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Application of bio-electrochemical methods in water treatment, Resource recovery

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Abstract

Examples of application of Microbial Fuel Cell (MFC) and Microbial Electrolysis Cell (MEC) in water treatment are reported. Anodic processes for organic matter degradation and cathodic processes for removal of copper and free radical species are under discussion. In applying this approach, the ionic form of copper (Cu2+) can be converted to elemental metal (Cu0) The results obtained in case of free radicals removal experiment demonstrates the potential of Microbial Fuel Cells to be used as a radical scavenging tool. The main advantage of this mode over the use of conventional antioxidant chemicals is the non-invasive nature of the process which provides opportunity to perform antioxidant protection and free radical neutralization without adding any reagents into the treated fluids or objects. Such actions are running without external source of energy and produce electricity. The bio-electrochemical behavior of the anode is also examined. Pioneering studies related to phosphorous mobilization in treatment of ferric phosphate (MFC) and pH elevation due to proton/electron interaction in MEC are studied as well. The experiments reveal the economically attractive opportunity to mobilize phosphorous (P) contained in conventional municipal wastewater treatment plants in form of ferric phosphate. Higher soluble P is advantageous for optimizing its chemical precipitation. The bio-electrochemical increase of pH over pH9 offers a non-reagent option to precipitate phosphorous in presence of sufficient ammonia and magnesium as struvite. Variety of cell architecture and materials of MFC and MEC are explored and viewed.

1. Introduction

Microbial Fuel Cells (MFC) are well known as bio-electrochemical systems capable to convert the chemical energy of organic substrates in to electricity. This is a result of the specific biochemical activity of the so-called Electrogenic microorganisms. The typical Microbial Fuel Cell usually consists of anode and cathode, connected by an external circuit and separated in different compartments by proton exchange membrane. In the anodic chamber, microbial decomposition (biological oxidation) of organic substrates generates electrons and protons that are transferred to cathode trough the circuit and membrane respectively. On the cathode surface they react with the final electron acceptor. Mostly O2 is applied as electron acceptor because of its abundance in nature. Recently, air-cathodes based on the gas-diffusion layers are in use, avoiding forced O2 provision at the cathode.

Different ions can be used as electron acceptor in the cathodic semi-reactions, such as manganese, copper and iron ions, nitrates, sulfate, etc., resulting in their chemical reduction and transformation into a preferable form. Recently, the processes involved in the MFCs are intensively studied as an alternative energy source and also as a method for wastewater treatment. Actually, the main benefit of this technology seems to be in the opportunity to mineralize organic matter to water and CO2 in anaerobic conditions. This perspective is promising since more that 50% of the wastewater treatment costs are due to the energy demand of aeration systems [1]. Another bio-electrochemical modification is the Microbial Electrolysis Cell (MEC) which is functioning at free electron acceptor condition and external potential applied between electrodes. The released protons from biological oxidation are transferred through proton exchange membrane to the cathode chamber, where the consumption of protons via hydrogen evolution results in a local pH increase.

Summarizing the above, it is clear that the bio-electrochemical processes offer promising alternative of the conventional processes for wastewater treatment. The paper describes different approaches of bio-electrochemical processes applied for water depollution and resource recovery. All the experiments reported are performed in the department of Water Treatment Engineering of Burgas Asen Zlatarov University, Bulgaria.

2. **Experimental**

2.1. MFC copper removal

Fresh fruits MFC used represent cylindrical anode and cathode chambers, separated by electro dialysis cation-exchange membrane [2]. . Each compartment had two ports for input and output flows. A schematic design of the system is shown in Fig1. Both electrodes were made of carbon cloth with circular section (D = 4.5 cm). The potential of the electrodes was measured versus calomel electrodes as reference. The anode and cathode were connected with an external electrical circuit with of 100 Ω resistor. The Anode and cathode chambers volume are 12.5 ml and 20 ml, respectively. The anode compartment was filed by granular activated carbon to provide biofilm formation and electron transduction to the electrode. The tested microorganisms were enriched in anaerobic conditions by inoculation of 0.5 ml sediment, collected from the bottom of "Yasna Polyana" dam in 20 ml nutrient medium containing: glucose – 15g/dm3; tryptone - 10 g/dm3; yeast extract - 5 g/dm3 and NaCl – 5 g/l and pH -7. After 96 hours of cell growth the enriched culture was suspended in fresh nutrient medium to a microbial concentration of 107 CFU/ml and loaded in the anode chamber of the MFC. The cathode chamber was filled by CuSO4 solution as donor of Cu2+ ions. The process was conducted at a temperature between 14-18 ºC.

During operation of the MFC the potential of electrodes and current were measured daily by Auto ranging digital millimeter Model MY-66. The concentration of dissolved copper was analyzed by DrLange Lasa100 automatic photometer and Hach Lange Copper LCK 329 cuvette test kit. The total organic content of the medium was experimentally examined by using of permanganate oxidation according to Kubel's method. Enriched mixed culture of electrogens from sediment of "Yasna Polyana" dam was inoculated in the anodic chamber. The anode and cathode reaction processes can be summarized as follow: In the anodic chamber the organic substrates are oxidized by bacteria to CO2, H+ and electrons. The electrons are transferred to the cathode compartment by the electric circuit and reduce the Cu2+ to Cu0. The protons penetrate the cation exchange membrane and reacts with sulphate ions resulting in formation of H2SO4. This leads to pH reduction in the cathode area near values of 3.5. The low pH of the medium was reported by other authors as favorable for Cu0 production [3]. The MFC was loaded with microbial culture suspended in nutrient medium as electron donor and constant circulation of 1dm3 CuSO4 solution with high concentration (1130 mg/dm3) was provided as electron acceptor in the cathode chamber. At these conditions the process depends on substrate availability and microbial activity. The results obtained are presented at Fig.2.

