to 280 Ω) with the change of the work surface of the electrodes. As shown in the Fig. 5 and Fig. 6, electrodes with maximum quantity of activated carbon, respectively maximum working surface of the electrode, give about 25 times higher levels of power, 3-fold higher levels of voltage and endure 10 times higher current loading of the fuel cell compared to the electrodes with no activated carbon.

2.3. Electrodes in anode compartment

Experiments with maximum quantity of activated carbon as electrode in the cathode compartment and different type (graphite rods or carbon wadding) and working surface (0.010 m^2 and 0.017 m^2) of the

electrodes in the anode compartment are carried out. A comparison of the levels of power and voltage as a function of current loading is shown in Fig. 5 and Fig. 6.

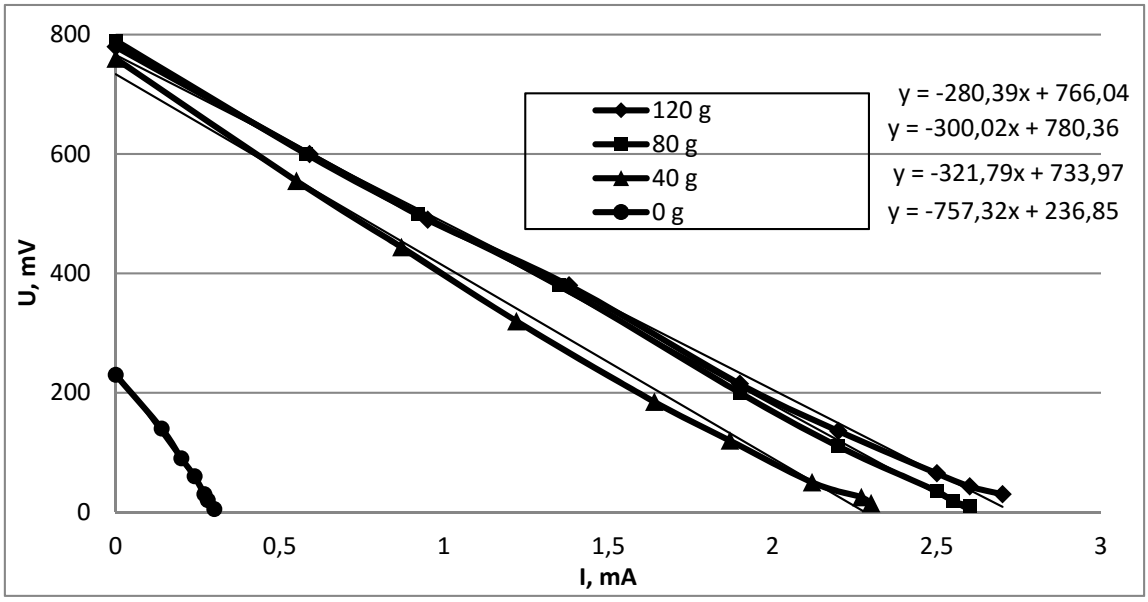


Fig. 6. Comparison of levels of voltage as a function of current loading of the fuel cell for different quantities of activated carbon

