SULFIDE-NITRATE FUEL CELL FOR ENVIRONMENTAL PURPOSES: A NOVEL CARBON PADDLING ELECTRODES

M. Martinov, E. Razkazova-Velkova, S. Stefanov

Institute of Chemical Engineering, Bulgarian Academy of Sciences,
Akad. G. Bonchev str., bld. 103, 1113 Sofia, Bulgaria

Abstract

Paddlings of structured activated carbon are used as electrodes in a fuel cell for sulfide oxidation and nitrate reduction. The influence on the electrochemical parameters of multiple uses at the same conditions are investigated as well as the rates of depletion of the sulfides and nitrates. Regeneration of the used paddlings by thermal desorption is conducted and the paddlings are retested.

The obtained electrical power rapidly decreases after the first use of the paddlings and after that the power level remains relatively constant. This is due to the wash up of some active centers over its surface. The thermal desorption increases the electrical properties of the cell. The depletion of sulfides and nitrates is within the ecological limits.

A conclusion can be made that the structured activated carbon paddlings can be successfully used as electrodes for continuous operation of a sulfide-nitrite fuel cell.

Keywords: *fuel cells, structured activated carbon, electrodes, nitrates, sulfides*

1. INTRODUCTION

The growing world population puts ever-increasing production requirements on all industries. This in turn increases the hazardous wastes from those industries. Some of the more hazardous and hard to neutralize wastes are sulfide- and nitrate-contaminated wastewaters.

The origins of sulfides can be generally divided into natural and anthropogenic ones. Volcanoes, thermal spring and closed deep water basins (where sulfides are formed from sulfur containing organic matter by the sulfate reducing bacteria) can be pointed out as natural. The main anthropogenic pollution with sulfides stems from the petroleum, leather, pulp and textile industries, sewage systems and wastewater treatment plants. The conventional methods for treatment of such effluents are absorption and adsorption (that can be combined with oxidation with strong oxidants (Cotrino R. et. al., 2007; Seredych et al., 2007; Wang, 2003; Yasyerli et al., 2002; Lemley et al., 1999; Tomar et al., 1994)), precipitation with metals (Henze et al., 1997) or biological oxidation (Kodama et al., 2003). Thermal and electrical methods for decomposition are also developed (Gerçe Özgül et al., 2008; Zaman et al., 1995; Wang et al., 2001). The Claus process is classical method but it requires high temperatures and specific catalysts (Capone et al., 1997).

The origins of nitrate pollution are households, industry and agriculture. After their reduction nitrites are produced that are much more harmful for the humans' health. There are several known processes for treatment and purification of nitrate-containing waters which can be generally grouped as physico-chemical and biological. Physico-chemical methods are reverse osmosis, ion exchange, electrodialysis, distillation and active carbon absorption (Mautner et al., 2017; Bhatnagar et al., 2010; Bhatnagar et al., 2011; Shrimali et al., 2001). These methods are very expensive, especially when large quantities of wastewaters are treated and result in waters with high concentration of nitrates that can lead to additional problems concerning their reduction and treatment.

The conclusion that can be derived is that all the conventional methods for wastewater treatment of sulfide- and nitrate-containing effluents are energy consuming and have high cost for both capital investment and exploitation.

Our aim is to neutralize wastewaters containing reducers (S^{2-} ions) and oxidizers (NO_3^- ions) by using both (in the anodic and cathodic compartments respectively) in a fuel cell and thus obtain electrical energy along with the neutralization of two hazardous substances.

One way to intensify the sulfide oxidation and nitrate reduction processes is to use microorganisms, but they have stringent requirements for the pH (about 7) of the solutions used.

An important element while constructing a fuel cell is the choice of the electrodes. The suitability of the electrodes for a long service life as well as a guarantee of constancy in electrical performance is of particular importance. Different carbon materials are often used as electrodes in the fuel cells (Guo K et al., 2015; Rimboud M et al., 2014; Santoro et al, 2013; Santoro et al, 2017; Liao et al, 2015; Liu et al, 2004). Along with their positive characteristics they have a certain disadvantages such as adsorption contamination by some of the products and relatively low mechanical resistance.

