

Investigation of Electrolysis Process Performance by Graphite Electrodes for De-Colorization of Phenolphthalein and Phenol Red from Aqueous Solution

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ABSTRACT

This study elucidates the de-colorization of phenolphthalein and phenol red from aqueous solution through electrochemical oxidation technique. An electrochemical reactor had 1 liter volume that used 2 graphite electrodes. Effect of electric power voltage, inter electrode distance and electrolyte concentration was investigated in this system.

It was found that the optimum conditions for completely removal of phenolphthalein was at voltage of 48 V, retention time of 9 minutes, distance between the electrode of 5 cm, and the salt concentration of 1.5 g/l. Also completely removal of phenol red was at voltage of 48 V, retention time of 8 minutes, distance between the electrode of 5 cm, and the salt concentration of 2 g/l. Phenol red and phenolphthalein COD removal efficiency was 85 and 80 percent respectively.

The results suggest that the electrolysis process is an effective way to removal of phenolphthalein and phenol red color from effluent, because of it can completely remove the color in a short time.

Keywords: De-colorization, Electrolysis, Graphite electrodes, Phenolphthalein, Phenol red

INTRODUCTION

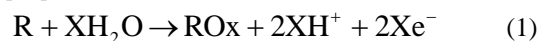
Color is a visual pollutant. Not only disrupt the aesthetic quality of surface waters, but effect on aquatic ecosystems by reducing light penetration [1]. Many of the organic compounds that cause pollution in natural water are chemical dyes that are used in industrial and domestic [2-3]. In absence of adequate treatment, colored effluents are dangerous for the environment. Dyes prevent the penetration of light into the water and will interfere photosynthesis and biological activities [1-4]. Also, it can be toxic for fish, fauna and flora in receiving water and these contaminants should be removed [5-7].

So far, for removing the color from water used the various physical, chemical and physico-chemical processes such as precipitation, chemical coagulation, sand filtration, ion exchange, adsorption on activated carbon, chemical oxidation (Cl₂, O₃, H₂O₂), membrane processes (NF, RO) and biological processes [8-10]. Although these methods are effective, but it is often inadequate and costly.

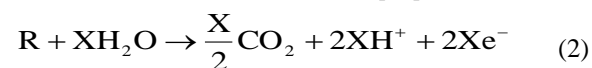
In recent years, electrochemical methods have been used for colouring wastewater treatment. Along with the increasing environmental restrictions on effluent discharge to the environment, more attention has to

use it [11]. This method has several advantages, including environmentally friendly, allowing purification of liquids, gases and solids, easy to set up, simple equipment, short retention time, low sludge production and higher density [12-13]. In this way, the electrons are the main cause of treatment. Oxidation reaction at the anode and reduction at the cathode occurs respectively. The efficiency of the process depends on parameters such as the type of electrode, pH, potential difference, electrical conductivity and the distance between the electrodes [14].

Electro-oxidation is one of the processes used in electrolysis. The overall process of anodic oxygen transport reaction occurs by the following where R is the organic reactor and ROx is oxidized product (Eq. 1) [15].

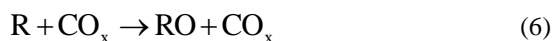
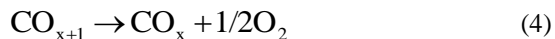
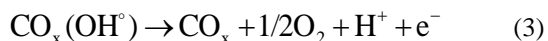


In addition, R can be mineralized by equation (2) that is known the combustion reaction [15].



If graphite electrodes are used, it has high electro-catalytic activity on the anode and oxidation occurs at the electrode surface. In the first stage anodic oxidation reaction, H₂O discharge at the anode to produce hydroxyl radicals. Followed by the second phase hydroxyl radicals react with oxygen already there oxide anode. With the ability to transfer oxygen from the hydroxyl radical to the anode oxide, oxide is formed above CO_x⁺¹. On the surface of the anode, active oxygen can create in two modes: (1) the physical absorption (hydroxyl radicals' absorbed OH^o), (2) to chemical absorption (oxygen in network MO_x⁺¹) [13].

