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The phosphate removal efficiency electrocoagulation wastewater using iron and aluminum electrodes

Đuričić, T.[a,*], Malinović, B.N.[a], Bijelić, D.[b]

[a]University of Banja Luka, Faculty of Technology, Stepe Stepanovica 73, 78000 Banja Luka,

[2]JP Dep-ot, Bulevar Živojina Mišića 23, 78000 Banja Luka, B&H

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***Corresponding author:**
E-mail: tijana.malinovic@unibl.rs
Phone: +387 65 334 067
Fax: +387 51 434 351

Abstract: Effects of electrolysis duration, initial phosphate concentrations and supporting electrolyte concentrations on the phosphate removal efficiency by electrocoagulation using either aluminum or iron electrodes were investigated in this study. All experiments were performed in a batch electrochemical reactor on synthetically prepared wastewater of the initial volume 0.2 L. The results indicate that increase of initial phosphate concentration has reduced removal rate, and by increasing the electrolysis duration removal efficiency increases. It was found that the aluminum electrode has higher removal efficiency (98.9%) compared to the iron electrode (93.5%) for 40 minutes of treatment (pH=3, j=1 mA/cm^2, γ_0=50 mg/L P–PO_4). The addition of supporting electrolyte (γ_{NaCl}=0.25 g/L) is achieved removal efficiency of 50.2% for Fe and 52.1% fo Al electrode in only 10 minutes of treatment, respectively.

INTRODUCTION

Phosphorus is a natural nutrient, unavoidable in surface water which appears almost always as a phosphate ion (House, 2012). Although precious nutrient highly valuable for the agriculture, phosphate released in extensive quantities into the surface waters, causes euthrofication.

Removal of the phosphate from the drinking waters and also from the wastewater started to draw the attention of the scientists and professionals from the 1960s (Vasudevan, Sozhan, Ravichandran, *et. al.*, 2008). As a perspective methods have proven electrochemical methods of wastewater treatment (El-Shazly, Daous, 2013). The electrochemical technologies have attracted a great deal of attention, because of their versatility, which makes the treatment of liquids, gases and solids possible and environmental compatibility. These methods are electrodialysis, electrooxidation, electroflocculation and electrocoagulation (Miranzadeh, Rabbani, Dehqan, 2012). This research is focused on the electrocoagulation treatment of synthetic wastewater loaded with phosphates. There are numerous studies on the removal of phosphorus from wastewater. Some of the studies related to electrochemical technology for wastewater treatment.

Electrocoagulation process of wastewater, and consequently water containing phosphates, has become very attractive for research in the last two decades. Initially, the research was based on the research of feasibility and applicability of the process of electrocoagulation treatment of wastewater containing phosphates to the testing of the basic parameters such as current density, electrolysis duration, temperature, initial phosphate concentration, the type and concentration of supporting electrolyte and their optimization (Behbahani, Moghaddam, Arami, 2010; Shalaby, Nassef, Mubarak, *et. al.*, 2014; Bektas, Akbulut, Inan, *et. al.*, 2004; Irdemez, Yildiz, Tosunoglu, 2006; Irdemez, Demircioglu, Yildiz, 2006; Irdemez, Demircioglu, Yildiz, *et. al.* 2006). After that was carried studies with different types of electrodes such as mild steel, stainless steel, aluminum ore, zinc, copper, etc. and was carried to compare them (Vasudevan, *et. al.*, 2008; Vasudevan, Lakshmi, Jayaraj, *et. al.*, 2008; Vasudevan, Lakshmi, Sozhan, 2009; Hong, Chang, Bae, *et. al.*, 2013). Process performance was achieved as in the batch reactor (Attour, Tuoati, Tlili, *et. al.*, 2014*)*, in a flow reactor with recirculation (El-Shazly, Daous, 2013; Lacasa, Canizares, Saez, *et. al.*, 2011), as well as in reactors which combine the electrocoagulation, electroflotation and the electrooxidation process (El-Masry, Sadek, Mekhemer, 2004).