The present paper aims to study the working characteristics of a structured activated carbon electrode. The reduction of the electric parameters during repeated use of the electrode has been investigated, as well as the possibility of it's regeneration.

2. MATERIALS AND METHODS

2.1. Experimental setup

The principle scheme of the fuel cell and the experimental installation are given in **Fig. 1.** It consists of two concentrically situated compartments (anodic (AC) and cathodic (CC)) with effective volume of 0.3 l each. The membrane (Fumapem®, S = 0.002 m^2, **Table 1.**) is placed on the bottom of the inner one. Continuous stirring with 300 rpm is assured in the anodic one. Both compartments of the fuel cell are equivalent and interchangeable.

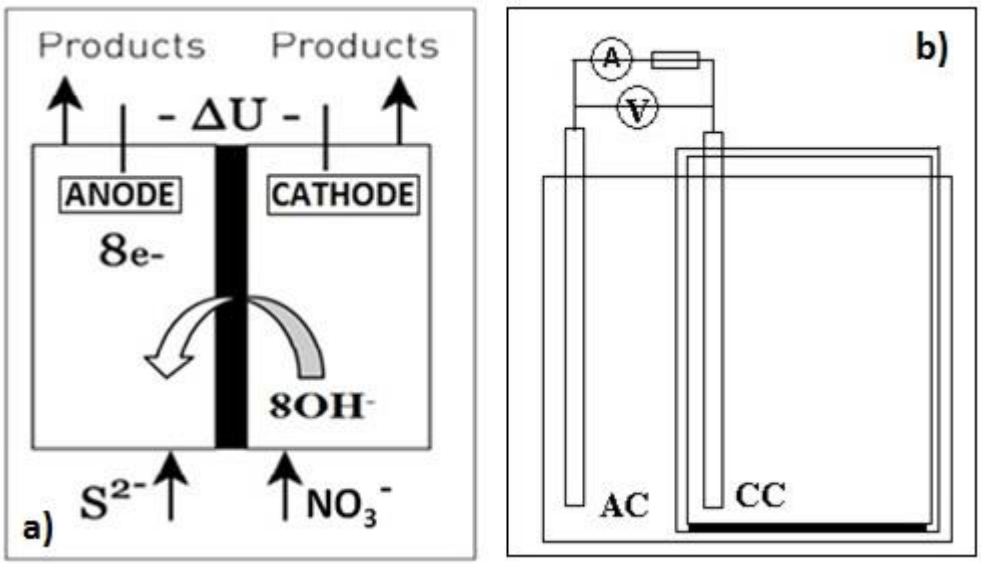

Fig. 1. Principle scheme of the sulfide-nitrate fuel cell

Membrane	Type of the membrane	Material of the membrane	Thickness, µm	El. Resist ($\Omega.cm^2$)	Purpose
Fumapem® FAA-3-PK-75 (OH form)	Anion exchange	Fumion® F Polymer	55	1.26	Separator in alkaline batteries

Table 1. Characteristics of the used membrane

The reactions are as follows:

Anode:

$S^{2-} + 6\ OH^- \rightarrow SO_3^{2-} + 3\ H_2O + 6\ e^-$

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

Total:

$S^{2-} + 8\ OH^- \rightarrow SO_4^{2-} + 4\ H_2O + 8\ e^-$

Cathode:

$2\ NO_3^- + 2\ H_2O + 4\ e^- \rightarrow 2\ NO_2^- + 4\ OH^-$

$2\ NO_2^- + 4\ H_2O + 6\ e^- \rightarrow N_2 + 8\ OH^-$

Total:

$2\ NO_3^- + 6\ H_2O + 10\ e^- \rightarrow N_2 + 12\ OH^-$

Pyrolyzed activated paddlings with surface area of 0.015 m^2 are used as electrodes in both compartments. The paddlings are prepared by a patented technology (Ljutzkanov et al., 2002) – pyrolyzation with simultaneous activation. **Fig. 2.** shows a SEM image of the activated paddling.