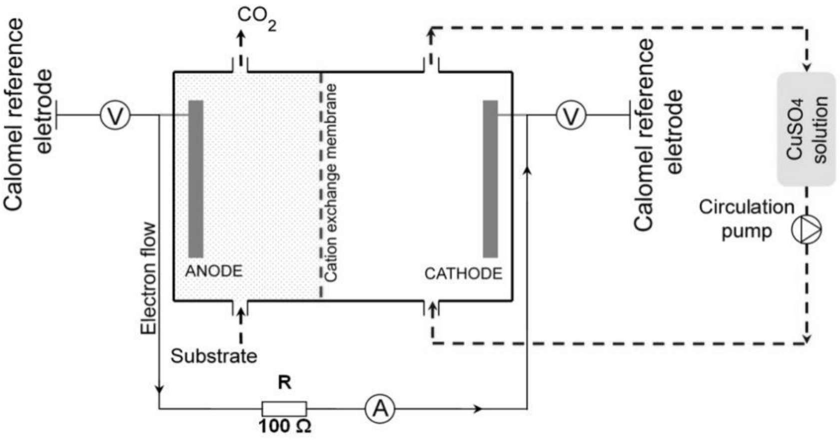

Figure 1: Design of Microbial fuel cell with main processes during exploitation
V – Voltmeter; A – Ammeter; R – Resistor.

There is a strong correlation between the electric current dynamics and substrate mineralization ratio. In the first days of cultivation the total organic contents was about 5000 mgO_2/dm^3 and maximum electric current 0.32 mA. A gradual decrease of organics concentration following the current curve slope was observed.

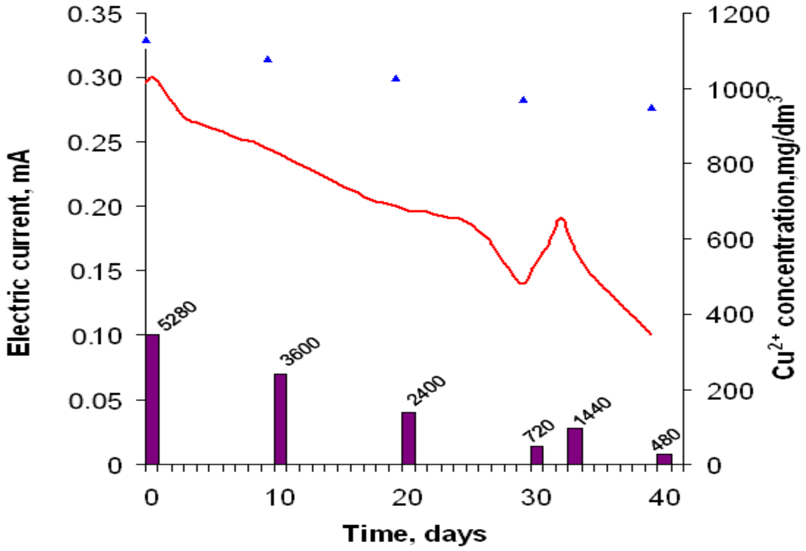

Figure 2: Electric current (-), Cu^{2+} concentration (▲) and organic content of the substrate (as mgO_2/dm^3 in the columns) in conditions of unlimited electron acceptors presence.

The final Cu^{2+} concentration reached was 200mg/l, i.e. about 80% copper removal was found. In examining the cathode chamber after the bio-electrochemical runs Cu precipitation products were identified on the cell walls. Two control MFC runs were done. In the first control the fuel cell was loaded with sterile medium for abiotic control. No electricity production was detected. This result demonstrates that the microbial activity drives the process. In the second control the mixed microbial culture was cultivated in the same nutrient medium in normal anaerobic conditions without any external acceptor of electrons. In this attempt a partial mineralization of the medium through fermentative metabolism and formation of lactic acid as final product of substrate utilization were observed.

The data obtained in this study demonstrate the potential of the Microbial fuel cells in copper removal from wastewater. The main point of interest is that this technology does not consume energy. Something more, MFCs are not just energy effective units – they produce energy during oxidation of the organic pollutants in the wastewaters.

2.2 Microbial Fuel Cell free radical scavenging

It's well known that the free radicals are a molecular species capable of independent existence that contains one or more unpaired electrons which makes them highly reactive. In the recent years the role of free radicals and oxidative stress as a negative processes affecting the living cells in molecular level has been elucidated. The activity of radicals was directly associated with cell aging and number of pathological processes, including neoplastic growth of tumors, metabolic and neuro-vegetative disorders [4].

Along with the metabolic processes themselves, the main source of free radicals in human body is food and the products obtained after it's oxidation during the storage and processing. For this reason, modern concept of food and life quality is linked with the effective anti-oxidation and free radical scavenging. Control of oxidation and elimination of the resulting free radicals is a critical factor in the production and storage of biologically active substances.

The conventional approach toward the free radicals which is applied both *in vivo* and *in situ* is based on the activity of so called antioxidants. They are usually natural compounds including some vitamins, polyphenols and other plant synthesized molecules. In the living cells themselves, there are several enzymes which poses antioxidant activity and they are crucial factors in oxidative stress protection [5]. However, in practical sense the application of chemical antioxidants in not always a proper solution. In certain cases adding external compounds to the products is not acceptable. Another drawback is related to the radical-chain reactions or pro-oxidant activities which are possible to occur in some cases after application of chemical antioxidants [6].