Attour *et al.* in their research indicate that the phosphate removal efficiency from wastewater at Al electrode was 90% after 15 minutes of treatment. The highest removal of phosphate was obtained at a initial concentration of phosphate 50 mg/L, as an supporting electrolyte used is 4,5 mM NaCl and at a current density 1 mA/cm^2 (Attour *et al.*, 2014). A comparison between the phosphate removal efficiency by using Al and Fe electrodes are investigated Behbahani *et al.* At pH=3 are achieved maximum removal efficiency, which amounts to 100% for Al electrodes and 84.7% for Fe electrodes. This highest removal efficiency at a pH=3 was obtained at a initial phosphate concentration of 400 mg/L and at a current density of 250 A/m^2 for both types of electrodes. The turbidity of the solution is higher for Fe electrode. In the sludge was found a greater amount of PO_4^{3-} for Al electrode, which indicate higher removal efficiency (Behbahani *et al*., 2010). During phosphate removal from the wastewater from the process of phosphating with zinc phosphate, pH 3 has proved as most effective. The highest phosphate removal was for 15 minutes of electrolysis. At optimal current density of 60 A/m^2 was removed 97.8% phosphate from wastewater (Kobya, Demirbas, Dedeli, 2010). In a series of research Irdemez *et al*. examined the impact of the initial phosphate concentration, current density and pH, as the main parameters of electrocoagulation Removal efficiency and reaction rate decreases with the increase of initial concentration of phosphate. According to their results, the removal efficiency increases with current density, therefore increasing energy consumption. It was found that the optimal initial pH-value of the wastewater is 3 (Irdemez *et. al.* 2006, Irdemez *et. al.* 2006, Irdemez *et. al.* 2006).

EXPERIMENTAL

Experimental part of the research is contained by the application of electrocoagulation proces for removing of phosphates from simulated wastewater. Experimental setup is shown on the Figure 1. The batch electrochemical reactor of 250 cm^3 capacity made from polypropylene with constant mixing was used, combined with two electrodes of the same area surface. The dimensions of the electrodes are 40x40x1 mm. The total effective area of one electrode is 17.2 cm^2, and the distance between 2 cm. Electrodes were connected to digital power source (Atten, APS3005SI; 30V, 5A) with the potentiostatic and galvanostatic operating options.

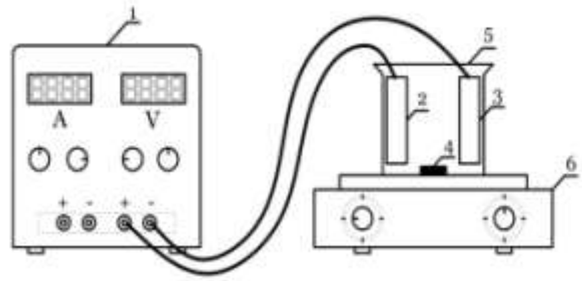

Figure 1. Schematic view of electrochemical reactor. 1 – source of electric power; 2 – anode; 3 – cathode; 4 – magnetic stir bar; 5 – electrochemical cell; 6 – magnetic stirrer)

All the experiments were performed at an ambiental temperature of sample and initial volume synthetic wastewater of 200 cm^3. Before each treatment electrodes were cleaned and degreased and the current density was set to a certain value. Used chemicals are of *p.a.* purity. In order to prepare synthetic wastewater of the particular concentration was used commercially available 99.3% potassium dihydrogen phosphate (KH_2PO_4), „Kemika“, Croatia. As supporting electrolyte was used 99.5% sodium chloride (NaCl), „Lachner“, Czech Republic. As an electrode material was used steel (EN 10130-91; max. 0.08% C, max. 0.12% Cr, max. 0.45% Mn, max. 0.60% Si) and aluminum (Al 99.5/EN AW-1050 A; max. 0.25% Si, max. 0.40% Fe, max. 0.05% Cu, max. 0.05% Mn, max. 0.05% Mg, max. 0.05% Ti, max. 0.07% Zn, min. 99.50% Al), which meet the required standards.