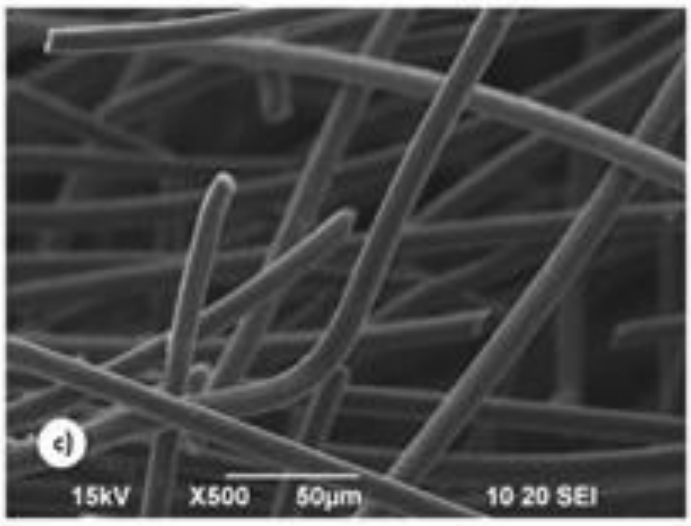

Fig. 2. SEM image of the activated paddling

2.2. Analytical procedures

The initial concentration of sulfides is determined photometrically by converting the sulfide ion to methylene blue by the addition of N,N-p-phenylen dymethyl diamine (Rees et al., 1971). Instead of using N,N-p-phenylen dymethyl diamine N,N- p-phenylen dyethyl diamine is used as it is proven to be more sensitive to S^{2-} ions. The measurement is conducted via VWR® UV-1600 PC spectrophotometer at $\lambda = 667$ nm.

The concentration of nitrates is determined by UV-spectrophotometry (Goldman and Jacobs, 1961). Appropriate volume of the sample is diluted to 50 ml and 1 ml of 1N HCl is added. The absorption of the sample is measured at $\lambda = 220$ nm. To avoid the interference of dissolved organic substances the absorbance of the samples is also measured at $\lambda = 275$ nm. Corrected absorption of nitrate sample (A_{corr}) is calculated using the following equation:

$$A_{corr} = A_{220nm} - 2*A_{275nm}$$

2.3. Experimental procedure

The external resistance is varied (1 – 1000 Ω) and the electrical parameters are measured. After linearization of the curve voltage vs current information about the internal resistance of the cell is obtained.

The exploitation characteristics of the cell are investigated at external resistance of 100 Ω by monitoring of the obtained voltage and current. The depletion of the pollutants is also observed.

Three sets of experiments are carried out (all sets of experiments are carried out with concentration of 500 mg/l for both pollutants):

1. Three consecutive experiments at the same conditions. They are conducted in order to estimate the decrease of the electrical parameters due to accumulation of part of the products into the electrodes, as well as to determine the mechanical stability of the pyrolyzed paddlings;
2. Experiments with regeneration of the paddling by thermal desorption of both compartments;
3. Experiments with regeneration of the anodic paddling by thermal desorption.

3. RESULTS AND DISCUSSION

3.1. Results for continuous use of the electrodes

Fig. 3. presents the obtained power as a function of the current for the initial three consecutive experiments. As shown the electrical parameters constantly decrease comparing each consecutive experiment. The most sudden drop-down of the electrical parameters is after the first use of the brand new paddlings. The electrical power is 2-3 times higher than that of the following experiments. Next figure (**Fig. 4.**) is more representative – it shows that the open circuit voltage is 35 % to 50 % higher for the first use of the electrode. **Fig. 5.** represents the obtained power as a function of time. As is the case of the previous figures the obtained power decreases with each consecutive experiment. The delay in maximum power output of the fuel cell is due to additional diffusion resistance of the paddlings – during the first hour additional substances enter the inner parts of the paddlings and provide additional reactants at the electrode surface.