The study is focused on testing the concept of using the reductive potential at the cathode of MFC in aiming to perform non-reagent free radical scavenging. The main idea is based on the electron and proton transfer via the electrode to the reactive molecules. The later play the role of terminal electron acceptors in the catholyte. The bio-electrochemical free radial scavenging method suggested could be a step further in order to overcome the above mentioned disadvantages of the chemical antioxidants.

The study employs DPPH (Aldrich Chemistry) as a model free radical and investigates the dynamics of its neutralization in the cathodic compartment of dual chamber MFCs. The MFC used was assembled as a cylindrical plastic reactor consist of two chambers separated by Nafion® 424 perfluorinted proton exchange membrane. The anode and cathode were made of carbon cloth with circular shape and diameter of 40mm. The electrodes are connected with external electric circuit with 1000Ω load. The total volume of cathodic and anodic compartments was 20 and 40 dm^3, respectively.

The Electrogenic culture enrichment is described elsewhere [2]. The changes in DPPH concentration were determined spectrophotometrically at 515 nm according to the Brand-Williams et al. method [7]. The effect of the treatment applied was expressed as percentage of the initial DPPH concentration (150 µM.). A control sample was prepared in the same manner but in abiotic conditions in order to evaluate the eventual free radical neutralization effects not related to the bio-electrochemical activity.

The results obtained in this set of experiments are presented on Fig. 3. The control sample lacks any dynamics and no neutralization was observed. In operational conditions the DPPH neutralization of about 95% was established. This rate of radical neutralization was achieved in 16 hours. The neutralization curve poses a typical first order kinetics with half-life of the tested free radical 3.5 hours. The relatively slower process is partially balanced by the deeper neutralization rate achieved by the MFC compering with the conventional chemical antioxidants [8,9]. Another advantage is that after reaching the maximum neutralization the DPPH levels remains stable while it is well known that the processes employing free radicals scavenging by antioxidants are often reversible [10]. The reversed reactions usually results in re-oxidation and re-activation of the radical molecules which is not possible in this case due to permanent electron (and proton) flow between anode and cathode.

The results demonstrate the potential of the Microbial Fuel Cells to be used as a radical scavenging tool. The main advantage of this approach over the conventional antioxidant chemicals is the non-invasive nature of the process which provides opportunity to perform antioxidant protection and free radical neutralization without adding any reagents into the treated fluids or objects.

2.3. Organic matter removal

It is well recognized that anaerobic digestion of sludge or concentrated wastewater, is usually a cheaper option than aerobic organic matter assimilation. However, the anaerobic effluent often requires further treatment to remove residual organics. These organic compounds are metabolic products of the anaerobic digestion (mainly volatile fatty acids). There are proofs that in case of applying MFC, these acids, such as acetate and butyrate, are effectively degraded in MFCs, even at low concentration. Therefore, MFCs can be used for post-treatment of these organic compounds to meet discharge standards while recovering some energy rather than employing energy intensive aerobic processes. Also there are positive examples of multi-stage treatment combining anaerobic digestion (AD) and MFC technologies may result in reduced accumulation of inhibitory by-products and allow effluent polishing the effluents [8]. The effect of MFC could be more prominent if the operating temperature of MFC is increased to 30 °C (a range of psychrophilic and mesophilic operating conditions), in both of effluent quality and electricity production.

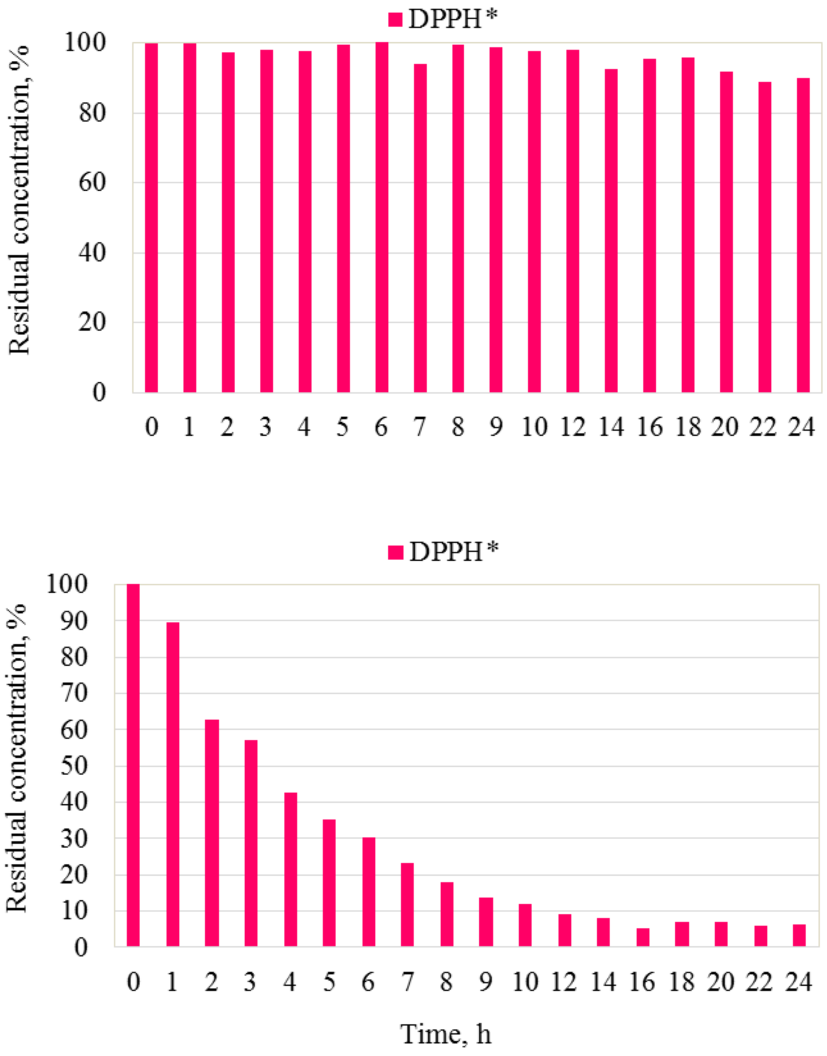

Figure 3: Changes in DPPH concentration A) in an open circuit MFC and B) in operational MFC.

