Advanced Engineering Science
http://publish.mersin.edu.tr/index.php/ades
e-ISSN 2791-8580

Importance of electrode type and configuration on reaction kinetics in removal of tetracycline antibiotic by electrocoagulation

Bahadır K. Körbahti *1, **Meltem Göktaş** 1

1 *Mersin University, Department of Chemical Engineering, Türkiye, korbahti@mersin.edu.tr; meltemgoktas969@gmail.com*

Cite this study: Korbahtı, B. K., & Göktaş, M. (2022). Importance of electrode type and configuration on reaction kinetics in removal of tetracycline antibiotic by electrocoagulation. Advanced Engineering Science, 2, 15-20

Keywords
Tetracycline
Electrocoagulation
Reaction kinetics
Aluminum electrode
Iron electrode

Research Article
Received: 08.01.2022
Revised: 13.02.2022
Accepted: 23.02. 2022
Published: 14.03.2022

Abstract

In this study, the effect of Al-Al, Al-Fe and Fe-Fe electrode configurations was investigated on reaction kinetics in removal of tetracycline antibiotic (TCY) by electrocoagulation. Response surface optimized reaction conditions were operated at 800 mg/L tetracycline concentration, 8 mA/cm^2 current density, 6 g/L NaCl electrolyte and 40°C reaction temperature at 60 min reaction time. The reaction kinetics study was carried out by nonlinear regression of the integral method with 95% confidence level on the basis of tetracycline concentration and COD concentration. The first order reaction rate equation was determined based on tetracycline concentration and reaction rate constants were calculated as 0.3919 min^{-1}, 0.2918 min^{-1} and 0.2885 min^{-1} for Al-Al, Al-Fe and Fe-Fe, respectively. The second order reaction rate equation was determined based on COD concentration and reaction rate constants were calculated as 4.67×10^{-4} mg^{-1}Lmin^{-1}, 4.32×10^{-4} mg^{-1}Lmin^{-1} and 4.28×10^{-4} mg^{-1}Lmin^{-1} for Al-Al, Al-Fe and Fe-Fe, respectively. The activation energy values based on tetracycline concentration were calculated as 3.020 kJ/mol, 0.866 kJ/mol and 0.805 kJ/mol for Al-Al, Al-Fe and Fe-Fe, respectively. Based on COD concentration, the activation energy values were determined as 9.413 kJ/mol, 10.085 kJ/mol and 9.825 kJ/mol for Al-Al, Al-Fe and Fe-Fe, respectively.

1. Introduction

Antibiotics are chemotherapeutic agents that inhibits or terminates the growth of microorganisms. They can be grouped by their chemical structure or mechanism of action and can be divided into subgroups such as β-lactams, quinolones, tetracyclines, macrolides, sulphonamides and others [1]. Antibiotics are being widely used in human medicine, veterinary medicine and in aquaculture to treat or prevent microbial infections. Wise [2] has been reported the worldwide annual consumption of antibiotics between 100,000 and 200,000 tons. Antibiotics are detected in hospital effluents, in municipal wastewater, and in sea, surface water and groundwater due to their consumption. Since antibiotics can be found in environmental matrices they are recognized as emerging pollutants [3]. Therefore, various processes have been investigated in order to remove the contamination arise from antibiotic sources [1].

Electrocoagulation is an efficient method that has been used for the treatment of many types of wastewaters [4]. Electrocoagulation involves the process of formation of coagulants by electrolytic oxidation of the sacrificial electrode, destabilization of the contaminants, particulate suspension, breaking of emulsions and aggregation of the destabilized phases to form flocs [5].