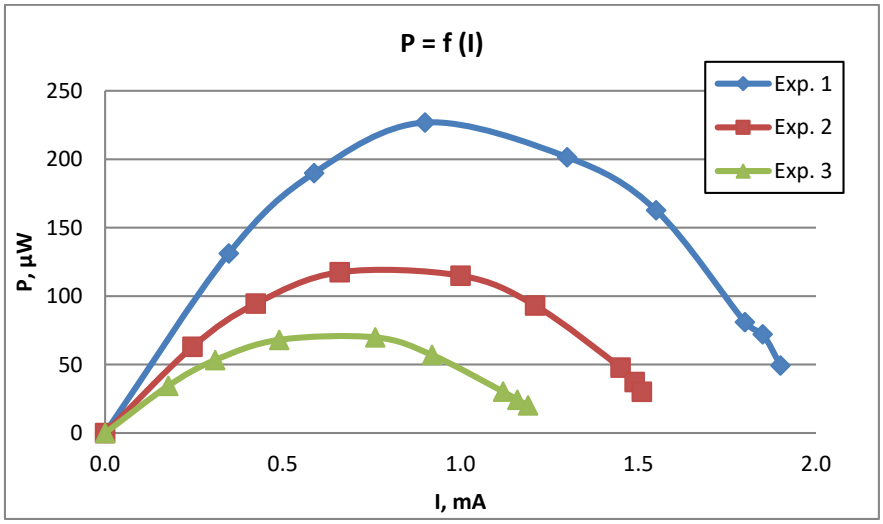

Fig. 3. Power as a function of the current

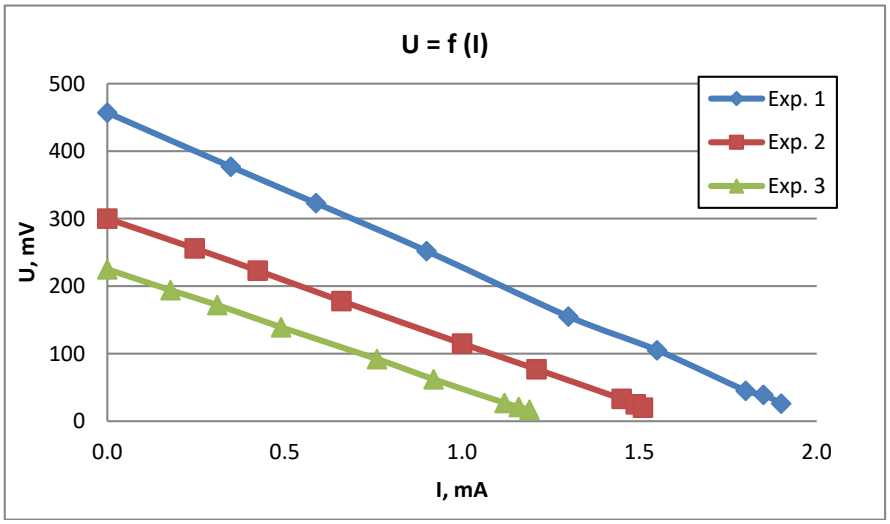

Fig. 4. Voltage as a function of the current

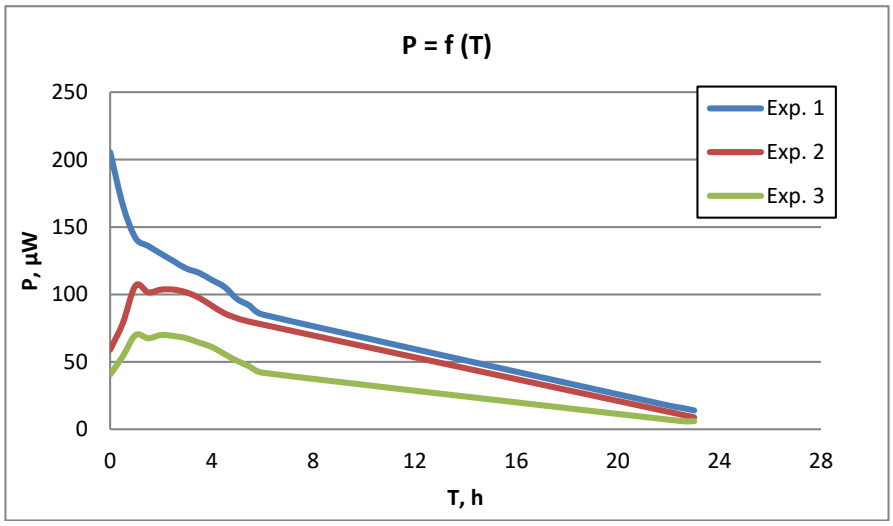

Fig. 5. Power as a function of time

The depletion of the components (**Fig. 6.** for sulfides and **Fig. 7.** for nitrates) follows the same tendency established from the previous figures, although the differences are not so radical. This can be explained with oxidation-reduction processes not on the surface of the electrodes (oxidation of sulfides in the volume of the solution) that