One of the factors governing the economics of biological processes for wastewater treatment is the sludge production. The cell yield of activated sludge, mostly applied in wastewater treatment, is estimated to be from 0.4 to 0.7 g VSS/ g BOD5. In consequence, the activated sludge process produces large amount of excess sludge which can amount to 60% of the total operation cost of an WWTP [9]. Typically, the anaerobic respiring microorganisms in digesters (e.g., methanogens and sulphate reducers) and fermentative bacteria amount around 0.13 g VSS/ g BOD5 [8, 9]. By fixing the biomass to a surface, biofilm reactors like MFCs reduce the amount of sludge for disposal. In general, the biomass yield appears to be low for MFCs in comparison to other anaerobic technologies [20]. Summarizing the above, the advantages of MFCs over the conventional aerobic treatment related to the low energy requirements and reduced sludge production are obvious. The research reported here was aimed to investigate the effects of a MFC based treatment of organics polluted wastewater. In applying to the anodic compartment (Fig.4) an organic load equivalent to permanganate oxygen demand 600 mgO2/L) a high extent of mineralization was observed. A typical degradation curve of the organic matter degradation process is shown in Fig.5, namely about 95% mineralization within 168 hours and full organic matter utilization in 360 hours. Such a Hydraulic Retention Time (168 h) is acceptable in practical realization of the MFC for organic matter degradation in wastewater treatment or sludge stabilization.

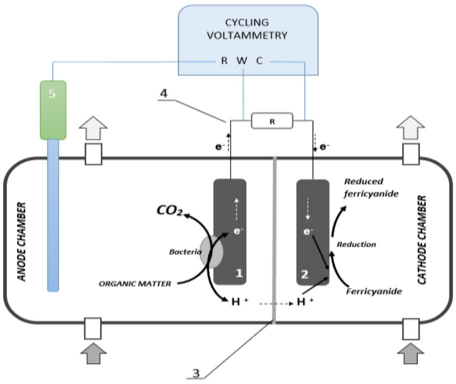

Figure 4: Anode (working electrode); 2 – Cathode (counter electrode); 3 - Proton exchange membrane; 4 – Load; 5 – Reference electrode.

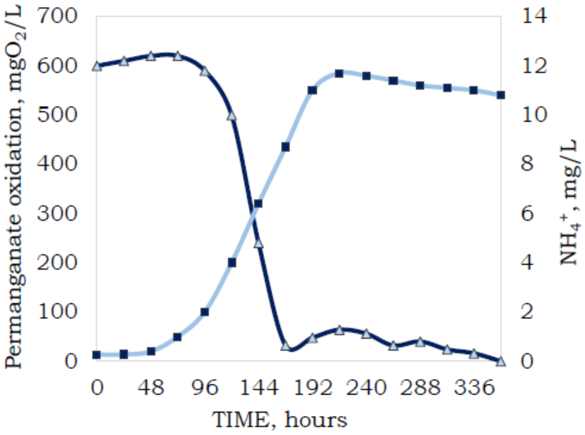

Figure 5: Typical MFC organic matter degradation curve.

2.4. Phosphorus removal

The limited Phosphorus resource [11] and its extensive consumption worldwide are the driving force towards phosphorus recycling from different residuals. One very promising alternative to phosphate rocks are residual sludge streams of some domestic and industrial wastewater treatment processes. Only in the EU, the total amount of excess sludge produced annually during sewage treatment reaches 11 million tons dry matter. This sewage sludge contains nearly 20% of the demand for phosphorus fertilizer for agriculture and food production in Europe.

Phosphate is removed in wastewater treatment plants either by chemical precipitation with iron or aluminium salts or by enhanced biological phosphorus removal (EBPR). The aim of the phosphorus recycling technologies under research is to recover the phosphorus out of the wastewater or the sludge matrix and to obtain an applicable phosphate fertilizer product such as magnesium ammonium-phosphate (MAP or struvite). MAP crystallization without sludge incineration is a suitable recovery process from both an economic and an environmental point of view, but has the drawback, that only a limited amount (25%) of the phosphorus in the wastewater stream can be recovered [12]. The major part of the phosphorus is in the form of insoluble Fe or Al phosphates accumulated into the activated sludge.

Transforming the chemically “locked” phosphates back into the soluble form is very important for the general yield during phosphorus recovery as struvite. Beside this, obtaining a condition suitable for struvite precipitation (as high pH values and chemical reagents to provide Mg ions) is also a challenge, especially in terms of development of environmentally friendly processes and fertilizer products applicable in so called organic farming.

A newly discovered path for phosphorus recovery from sewage sludge is the mobilization of orthophosphates from iron phosphate (FePO4) by microbial fuel cell power. An electrical current is achieved in the microbial fuel cell by attaching bacteria like *Escherichia coli* to an anode which the bacteria use as electron acceptor (Figure 6). With a proton exchange membrane the anode cell is separated from the cathode cell. The electric flow provides reductive conditions next to the cathode. Thus dissolution of up to 82% of the FePO4 has been achieved. This technique can be combined with struvite crystallization by adding magnesium chloride and ammonium hydroxide in stoichiometric ratio [13].