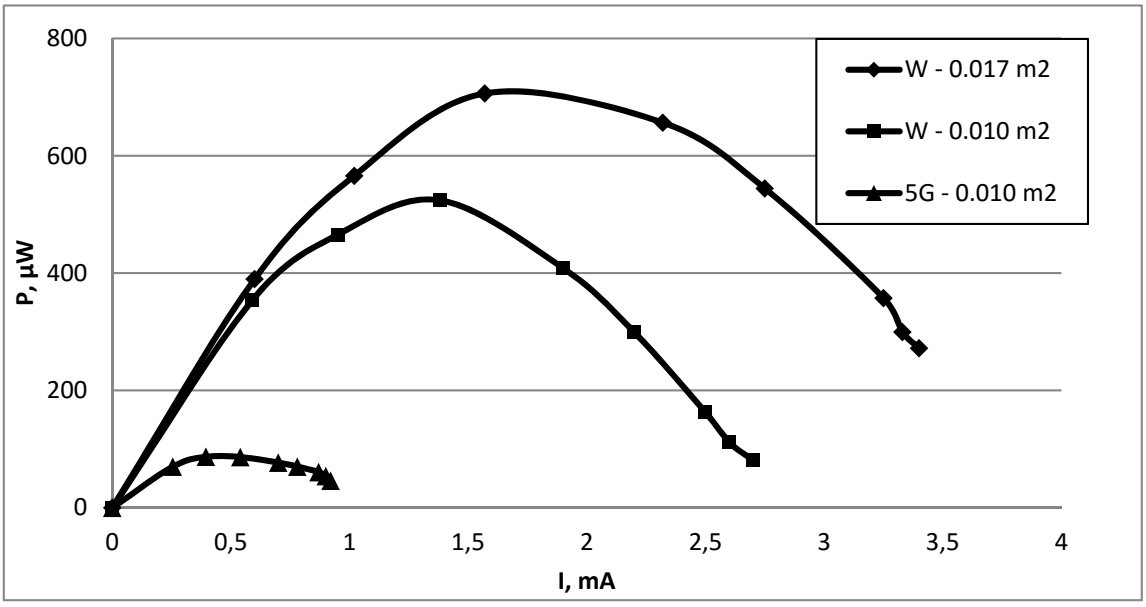


Fig. 7. Comparison of level of powers as a function of current loading of the fuel cell for different type of electrodes

In each of the figures we have a comparison of the one side of electrodes with same material and different working surface and the different material and equal surface from another side. Fig. 7. and Fig. 8 show clearly differences in the performance of the electrodes depending on the type (material) and the working surface. Electrode made of carbon wadding (with equal surface) gives about 5 times higher levels of power of the fuel cell and endure 3 times higher current loading when compared with

graphite rods. The levels of voltage produced by the fuel cell are 2-fold higher in the electrodes made of the carbon wadding compared to the graphite rods with equal working surface.

Increasing the working surface of the electrodes (made of equal material) by 70% gives an increase of up to 50% in power output, voltage and current loading.

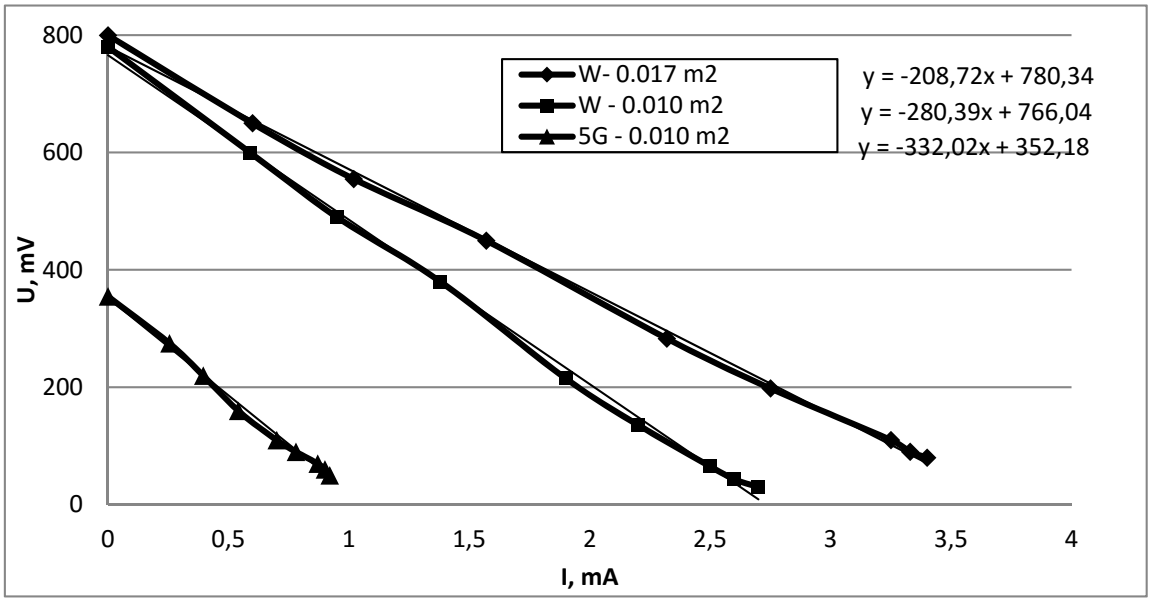


Fig. 8. Comparison of levels of voltage as a function of current loading of the fuel cell for different type of electrodes

Fig. 8 shows the difference in internal resistance of the cell, which decreases (from 382 to 208 Ω) with the change of the working surface and the material of the electrodes. As shown in the figures, the highest levels of power, voltage and current gives the configuration with the lowest internal resistance.

2.4. Influence of the optimization of the design of the electrodes on the power and depletion of the sulphides over time

Experiments with maximum quantity of activated carbon as electrode in the cathode compartment and different type (graphite rods or carbon wadding) and working surface (0.010 m^2 and 0.017 m^2) of the electrodes in the anode compartment are carried out. A comparison of the levels of power, depletion of sulphides and nitrates over time is shown in Fig. 9, Fig. 10 and Fig. 11.