In electrocoagulation, Fe^{2+} and Al^{3+} ions generate with iron or aluminum sacrificial anodes and these ions immediately undergo spontaneous reactions to produce hydroxides and polyhydroxides [5,6]. The reactions with Fe and Al anodes are given in Equations 1-9, respectively. Fe^{2+} ions generated by electrochemical oxidation of Fe anode may form monomeric ions and polymeric hydroxy complexes depending on the pH of the solution [5,6]. $Fe(OH)_2$ precipitates remaining in equilibrium with Fe^{2+} at pH > 5.5 up to pH 9.5 or with monomeric species such as $Fe(OH)^+$, $Fe(OH)_2$ and $Fe(OH)_3^-$ at higher pH values [6].

$$\mathrm{Fe \rightarrow Fe^{2+} + 2e^-} \tag{1}$$

$$\mathrm{2H_2O + 2e^- \rightarrow 2OH^- + H_2} \tag{2}$$

$$\mathrm{Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2} \tag{3}$$

In the presence of dissolved O_2 gas, insoluble $Fe(OH)_3$ is generated and released protons can be directly reduced to H_2 gas at the cathode [6].

$$\mathrm{4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+} \tag{4}$$

$$\mathrm{8H^+ + 8e^- \rightarrow 4H_2} \tag{5}$$

$$\mathrm{4Fe + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2} \tag{6}$$

$Fe(OH)_3$ precipitate can be in equilibrium with soluble monomeric species like Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^{2+}$, $Fe(OH)_3$ and $Fe(OH)_4^-$ depending on the pH range [6]. The polymeric hydroxy complexes may be $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ [5].

Al^{3+} ions generated by electrochemical oxidation of Al anode may form monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$ in acidic medium and $Al(OH)_4^-$ in alkaline medium [5,6]. Al^{3+} ions on hydrolysis may generate $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$ and the hydrolysis products may form many monomeric and polymeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ over a wide pH range [5,6].

$$\mathrm{Al \rightarrow Al^{3+} + 3e^-} \tag{7}$$

$$\mathrm{3H_2O + 3e^- \rightarrow 3OH^- + \tfrac{3}{2}H_2} \tag{8}$$

$$\mathrm{Al + 3H_2O \rightarrow Al(OH)_3 + \tfrac{3}{2}H_2} \tag{9}$$

The reactions involving chlorine ions in Equations 10-12 could also occur in the presence of NaCl supporting electrolyte [7]:

$$\mathrm{2Cl^- \rightarrow Cl_2 + 2e^-} \tag{10}$$

$$\mathrm{Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+} \tag{11}$$

$$\mathrm{HOCl \rightleftharpoons OCl^- + H^+} \tag{12}$$

In electrocoagulation, the pollutants can be removed by insoluble flocs of $Fe(OH)_3$ and $Al(OH)_3$ by surface complexation or electrostatic attraction [5,6]. The excess amount of aluminum and iron ions in the solution also feasible by anodic corrosion with Cl^- ions [6]. In this study, the effect of Al-Al, Al-Fe and Fe-Fe electrode configurations was investigated on reaction kinetics in removal of tetracycline antibiotic (TCY) by electrocoagulation in the presence of NaCl supporting electrolyte in a batch electrochemical reactor. The reaction kinetic models were developed with the nonlinear regression of the integral method on the basis of tetracycline concentration and COD concentration.

2. Material and Method

Tetracycline hydrochloride (Sigma-Aldrich), mercury sulfate (Merck), sodium chloride (Merck) and acetonitrile (Merck) were received in extra pure grade. Double distilled water was produced in our laboratory. Batch electrochemical system was equipped with jacketed electrochemical reactor, Ametek Sorensen XFR 60-46 programmable DC power supply, Lauda RE 620S refrigerated circulating water bath with thermostat control, Heidolph RZR 2021 mechanical mixer, Heidolph PD 5206 peristaltic pump and thermometer. Aluminum and iron electrodes were obtained from local sources and used as anode and cathode with 120 cm^2 surface area. The reaction volume was 600 mL and mechanically stirred at 500 rpm. Samples were taken from the reaction medium at regular intervals for HPLC and chemical oxygen demand (COD) analysis. HPLC analysis were done using Inertsil ODS-3 column (5 mm, 4.6×250 mm) in a Shimadzu Prominence LC-20AD Liquid Chromatography. Gradient mobile phase was acetonitrile and water (50/50) (v/v) at a flow rate of 1.5 mL/min. UV/Vis detection wavelength of tetracycline antibiotic was at 254 nm. Column temperature was set at 40°C. Injection volume was 40 mL. Merck Spectroquant® TR 420 thermoreactor and Nova 60 photometer were used for the COD analysis.