In the presence of oxidizable organic materials, physical absorption of reactive oxygen (OH^o) makes full use of organic materials and chemical absorption contributes in the formation of selective oxidation products, in accordance with the following reaction:



One of the main wastewater contained colors is textile wastewater. The large quantities of textile industries in wastewater contain chemicals, which cause a significant environmental problem [16-18]. The three most important of environmental impacts are biological oxygen demand (BOD), toxicity and color [8]. The common methods for color removal are: adsorption, coagulation, chemical oxidation, and advanced oxidation processes. However, these processes are quite expensive and involve several operational problems [19]. Among various techniques, electrochemical treatment of organic compounds is very popular due to simplicity, efficiency, short process period, and low produced sludge [20].

Electrochemical methods have been successfully used in color wastewater treatment. For example Daneshvar and Jafarzadeh were able to remove color from Naghshe-Jahan-Tabriz Company's wastewater by electrochemical method with iron electrodes. They achieved to 94 percent removal efficiency with 80-90 A/m² current density in 8 minutes reaction time [21].

Jia and colleagues were removed color and COD of color wastewater with activated carbon fiber (ACF) electrode. Removal efficiency for color and COD were 90% and 80% respectively with 25 volt at 60 minutes [14].

In another study, Radha and colleagues were removed color and COD from textile wastewater with graphite electrode as anode and stainless steel

electrode as cathode. They could remove color and COD with removal efficiency 96% and 68% respectively, with 0.6 A current at 60 minutes [13].

In recent years, many investigations have been especially focused on the use of different anode materials such as lead dioxide, glassy carbon [22], Sb doped SnO₂ [23], Ti/IrO₂, and platinum [24] in electrochemical treatment process. However, some of tested anode materials have been shown to rapidly lose efficacy due to surface fouling (such as glassy carbon) [22], but others not only have selectively oxidized pollutants without significant lose efficacy but also cause complete mineralization of organics to CO₂ (such as Ti/IrO₂, Pt, SnO₂) [24]. Graphite was used as an anode during electrochemical treatment that it is cost benefit and gives satisfactory results [25].

The aim of this work was to study electrochemical oxidation of phenolphthalein and phenol red in synthesized wastewater on a laboratory scale by using graphite electrodes. In this view, the effect of operating parameters such as electric power voltage, inter electrode distance and electrolyte concentration on the complete color removal of point of appropriate retention time was determined.

MATERIALS AND METHODS

Experimental set-up

Experiments were carried out in a square electrochemical glass batch reactor (having dimensions 14cm × 11.5 cm × 11.5 cm) in laboratory scale at ambient conditions. The batch experimental device is schematically shown in Fig. 1. The reactor was filled with 900 ml volume of wastewater and pH was adjusted by 1 N sodium hydroxide at 6.5. Graphite rod was used as anode and cathode electrodes with a dimension of 1 cm × 1 cm × 13.5 cm. The electric power was supplied with regulated DC power supply. NaCl (99%) was used as electrolyte solution. Experiments were carried out at a constant concentration of phenolphthalein (500 mg/l) and phenol red (5000 mg/l); different electrode gap of 3, 5, 7 and 9 cm; different electric power voltage of 12, 24, 48 V; and different NaCl concentration of 0.5, 1, 1.5, and 2 mg/l. As the experiment proceeded, the wastewater sampling was done at interval times to analyze COD.

All experiment was performed in triplicate and average values were analyzed with descriptive statistic by excel software.

Materials and instruments

Phenolphthalein and phenol red were bought from Merck Company. Principal characteristics of these compounds are given in Table 1. Dye concentration was measured using spectrophotometer (DR5000,

HACH) at a wavelength corresponding to the maximum absorbance of 552 and 431 nm for Phenolphthalein and phenol red, respectively. The detection limit was measured about 0.001 mg/l. A gentle magnetic stirring rate of 200 rpm was applied to the solutions in all tests (ALPHA/AG-5054).

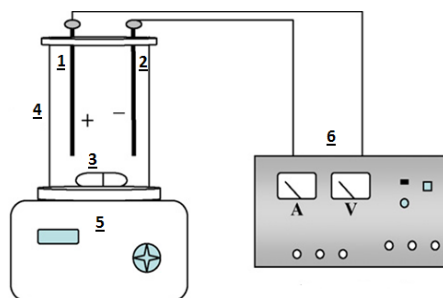
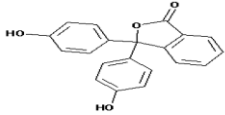
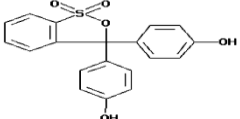


Fig. 1 Diagram of the experimental setup for the electrolysis process (1- anode; 2-cathod; 3- magnet; 4- batch reactor; 5- magnetic stirrer; 6- DC power supply)