does not lead to an increase of the obtained power. Although differences in the obtained power and the depletion are substantial, the internal resistance of the fuel cell is relatively constant (180 Ω ± 5%).

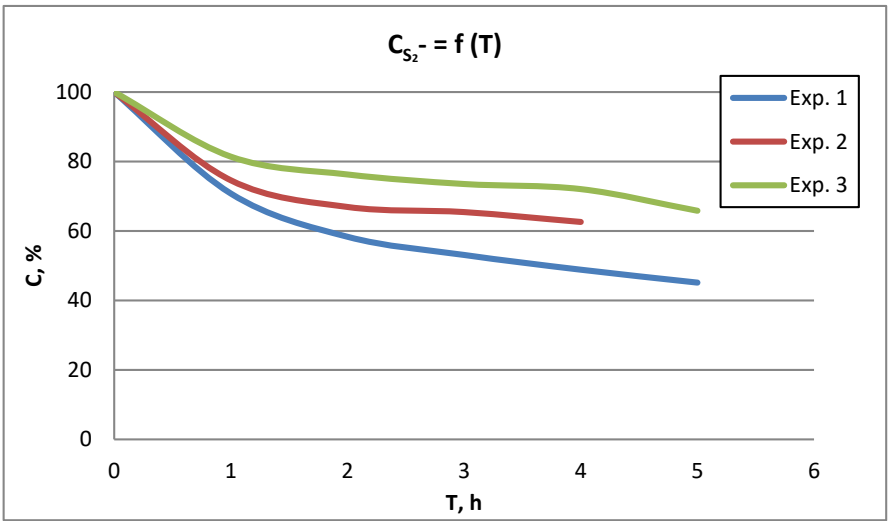

Fig. 6. Sulfide depletion

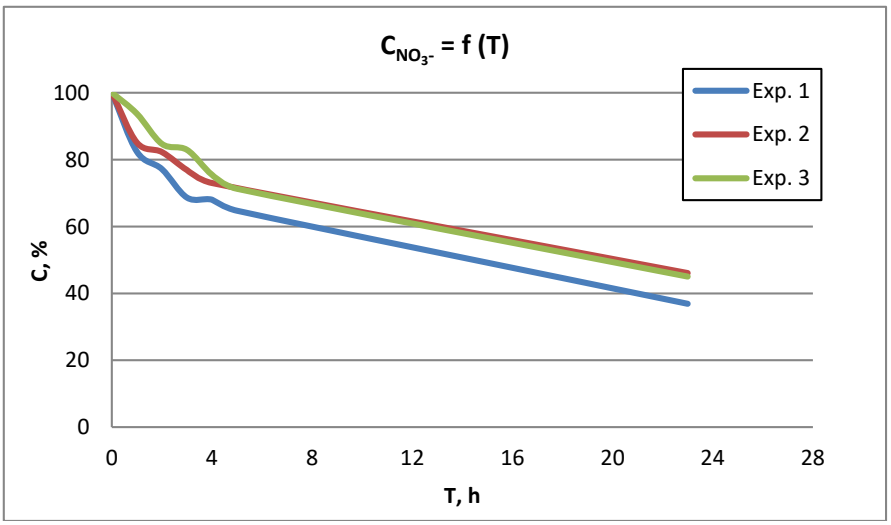

Fig. 7. Nitrate depletion

3.2. Results for thermal regeneration of the electrodes of both compartments

The thermal regeneration is conducted by boiling the paddlings with the same volume of distilled water and thoroughly rinsing it with cold distilled water afterwards.