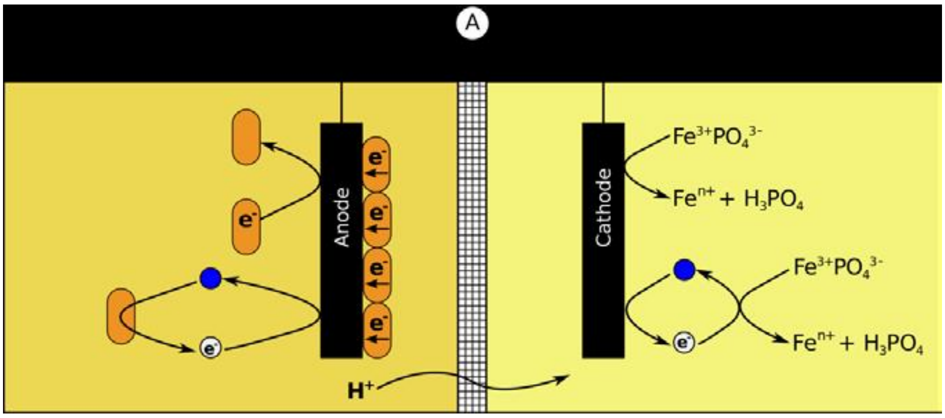

Figure 6: Electrochemical mobilization of orthophosphates [Fischer et al., 2011].

The "Fisher" approach was applied in treatment of residual sludge form municipal Wastewater Treatment Plants. The Microbial Fuel cell used in studying the FePO4 mobilization was designed as a cylindrical reactor with two chambers separated by cation exchange membrane. The volumes of anodic and cathodic chambers are 20 and 10 ml, respectively. Each compartment had two ports for input and output flows. Both electrodes were made of carbon cloth with circular section. The anode compartment was filed by granular activated carbon to provide better biofilm formation and electron. The anode and cathode were connected with an external electrical circuit loaded with an 100 Ω resistor (Fig. 7). The conditions for electrogens isolation are given elsewhere [14].

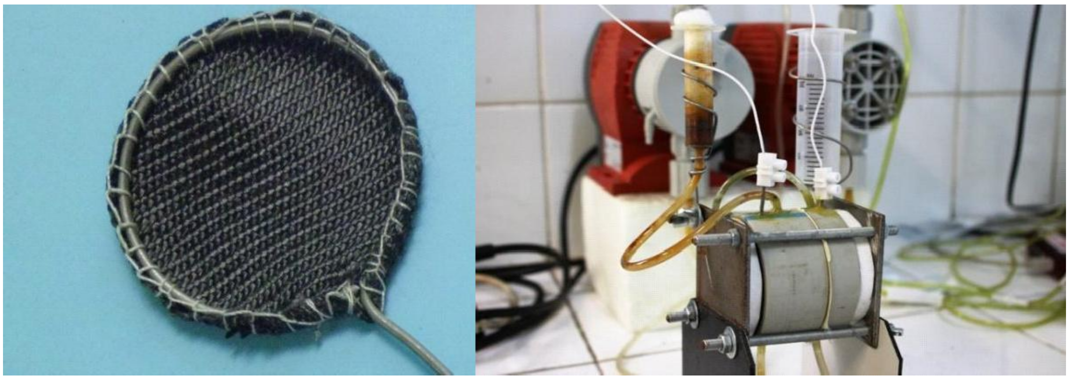

Figure 7: Design of the MFC reactor (**A**) and the carbon cloth electrodes (**B**) designed and used in phosphate dissolution experiments.

During operation of the MFC the potential difference between the electrodes was measured and recorded in 10 minutes intervals by *data acquisition system* connected to PC equipped with specific software. Ferric phosphate used in this study was synthesized in our lab by imitating the coagulation procedure applied during conventional waste water treatment. The procedure includes phosphoric acid dilution and coagulation of phosphates as ferric phosphate by adding equimolar concentration of $FeCl_3$. During the coagulation and synthesis the pH was adjusted to 3.2 by adding NaOH to the reagent mixture. The low pH values prevents formation of Fe(OH)3 which is parasitic reaction during this synthesis.

The results, Fig.8, reveal the potential of the electrochemical phosphate mobilization to provide addition *ortho*-phosphates for MAP precipitation. We tested the performance of two types of separator membranes – Nafion-Proton Exchange Membrane (PEM) and the cheaper and less specific Ralex-Cathion Exchange Membrane (CEM). The results obtained were very comparable and in the next stages of the work we decided to use the CEM. In the first set of experiments the reductive conditions in the cathode chamber of the MFC was used toward model suspension of ferric phosphate with different concentration. We observed maximal and average dissolution rates of **Q_{max}** = 7.08 $mgPO_4.h^{-1}$ and **Q_{av}** = 4.06 $mgPO_4.h^{-1}$ with tendency for better dissolution in the reactors with higher concentration of $FePO_4$ (450 mg/l). This is implication of the typical MFC behavior and correlation between the electric current obtained from the cells and the presence of electron acceptors. From the electrochemical point of view in such a system the Fe^{3+} plays a role of terminal acceptor of electron and higher concentrations of $FePO_4$ leads to generation of higher voltage, current and faster cathode reactions.

The real fluids obtained from activated sludge digestion, which will be the potential target of this technology, are characterized by very high organic content. It is known that the variety of organic molecules can affect the electrochemistry of the fuel cells by providing alternative acceptors and shifting the cathode reactions to different "parasitic" processes. To evaluate the influence of organics in the activated sludge on the above described process an experiment for phosphate mobilization in model fluid prepared by suspending the $FePO_4$ in activated sludge filtrates with COD 1500 $mgO_2.l^{-1}$ was performed (Fig.9).