Before each experiment, in accorcdance to the literature data, was adjusted the optimum pH-value of the synthetic wastewater (pH=3) with HCl (Irdemez *et. al.* 2006, Behbahani, *et. al.*, 2010, Kobya, *et. al.*, 2010). Treated synthetic wastewater after each experiment was collected and filtered through filter paper „Filtres Fioroni“, France (Ref.:0015A00007; size:125 mm; qty.: 1000). Prepared samples of synthetic wastewater before and after treatment were analyzed on the following parameters: phosphorus content (P-PO_4), total dissolved substances (TDS), pH, electrolyte resistivity (ρ) and conductivity (κ). *TDS*, ρ and κ are determined on the multimeter (Consort C861), and a phosphorus concentration spectrophotometrically (λ_{max}=410 nm) in the UV-VIS spectrophotometer (Perkin-Elmer, LAMBDA 25) according to a standard method (APHA, 1999). The composition of the resulting precipitate is determinate using the FTIR spectroscopy (Bruker, Tensor 27).

RESULTS AND DISCUSSION

Results for the phosphate removal by electrocoagulation are expressed by mass concentration (mg/L) and phosphate removal efficiency, *Eu*, in percent calculated by the followed equation:

$$E_U = \frac{\gamma_i - \gamma_f}{\gamma_i} \times 100\ \% \qquad (1)$$

There the γ_i and γ_f are the initial and the final concentration of the phosphate in mg/L.

Figure 2 show the influence of the electrolysis duration (2.5; 5; 10; 30; 40 min) on the reduction of phosphate concentration by using iron and aluminum electrodes, respectively. Used current density was j=1 mA/cm^2 which, in accordance to the literature, was cited as the optimal current density (Attour *et al.*, 2014). Experiments were performed without the presence of supporting electrolyte and the initial concentration of phosphate γ_0=50 mg/L. It can be seen that the aluminum electrode has a slightly greater removal efficiency (98.9%) compared to the iron electrode (93.5%), for 40 minutes of treatment, which is in accordance with previous studies (Behbahani, *et. al.*, 2010).

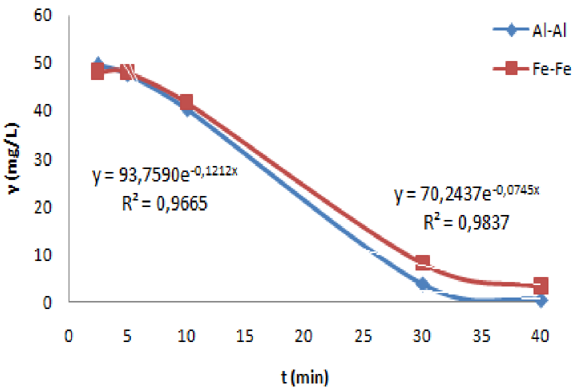

Figure 2. Phosphate concentration in relation to the electrolysis duration for iron and aluminum electrodes (j=1 mA/cm^2, t=40 min, γ_0=50 mg/L, pH=3)

The influence of the concentration of supporting electrolyte on the phosphate removal efficiency for both electrode pairs was examined in previous research and shown in Figure 3 (Malinovic, Djuricic, Bjelajac, 2016). It was found that the optimal concentration of supporting electrolyte γ_{NaCl}=0.25 g/L, which is significantly lower concentration compared to the previously published recommendations (Attour *et al.*, 2014; Kuokkanen, Kuokkanen, Ramo, 2014). For the case of aluminum electrodes, highest removal efficiency at a concentration of γ_{NaCl}=0.25 g/L was E_u=52.1%, while for the iron electrode highest removal efficiency was E_u=50.2% at a same experimental conditions.

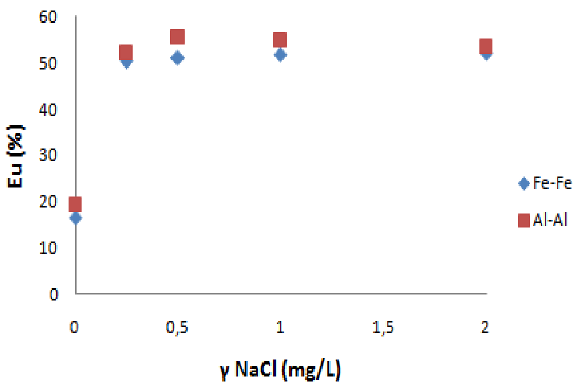

Figure 3. Removal efficiency in relation of concentration of NaCl (j=1 mA/cm^2, t=10min) (Malinovic, *et. al. 2016*)