Fig. 8. is a comparison between the treated electrodes in both compartments and the third of the initial experiments. It can be seen that the power is higher than that of the non regenerated electrodes. However the power of the brand new electrode (**Fig. 3.**) can not be achieved due to blockage of some active centers or mechanical tearing some of them out. The figures for the depletion (**Fig. 9.** and **Fig. 10.**) in these cases also demonstrate the successful recovery of the electrodes.

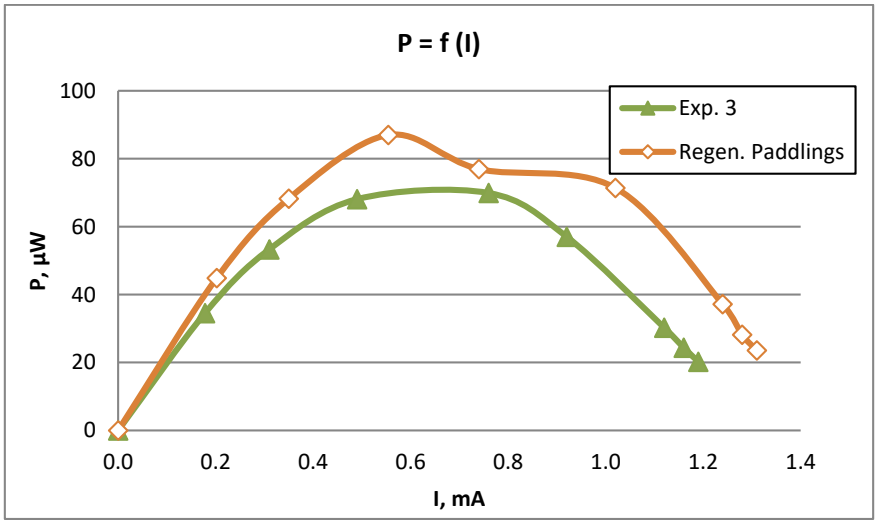

Fig. 8. Power as a function of the current

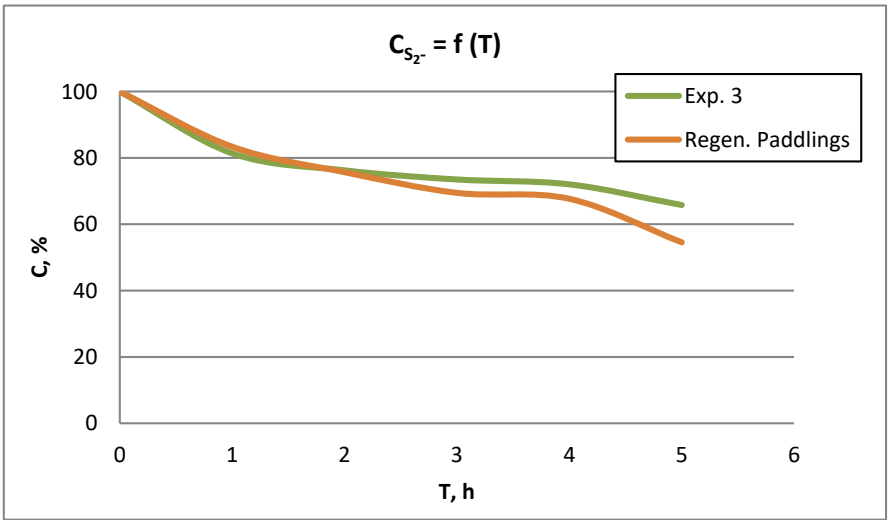

Fig. 9. Depletion of sulfides

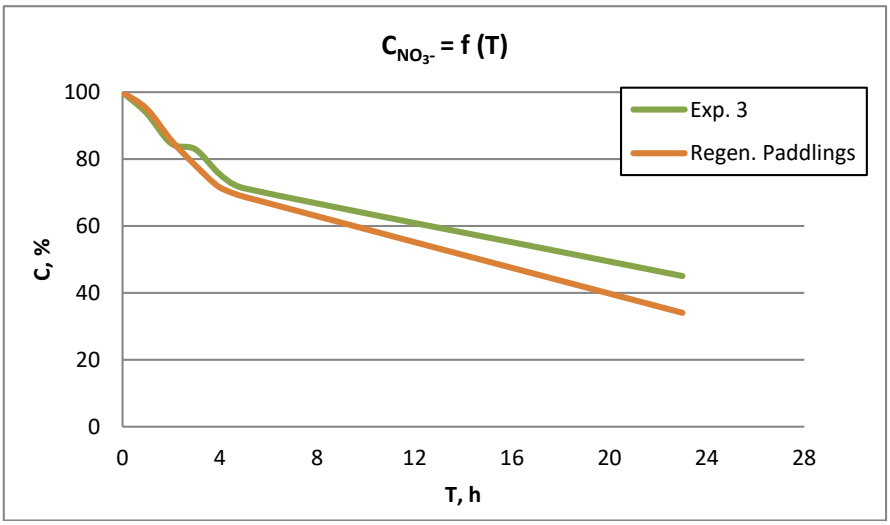

Fig. 10. Depletion of nitrates

3.3. Results for thermal regeneration of the anodic electrodes.

Fig. 11. is a comparison of the second and third consecutive experiments, regenerated electrodes in both compartments and regenerated electrode in the anodic compartment. The conclusion derived from this figure is that regeneration of both electrodes has to be done and the regeneration of the cathodic paddling is more essential.