3. Results and Discussion

The response surface optimized reaction conditions were operated at 800 mg/L tetracycline concentration, 8 mA/cm^2 current density, 6 g/L NaCl electrolyte and 40°C reaction temperature at 60 min reaction time in order to determine the reaction kinetics in removal of tetracycline antibiotic by electrocoagulation. The reaction kinetics study was carried out by nonlinear regression of the integral method based on tetracycline concentration and COD concentration. Nonlinear regression is the modeling of the observational data by a function which is a nonlinear combination of the model parameters and depends on one or more independent variables. The experimental reaction kinetics data were processed for the nonlinear models using CurveExpert Professional 2.7 software.

The nth order reaction kinetics can be expressed in Equation 13 [8,9] and by integrating with the boundary conditions in Equation 14, the solutions of first order and second order reaction kinetics can be obtained in Equations 15 and 16, respectively.

$$\frac{dC_A}{dt} = -kC_A^n \tag{13}$$

$$\begin{aligned} @\ t = 0 \quad &\Rightarrow \quad C_A = C_{Ao} \\ @\ t = t \quad &\Rightarrow \quad C_A = C_A \end{aligned} \tag{14}$$

The solution of first order reaction kinetics for n=1:

$$C_A = C_{Ao}e^{-kt} \tag{15}$$

The solution of second order reaction kinetics for n=2:

$$C_A = \frac{C_{Ao}}{1 + C_{Ao}kt} \tag{16}$$

The reaction rate constant, k, is strongly dependent on the reaction temperature and this temperature dependence could be correlated by Arrhenius equation with the activation energy of the reaction as in Equation 17 [8,9]. The activation energy of the reaction is defined as the minimum energy that must be possessed by reacting molecules before the reaction will occur [8].

$$k = k_o e^{\frac{-E_a}{RT}} \tag{17}$$

In Equation 17, k_o is pre-exponential constant, R is gas constant as 8.314 J/(mol.K), T is absolute temperature in K and E_a is the activation energy in J/mol. The nth order reaction rate can be obtained in Equation 18 by substituting Equation 17 in terms of activation energy. Finally, the solutions of first order and second order reaction kinetics can be obtained in Equations 19 and 20, respectively.

$$\frac{dC_A}{dt} = -\left(k_o e^{\frac{-E_a}{RT}}\right) C_A^n \tag{18}$$

The solution of first order reaction kinetics with activation energy (n=1):

$$C_A = C_{Ao} e^{-\left(k_o e^{\frac{-E_a}{RT}}\right)t} \tag{19}$$

The solution of second order reaction kinetics with activation energy (n=2):

$$C_A = \frac{C_{Ao}}{1 + C_{Ao}\left(k_o e^{\frac{-E_a}{RT}}\right) t} \tag{20}$$

Equations 19 and 20 were solved by nonlinear regression using CurveExpert Professional 2.7 software and the kinetic model results with the experimental reaction kinetics data were demonstrated in Figure 1 and Figure 2 for tetracycline removal and COD removal by electrocoagulation with Al-Al, Al-Fe and Fe-Fe electrode configurations, respectively. Tetracycline removal and COD removal was achieved with the insoluble flocs of $Fe(OH)_3$ and $Al(OH)_3$ by surface complexation or electrostatic attraction as well as by indirect oxidation due to the formation of $HOCl/OCl^-$ redox oxidants in the aqueous medium by Cl_2 discharge on the anode. The initial electrochemical degradation rate of tetracycline antibiotic was found higher than the COD removal. This result showed that the formation of intermediates and by-products were removed at a much lower reaction rate.