In each of the figures we have a comparison of the electrodes with same material and different working surface from one side and the different material and equal surface from the other. Fig. 9, Fig. 10 and Fig. 11 show clearly differences in the performance of the electrodes depending on the material and the working surface.

In respect the energy component of the performance of the fuel cell, obtained data for energy production are represented in Fig. 9. Electrode made of carbon wadding (with equal surface) gives about 0.85 mW per hour (20 mWh per 24 h) compared to about 0.1 mW per hour (2.4 mWh per 24 h) for graphite rods electrode or 8.5 times higher levels of power of the fuel cell. Increasing the working surface (with equal material of the electrodes) by 70% gives an increase of up to 50% in power output (0.85 mW per hour (20mWh per 24 h) compared to about 1.25 mW per hour (30 mWh per 24 h)).

In respect the environmental component of the performance of the fuel cell, the data on the depletion of sulphides and nitrates are shown in Fig. 10 and Fig. 11.

A fuel cell operating with electrodes made of carbon wadding gives twice as efficient depletion of sulphides and nitrates, compared with a cell operating with graphite rods (with the same working surface).

Increasing the working surface of the electrodes (made of the same material) by 70% increases the rate of oxidation of the sulphides by up to 20% and the rate of reduction of the nitrates by up to 10%.

Despite the depletion of nitrates in the fourth hour is more of 90%, the cell continues to produce comparable energy performance for up to 24 hours. The explanation for this is that all nitrates are not reduced to nitrogen and thereby come out from the process. A large portion of the nitrates is absorbed into the activated carbon and the reduction process continues in the volume of the electrodes.

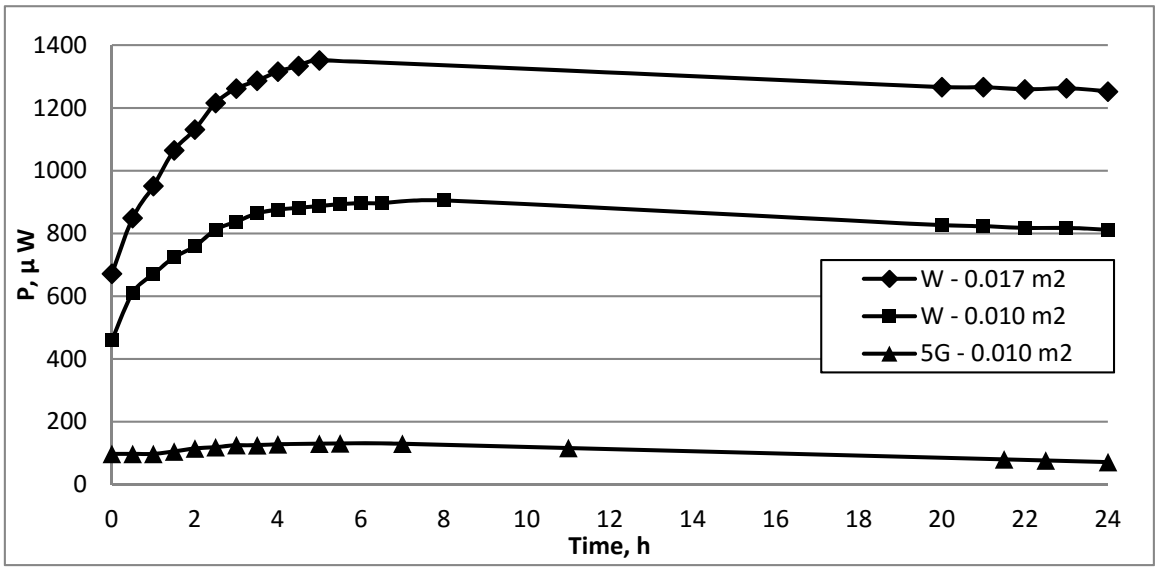


Fig. 9. Comparison of levels of power as a function of time for different types of electrodes