By increasing the initial phosphate concentration in wastewater removal efficiency linearly decreases in the case of the both electrode pairs (Malinovic, Atlagic, Malinovic, 2016; Malinovic, Malinovic 2016) (Figures 4 and 5). At optimum current density j=0.25 mA/cm^2 [19] and optimum concentration of supporting electrolyte γ_{NaCl}=0.25 g/L removal efficiency is increased by reducing initial phosphate concentration in wastewater (25, 50 i 100 mg/L), which is in accordance with with previous researche (Irdemez, *et. al.* 2006). Efficiency was the highest at initial phosphate concentration γ=25 mg/L and amounts Eu=62.6% (Al), Eu=63.4% (Fe). The lowest removal efficiency was at initial phosphate concentration γ=100 mg/L and amounts Eu=29.8% (Al) and Eu=30.3% (Fe).

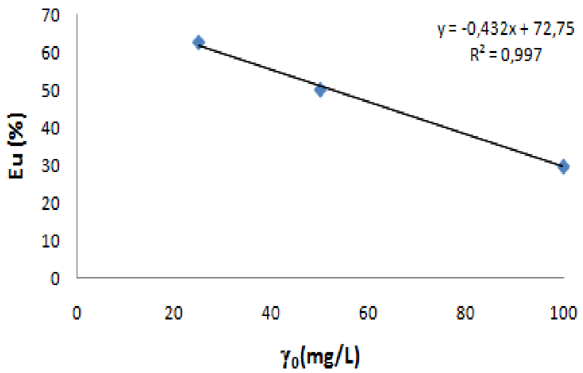

Figure 4. Removal efficiency in relation of initial phosphate concentration in wastewater, for Al electrodes (j=0.25 mA/cm^2, γ_{NaCl}=0.25 g/L, t=10 min) (Malinovic, *et. al. 2016*)

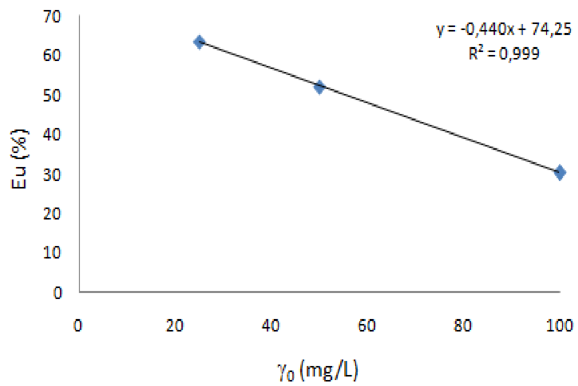

Figure 5. Removal efficiency in relation of initial phosphate concentration in wastewater, for Fe electrodes (j=0,25 mA/cm^2, γ_{NaCl}=0,25 g/L, t=10 min) (Malinovic, *et. al. 2016*)

In some of the previous studies electrocoagulation phosphate was researched the kinetics of the process, where concluded that the process follows a first order reaction kinetics (El-Shazly, Daous, 2013; Shalaby, Nassef, *et. al.*, 2014; Zhang, Zhang, Wang, 2013). At the experimental conditions (j=1 mA/cm^2, γ_0=50 mg/L, pH=3), the dependence of $ln(C_0/C)$ of the electrolysis duration (min) shows a linear relationship (Figure 6). It can be concluded that the electrocoagulation process can be described by a first order rate, which confirming the relatively high correlation coefficient for iron (R^2=0.9837) and aluminum electrodes (R^2=0.9665). Reaction rate constants of electrocoagulation phosphate amounts k=-0.0745 min^{-1} (Fe) and k=-0.1212 min^{-1} (Al), respectively. Based on the processed data (Figure 2), equation 2 and 3 representing the dependence of the phosphate concentration variation of the electrolysis duration in electrocoagulation process using iron or aluminum electrode.