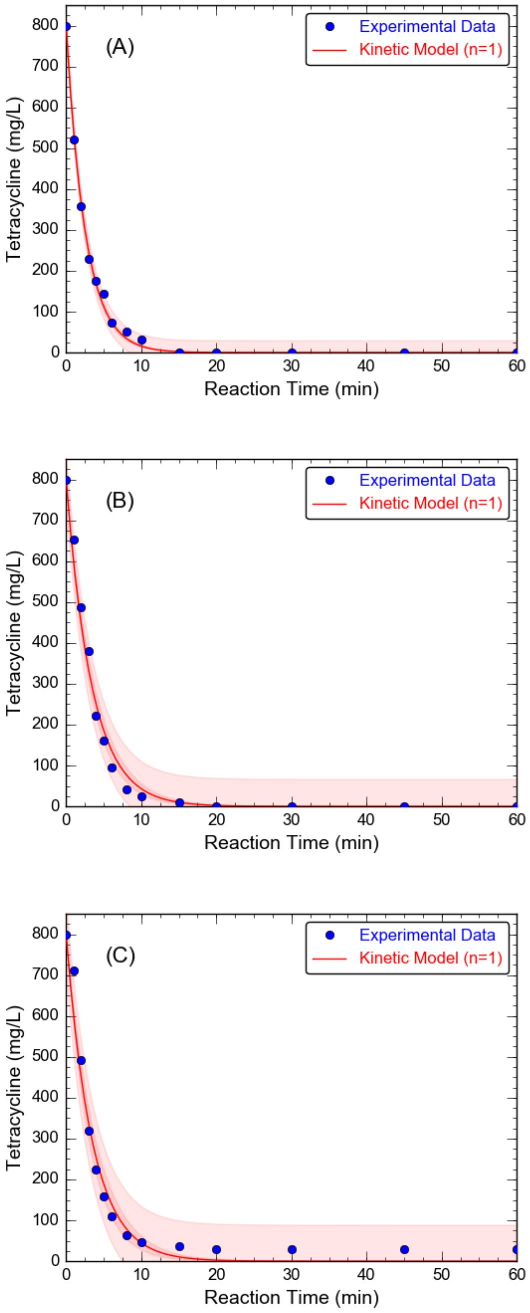

Figure 1. Tetracycline removal by electrocoagulation with (a) Al-Al electrodes, (b) Al-Fe electrodes, (c) Fe-Fe electrodes ($[TCY]_o$=800 mg/L)

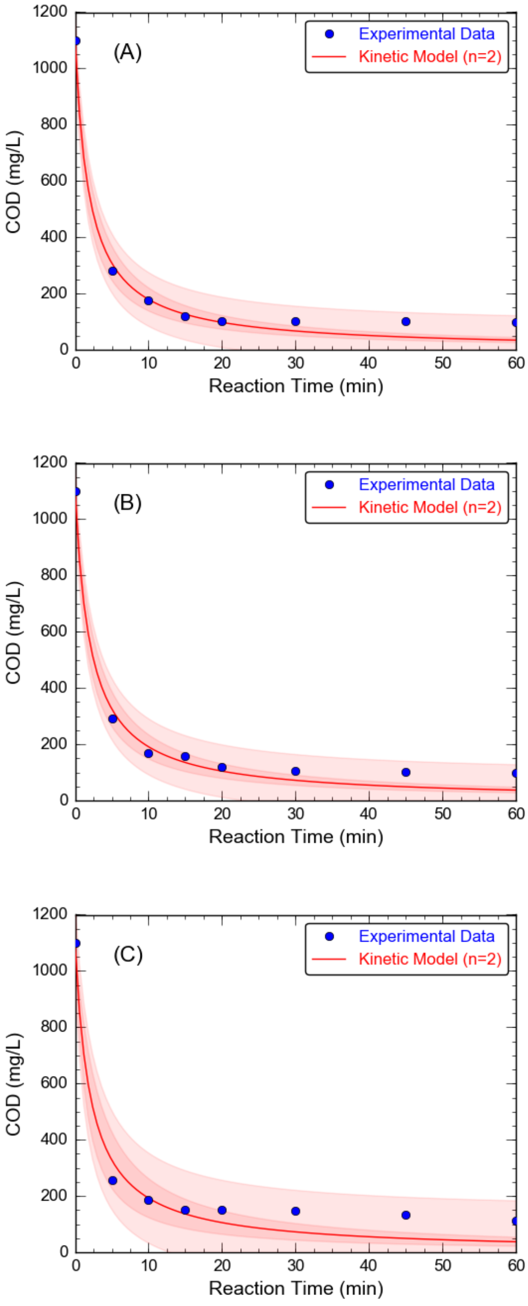

Figure 2. COD removal by electrocoagulation with (a) Al-Al electrodes, (b) Al-Fe electrodes, (c) Fe-Fe electrodes ($[COD]_o$=1100 mg/L)