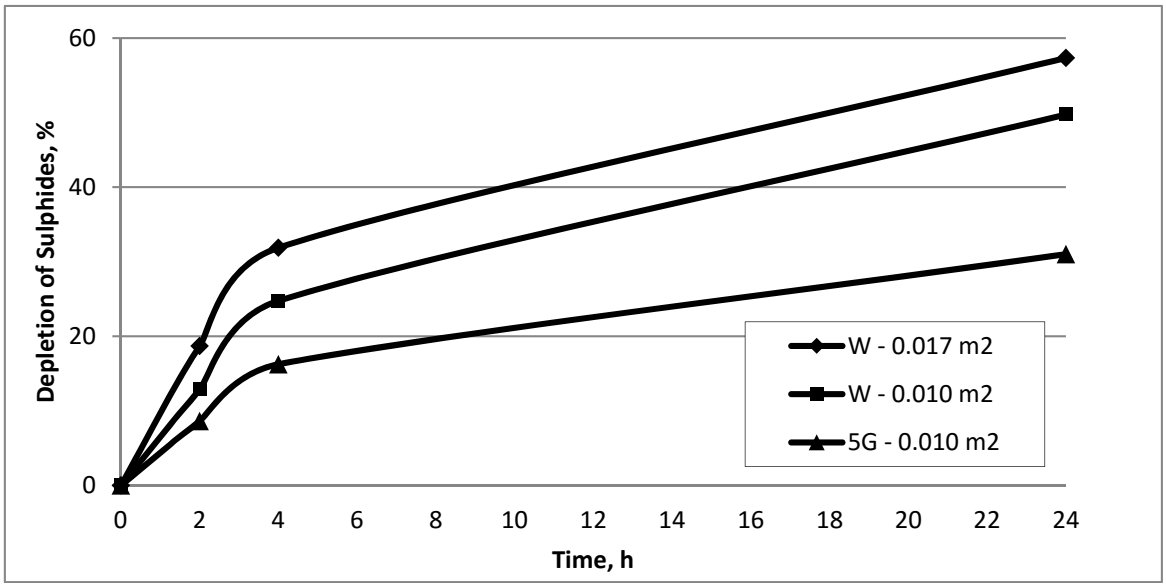


Fig. 10. Comparison of the levels of depletion of sulphides as a function of time for different types of electrodes

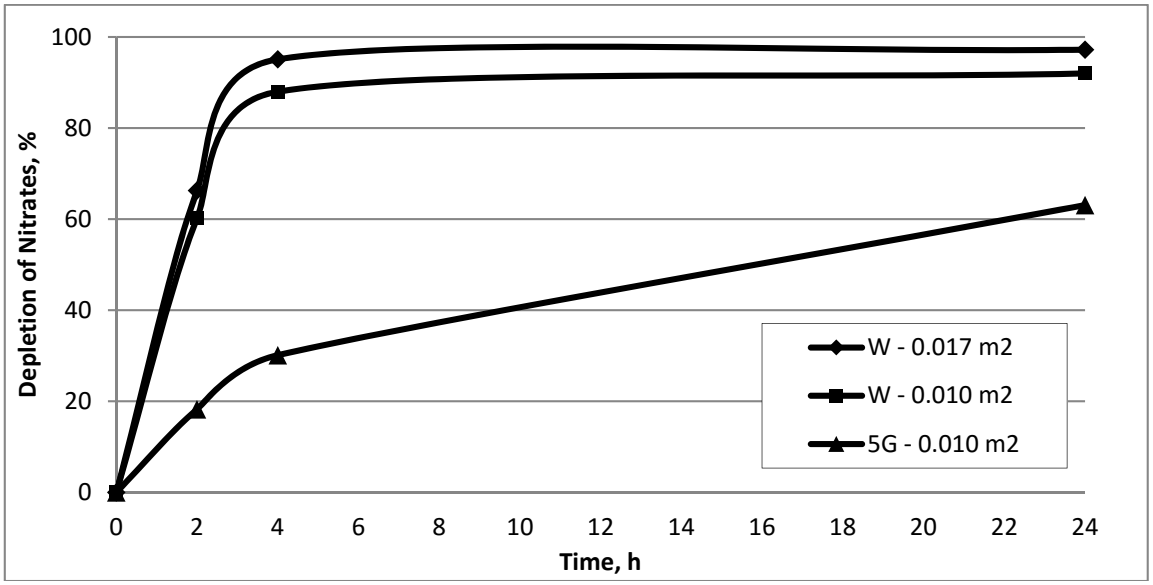


Fig. 11. Comparison of the level of depletions of nitrates as a function of time for different type of electrodes

CONCLUSION

Simultaneous removal of sulphates and nitrates from wastewaters by electrochemical way is carried out. The processes are carried out in newly designed fuel cells and as a result energy is released which can be used. Improving the energy efficiency of the fuel cell by minimizing internal losses by optimizing the material, design and position of the electrodes is done.

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