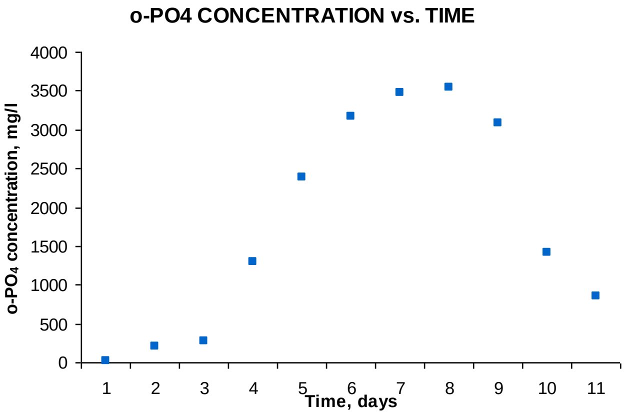

Figure 8: Phosphate concentration dynamics during electrochemical mobilization of $FePO_4$.

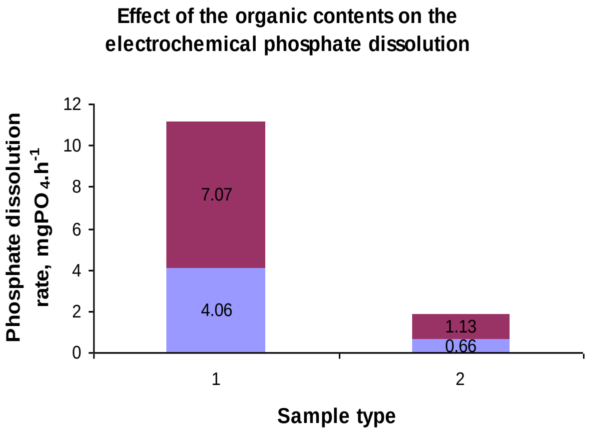

Figure 9: Electrochemical phosphate dissolution rates in the presence of high organic content (bar 2) compared to the rates in reagent mixture without organics (bar 1) – Maximal Dissolution Rates in purple; Average Dissolution Rates in Blue

The negative influence of the organic matter on the process kinetics is probably a result of electrochemical conditions break down due to lower cathode potential caused by the presence of biodegradable organics in the cathodic space. We have to point that even at these conditions the electrochemical reduction and mobilization is possible and we observed dissolution of 111 mg/l phosphates in 168 hours.

In the last stage of the experimental work we applied the MFC phosphate dissolution toward real fluids obtained from residual WWTP activated sludge. A dried digested sludge was re-suspend in water to concentration of 15 g/l and loaded this suspension into the cathodic chamber of the MFC. In parallel, a control sample with the same content was prepared and placed in anaerobic conditions for evaluation of the eventual microbial co-mobilization of phosphate due to biological activity in sludge. The results obtained are presented in Fig.10. The results demonstrated the ability of the studied system to release *ortho*-phosphates from ferric phosphate in real conditions.

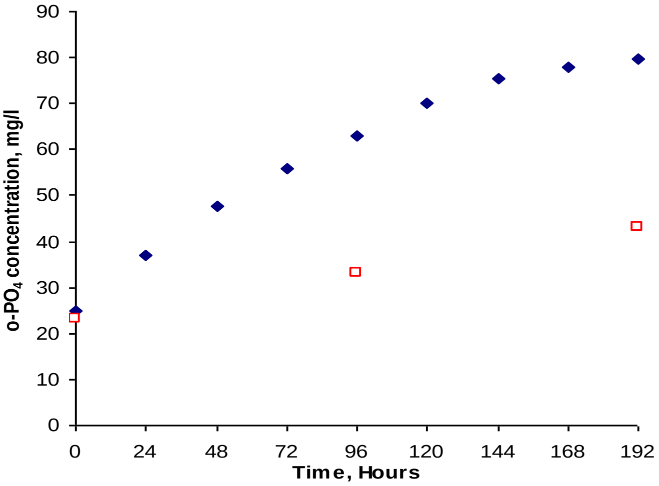

Figure10: Ortho-Phosphate concentration in dried sludge suspension treated in MFC (♦). □ - control sample.

2.5. *Non- reagent pH elevation in Microbial Electrolysis Cell (MEC).*

The study was aimed to take advantage of protons and electrons recombination in the cathodic chamber of MEC leading to “disappearance” of protons and consequently, to pH increase. The schematic representation of the cell and the actual reactor used in the investigation are shown in Fig.11. The MEC is a cylindrical reactor with two sections separated by ion exchange membrane. The electrodes were made of carbon cloth. They are connected to the external power source. In this electric circuit a potentiometer to control the voltage applied to the cell was placed. For direct pH measurement and record a pH electrode was placed into the cathodic chamber. The preparation of microbial culture and growth medium was performed according to the above mentioned procedure.