The reaction order and the reaction rate constant values were found by nonlinear regression of the integral method with 95% confidence level as outlined in Table 1. The reaction order was determined as 1 for tetracycline removal and as 2 for COD removal. The relationships developed between the parameters were in very good agreement according to the regression coefficients.

Table 1. Reaction order and reaction rate constant values for removal of tetracycline antibiotic by electrocoagulation with Al-Al, Al-Fe and Fe-Fe electrode configurations

Parameter	Electrode configuration	Reaction order	Reaction rate constant	R^2
Tetracycline removal	Al-Al	1	0.3919 min^{-1}	0.9970
	Al-Fe	1	0.2918 min^{-1}	0.9872
	Fe-Fe	1	0.2885 min^{-1}	0.9764
COD removal	Al-Al	2	4.67×10^{-4} $mg^{-1}Lmin^{-1}$	0.9888
	Al-Fe	2	4.32×10^{-4} $mg^{-1}Lmin^{-1}$	0.9877
	Fe-Fe	2	4.28×10^{-4} $mg^{-1}Lmin^{-1}$	0.9665

The first order reaction rate constants based on tetracycline concentration were calculated as 0.3919 min^{-1}, 0.2918 min^{-1} and 0.2885 min^{-1} for Al-Al, Al-Fe and Fe-Fe, respectively. Based on COD concentration, the second order reaction rate constants were determined as 4.67×10^{-4} $mg^{-1}Lmin^{-1}$, 4.32×10^{-4} $mg^{-1}Lmin^{-1}$ and 4.28×10^{-4} $mg^{-1}Lmin^{-1}$ for Al-Al, Al-Fe and Fe-Fe, respectively. The second order behavior can be attributed to the existence of an energized and unstable form for the reactant [9]. It is known that reaction rate constants drastically affect the rate of the reactions. According to these results, the reaction rates with electrode configurations were found as Al-Al > Al-Fe > Fe-Fe for both tetracycline removal and COD removal. It can be concluded that $Al(OH)_3$ flocs more rapidly destabilize the pollutants in the solution than $Fe(OH)_3$ flocs. In addition, the use of hybrid configuration was increased the reaction rate slightly than using single Fe electrodes in the electrocoagulation.

The activation energy values were obtained in Table 2 by nonlinear regression of the experimental reaction kinetics data with 95% confidence level. The activation energy values based on tetracycline concentration were calculated as 3.020 kJ/mol, 0.866 kJ/mol and 0.805 kJ/mol for Al-Al, Al-Fe and Fe-Fe, respectively. Based on COD concentration, the activation energy values were determined as 9.413 kJ/mol, 10.085 kJ/mol and 9.825 kJ/mol for Al-Al, Al-Fe and Fe-Fe, respectively. It was reported that fast reactions generally have small activation energy values and E_a is typically less than 40 kJ/mol for diffusion-controlled homogeneous reactions [10-12]. The activation energy values of COD removal are higher than the values of tetracycline removal confirming that COD removal is much more difficult than tetracycline removal due to the recalcitrant nature of the degradation products. The activation energy values with electrode configurations were found as Fe-Fe < Al-Fe < Al-Al for tetracycline removal and Al-Al < Fe-Fe < Al-Fe for COD removal. The results indicated the requirement of Fe-Fe electrode configuration in tetracycline removal and Al-Al electrode configuration in COD removal for the minimum activation energy.