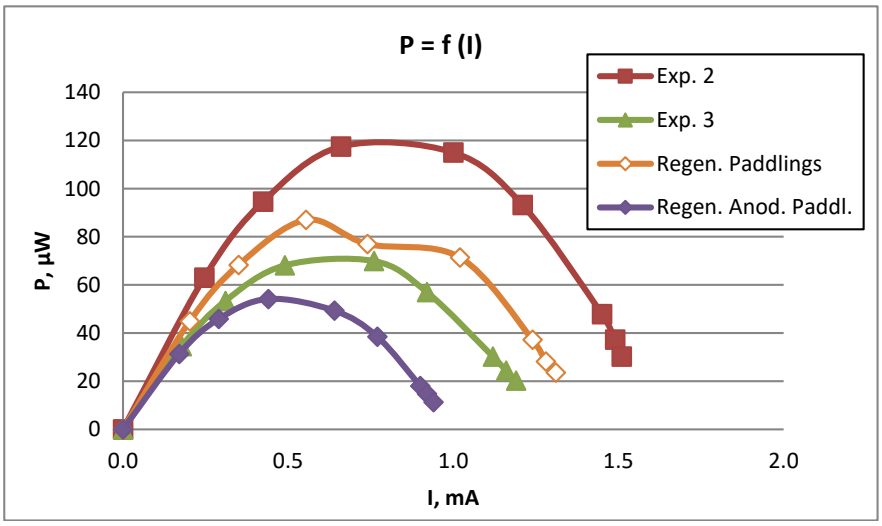

Fig. 11. Power as a function of the current

4. CONCLUSIONS

The brand new electrode of activated paddling shows very good performance characteristics. Due to blockage of some active centers or mechanical tearing of parts of the finest fibers those characteristics can not be replicated. In the following experiments the electrodes function but the blockage of active centers and the mechanical tearing continues.

The thermal regeneration of the paddlings leads to a satisfactory recovery and nearly constant levels of electrical output after consecutive usage.

The most essential result of the conducted investigation is that the depletion of the pollutants is nearly constant in all cases and does not decrease significantly with continuous use of the same paddlings.

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