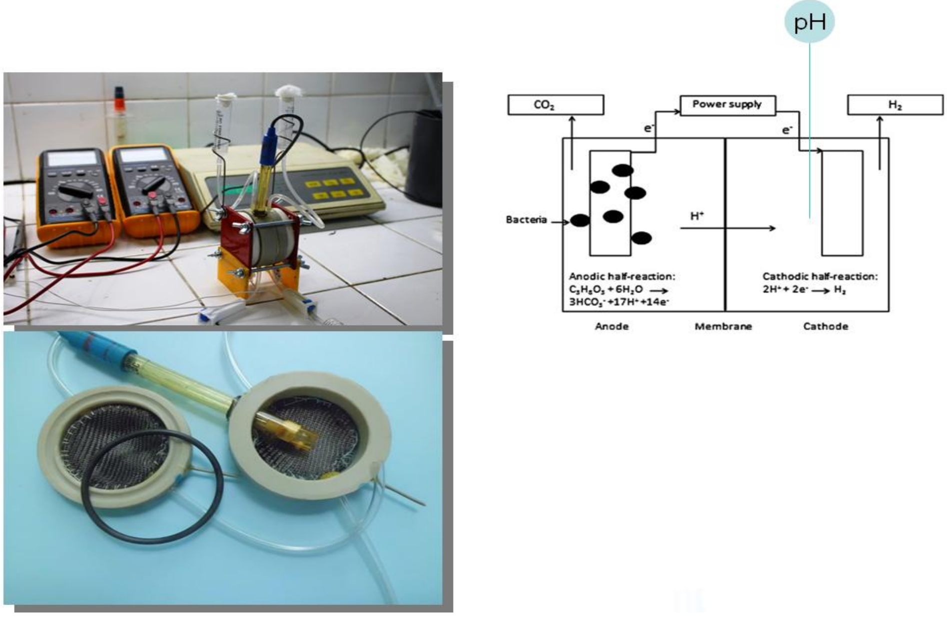

Figure 11: Microbial Electrolysis Cell (MEC) used for electrochemical pH elevation and overview of the experimental design and mechanisms.

The influence of the external voltage applied and membrane type in the pH elevation process was studied. For this purpose a model reagent mixture of $MgCl_2$ and $(NH_4)_2HPO_4$ in equimolar ratios and external voltages of 200, 700 and 1200 mV was used. The best results regarding the pH elevation were obtained after application of 1200 mV external voltage. In this condition very high pH elevation rate of 0.08 units per hour was observed.

Experiments, Fig.12, with a mixture of real digested sludge filtrate and brine (as a source of magnesium) was applied as well. The mixture was prepared to provide phosphate and magnesium mole ratio of 1:2.

The results obtained show a slower pH elevation rate compared to the synthetic solution, which is probably due to the complex composition of the reagent mixture and presence of alternative (to H^+) electron acceptors which affects the efficiency of process. However, the MEC was still able to elevate the pH of the fluid to the desired valued of 9-9.5 in 24-36 hours. As a result of this the *ortho*-phosphate concentration in the cathode medium dropped from 143 mg/l to 37 mg/l.

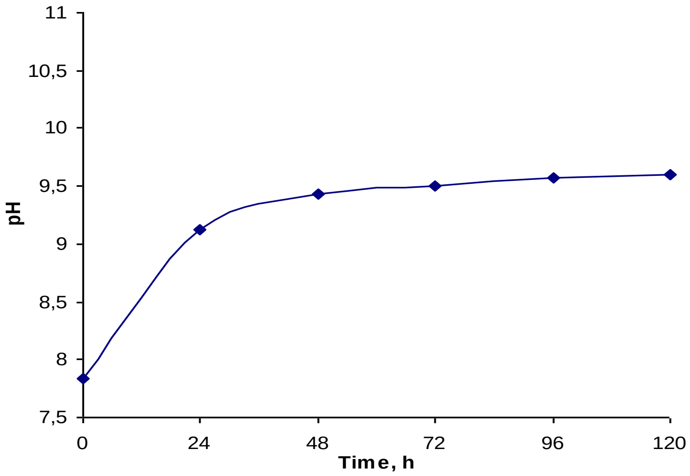

Figure 12: pH values vs. time in experiments for MEC treatment of digested sludge filtrate and brine mixture (1200 mV external voltage).

2.6. Microbial Desalination Cell (MDC)

MDCs are similar to MFCs but they differ in the fact that the latter consist of three chambers (i.e., the cathodic, anodic and desalination chambers). These chambers are separated using membranes. A cation exchange membrane (CEM) is used between the cathode and the desalination chamber, whereas an anion exchange membrane (AEM) is used between the anodic and desalination chambers. The anolyte and the catholyte are identical to those used in MFCs, but the desalination chamber is loaded with salt water. The AEM prevents the transfer of protons that are produced in the anodic chamber to the desalination side, and facilitates the transfer of negative ions, in the sea water, towards the anode. The principals of MDC work are shown in Fig. 12.

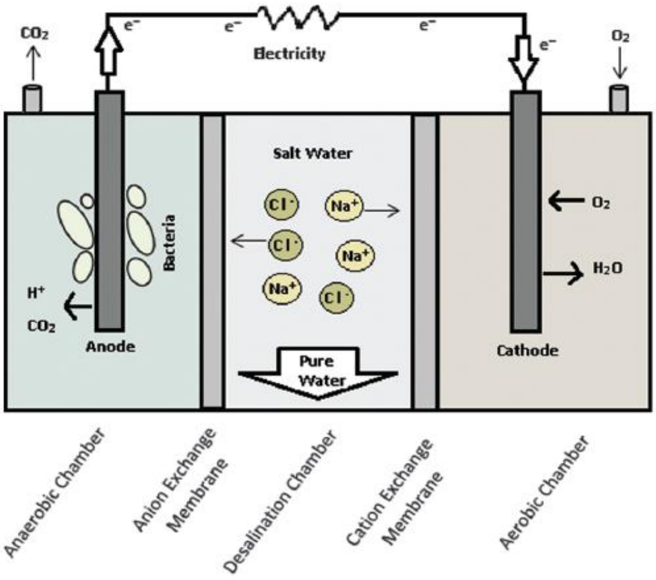

Figure12: MDC principals.

The anodic chamber of the reactor was filled with activated carbon to provide better conditions for biofilm formation and to expand the anodic surface in order to obtain better electron transfer. Details of the experimental are given elsewhere [15]. The plot of the potential between electrodes (mV) vs. time is shown in Fig.13.