$$\gamma = 70{,}2437 e^{-0{,}0745x} \quad (2)$$

$$\gamma = 93{,}7590 e^{-0{,}1212x} \quad (3)$$

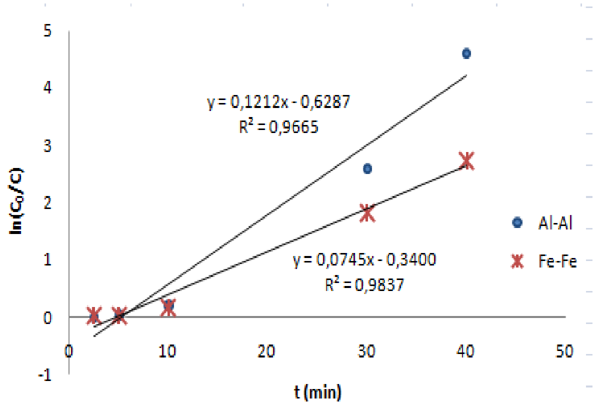

Figure 6. The dependence of ln(C_0/C) of the electrolysis duration (j=1 mA/cm^2, γ_0=50 mg/L P-PO_4, pH=3)

By using Fourier transform infrared spectroscopy (FTIR) method, can be determine characteristics of the obtained sediment. Using iron electrodes in the electrocoagulation process it was obtained an amorphous precipitate of iron hydroxide, and the sediment has a polymeric structure (Inan, Alaydin, 2014). For the case of aluminum electrodes, at acidic pH values, free Al^{3+} ion and $Al(OH)^{2+}$ hydroxocomplex species are predominate. Precipitation of phosphate involves the dissolved cations Al^{3+} and Fe^{3+} when iron or aluminum is present in the water, $FePO_4{\cdot}2H_2O$ and $AlPO_4{\cdot}2H_2O$ or mixed $Al(OH)_3$–$AlPO_4$ and $Fe(OH)_3$–$FePO_4$ form (Kobya, *et. al.*, 2010). In Figure 7 is shown capture FTIR spectroscopic analysis of resulting sediment after the treatment of synthetic wastewater by using aluminum electrodes.

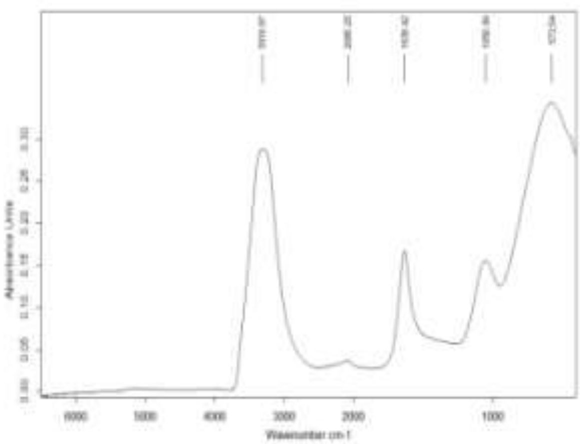

Figure 7. FTIR absorption spectrum of the resulting sediment (Al electrodes)

CONCLUSION

Using aluminum electrodes in the electrocoagulation process results a higher phosphate removal efficiency from the wastewater, in relation to the iron electrode. By increasing the electrolysis duration decreases phosphate concentration in wastewater. Based on the results, recommended concentration of the supporting electrolyte is concentration of 0.25 g/L. Increased removal efficiency is achieved with lower initial concentrations of phosphate.

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Summary/Sažetak

U ovom radu ispitan je uticaj vremena trajanja elektzrolize, početne koncentracije fosfata i koncentracije pomoćnog elektrolita na efikasnost uklanjanja fosfata elektrokoagulacijom, primjenom aluminijumskih ili željeznih elektroda. Svi eksperimenti su izvedeni u šaržnom elektrohemijskom reaktoru na sintetički pripremljenoj otpadnoj vodi početnog volumena 0.2 L. Rezultati pokazuju da sa porastom početne koncentracije fosfata smanjuje se efikasnost uklanjanaja, a sa porastom vremena trajanja elektrolize raste i efikasnost uklanjanja fosfata. Aluminijumske elektrode pokazuju veću efikasnost uklanjanja (98.9%) u poređenju sa željeznim elektrodama (93.5%) u toku 40 minuta tretmana (pH=3, j=1 mA/cm^2, γ_0=50 mg/L P–PO_4). Dodatkom pomoćnog elektrolita (γ_{NaCl}=0.25 g/L) postignuta je efikasnost uklanjanja od 50.2% za Fe, odnosno 52.1% za Al, za samo 10 minuta tretmana.