Table 2. Activation energy and pre-exponential constant values for removal of tetracycline antibiotic by electrocoagulation with Al-Al, Al-Fe and Fe-Fe electrode configurations

Parameter	Electrode configuration	Activation energy (kJ/mol)	Pre-exponential constant	R^2
Tetracycline removal	Al-Al	3.020	1.2505 min^{-1}	0.9970
	Al-Fe	0.866	0.4071 min^{-1}	0.9872
	Fe-Fe	0.805	0.3931 min^{-1}	0.9764
COD removal	Al-Al	9.413	0.0174 $mg^{-1}Lmin^{-1}$	0.9888
	Al-Fe	10.085	0.0208 $mg^{-1}Lmin^{-1}$	0.9877
	Fe-Fe	9.825	0.0187 $mg^{-1}Lmin^{-1}$	0.9665

4. Conclusion

In this study, the effect of Al-Al, Al-Fe and Fe-Fe electrode configurations was investigated on reaction kinetics in removal of tetracycline antibiotic by electrocoagulation in the presence of NaCl supporting electrolyte in a batch electrochemical reactor. The reaction order was determined as 1 for tetracycline removal and as 2 for COD removal with nonlinear regression of the integral method. According to the calculated values of the reaction rate constants, the reaction rates with electrode configurations were found as Al-Al > Al-Fe > Fe-Fe for both tetracycline removal and COD removal. The activation energy values with electrode configurations were determined as Fe-Fe < Al-Fe < Al-Al for tetracycline removal and Al-Al < Fe-Fe < Al-Fe for COD removal. The results showed that Fe-Fe electrode configuration is feasible in tetracycline removal and Al-Al electrode configuration is feasible in COD removal for the minimum activation energy. $Al(OH)_3$ flocs more rapidly destabilize the pollutants in the solution than $Fe(OH)_3$ flocs. The use of hybrid configuration was increased the reaction rate slightly than using single Fe electrodes in the electrocoagulation.

Acknowledgement

The authors gratefully acknowledge Mersin University Scientific Research Projects Center (MEÜ BAP) for the financial support.

Funding

This study was supported by Mersin University Scientific Research Projects Center (MEÜ BAP) with Grant No. 2019-3-TP2-3823.

Author contributions

Bahadır K. Körbahti: Conceptualization, Methodology, Writing-Reviewing and Editing. **Meltem Göktaş:** Investigation, Data collection, Writing-Original draft preparation.

Conflicts of interest

The authors declare no conflicts of interest.

References

1. Kümmerer, K. (2009). Antibiotics in the aquatic environment-A review-Part I. *Chemosphere*, 75, 417-434.
2. Wise, R. (2002). Antimicrobial resistance: priorities for action. *Journal of Antimicrobial Chemotherapy*, 49, 585-586.
3. Homem, V. and Santos, L. (2011). Degradation and removal methods of antibiotics from aqueous matrices-A review. *Journal of Environmental Management*, 92, 2304-2347.
4. Khandegar, V. and Saroha, A.K. (2013). Electrocoagulation for the treatment of textile industry effluent-A review. *Journal of Environmental Management*, 128, 949-963.
5. Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J. and Cocke, D.L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials*, B114, 199-210.
6. Brillas, E. and Martínez-Huitle, C.A. (2015). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied Catalysis B: Environmental*, 166-167, 603-643.
7. Chen, G. (2004). Electrochemical technologies in wastewater treatment, *Separation and Purification Technology*, 38, 11-41.
8. Fogler, H.S. (1992). *Elements of Chemical Reaction Engineering*, Prentice Hall International Editions, USA.
9. Levenspiel, O. (1999). *Chemical Reaction Engineering*. John Wiley & Sons, USA.
10. Körbahti, B.K. and Demirbüken, P. (2017). Electrochemical Oxidation of Resorcinol in Aqueous Medium Using Boron-Doped Diamond Anode: Reaction Kinetics and Process Optimization with Response Surface Methodology. *Frontiers in Chemistry*, 5, 75.
11. Körbahti B.K. and Artut, K. (2010). Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes. *Desalination*, 258, 219-228.
12. Samet, Y., Chaabane Elaoud, S., Ammar, S. and Abdelhedi, R. (2006). Electrochemical degradation of 4-chloroguaiacol for wastewater treatment using PbO_2 anodes. *Journal of Hazardous Materials*, B138, 614-619.