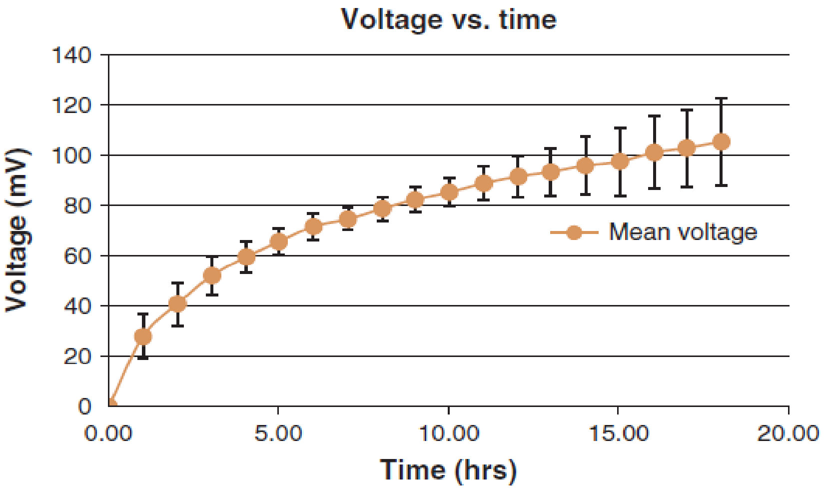

Figure 13: Plot of average voltage versus time (the error bars are standard deviations).

A maximum voltage of 105 mV is reached within 20 hours. An average power density of 1.54 mW/m^2 was achieved using our cell. Additionally, the cell is able to achieve 62% desalination in 20 hours. It can be seen from the above graph that, the voltage is steadily increasing with time due, in part, to the activated carbon which supports a stronger bacterial community/culture and increased electron transfer in the anodic chamber, through the formation of a biofilm. Also the combination of protons, electrons and oxygen that closes the circuit of the MDC is made easier by the addition of activated carbon that provides more sites for this combination to occur. The percentage desalination depends on various factors including the membrane type. In our experiments, the cellulose membrane yields 62% desalination. The experimental results are summarized in Table 1.

Parameter	Average
TDS of salt water (i)	4
TDS of salt Water (f)	15.274
Percent desalination	61.815
TDS; of anode (i)	5.774
TDS of anode (f)	14.414
TDS; of cathode (i)	4.902
TDS of cathode (f)	14. 216
Voltage (mV)	77.044
Power density (mW/m^2)	1.546

Table 1: Experimental results of our MDC.

Note: TDS;: initial total dissolved salt in (g/L),
TDS: final total dissolved salt in (g/L); (i) – initial; (f) final

Based on the study performed, it can be concluded that the power generated by the cell is efficient enough to self-sustain the cell for desalination. Therefore, this technology has the potential to be used to integrate a waste water treatment plant and a desalination facility. MDCs can also be used as a pretreatment process for reverse osmosis (RO), thereby minimizing the operating cost of these water treatment facilities.

Conclusions

The bio-electrochemical processes applied in water treatment are promising alternative of the conventional processes, such as the aerobic organic matter removal, heavy metal conversion and separation by chemical precipitation or ion exchange, nitrogen removal by the conventional bio-nitrification/denitrification; phosphorus removal (EBPR) and membrane water desalination.

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References

1. Yemendzhiev H., Peeva G., Bonev B., Midyurova B., Rasheva M., Nenov V**.,** *Efficacite energetique – Sources d'energies renouvelables – Protection de l'environnement, ed.: M. Feidt and Vl. Lazarov, Avangard Prima, Sofia,* (2012) 412.
2. Nenov V., Yordanova G., Bonev B., *Proc. of ICWEE 2011 Conference, Sharjah, UAE,* (2011) 14.
3. Tao H. C., Liang M., Li W., Zhang L. J., Ni J. R., Wuc W. M., *J. Haz. Mater.*, 189 (2011) 186.
4. Valko M., Jomova K., Rhodes C. J., Kuča K., Musílek K., *Arch. Toxicol.* 90 (2016) 1.
5. Carocho M., Ferreira I., *Food Chem. Toxicol., 51 (*2013) 15.
6. Mohanakrishna G., Srikanth S., Pant D., *Applied Environmental Biotechnology: Present Scenario and Future Trends, Springer India* (2015) 145.
7. Brand-Williams W., Cuvelier M.E., Berset C., *LWT.* 28 (1995) 25.
8. Otohinoyi D.A., Ekpo O., Ibraheem O., *Int. J. Biol. Chem. Sci.*, 8 (2014) 1262.
9. Abbasi B., Dullstein S., Rabiger N., *Water Res.*, 34 (2000) 139.
10. Rittmann B. E., McCarty P. L., *Environmental Biotechnology: Principles and Applications, McGraw-Hill Book Co., New York,* (2001) 768.
11. Michael Reilly., *New Scientist*, (2007) 194.
12. Lüscher C., Nättorp A., *Sciences, Recovering Phosphorus and Closing the Nutrient Cycle, Research Report 2009/2010 University of Applied Sciences Northwestern Switzerland School of Life Sciences*, (2010) 565.
13. Fischer F., Bastian C., Happe M., Mabillard E., Schmidt N., *Bioresource Technology* 102 (2011) 5824.
14. Nenov V., Jemendjiev H., Peeva G., Bonev B., Zerrouq F., *J. Mater. Environ. Sci.* 7 (2016) 113.
15. Aidan A., Husseini G. A., Yemendzhiev H., Nenov V., Rasheed A, Chekkath H., Al-Assaf Y., *Advanced Science, Engineering and Medicine* 6 (2014) 1.

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