Table 1. Main characteristics of Phenolphthalein and phenol red

| Dye | Chemical structure | Chemical group | λ_{\max} (nm) | Molecular weight (g/mol) |
|-----------------|--|-------------------------|-----------------------|--------------------------|
| phenolphthalein |  | Hydroxyl triarylmethane | 552 | 318.32 |
| phenol red |  | Triarylmethane | 431 | 354.39 |

RESULTS AND DISCUSSION

In this study, for decolonization used electrolysis process with graphite electrodes. The variable's effects of voltage, the concentration of NaCl and the distance between the electrodes were evaluated on color removal efficiency based time. Results are shown in figures 2 to 5.

In investigation, the effect of electric power voltage on the time required for color removal reaches 100%; different current voltage was studied from 12 to 48 V. As saw in Fig. 2 and 3, increasing current voltage results in increasing removal efficiency. This result is agreement with Faraday's law that which the hypochlorite content increases with voltage [26]. At a constant electrode distance of 3 cm, the time require for complete removal of phenolphthalein and phenol red was 26 and 30 min, respectively, at current voltage of 48 V. However, this time increased to 95 and 120 min, respectively, when voltage decreased to 12 v. The phenolphthalein and phenol red removal increased about 72% and 70%, respectively, as electric power voltage increased from 12 to 48 V at inter electrode distance of 3 cm. The higher electric power voltage can lead to the formation of higher free radicals such as $\bullet\text{OH}$, $\bullet\text{O}$, H^+ and OCl^- , etc. [27]; which can oxidize organic matter included in wastewater. More hydroxyl and hypochlorite radicals

are generated in solution at higher current density because of higher oxidation of organic matter included in wastewater and consequently decreasing in removal time [13]. Piya-arehtam [28] and Dalvand [29] obtained the same results.

The effect of inter electrode distance is investigated between 3 and 9 cm as shown in Fig. 2 and 3. The results show dye removal increases slightly with decreasing electrode gap. In a fixed electric power voltage, when the inter electrode distance was increased from 3 to 9 cm, the time required for dye removal of 100% increased around 30 min for both dyes studied. These results are agreement with those found in the study of Aoudj [30] and Xu [31]. In the electrolysis process, there is a close relationship between the electric power voltage, current density and the distance of electrodes. When the electrodes distance increase, the electrical current was decreased which cause less interaction of ions with hydroxyl. Therefore, to achieve a certain current density, the voltage must be increased. In other words, this is because that the shorter distance will speed up the anion discharge on the anode and improve the oxidation [31].

Generally, NaCl was used as supporting electrolyte to obtain the conductivity in the oxidation process. The influence of NaCl concentration on the dye

removal rate has been tested for three different concentrations with an initial dye concentration of 500 and 5000 mg/l of phenolphthalein and phenol red and the electric power voltage of 48 V. The effect of NaCl concentration on the time required for dye removal of 100% is shown in Fig. 4 and 5.

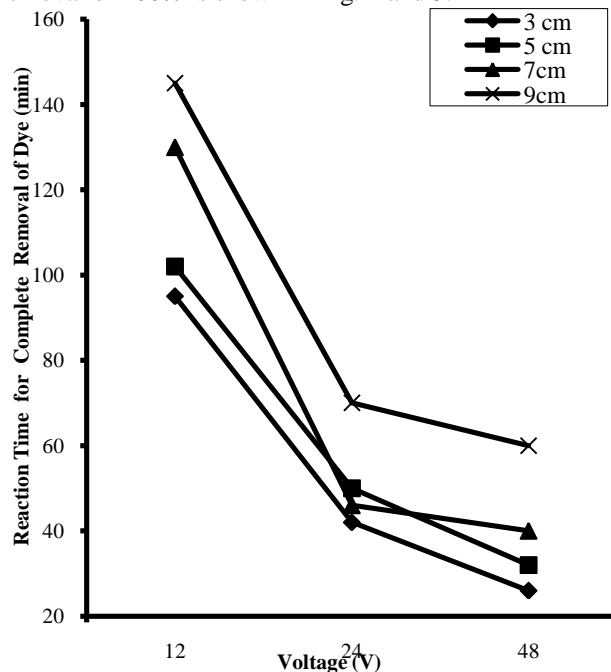


Fig. 2. The effect of electric power voltage on phenolphthalein removal efficiency at various inter electrode distances of 3, 5, 7 and 9 cm

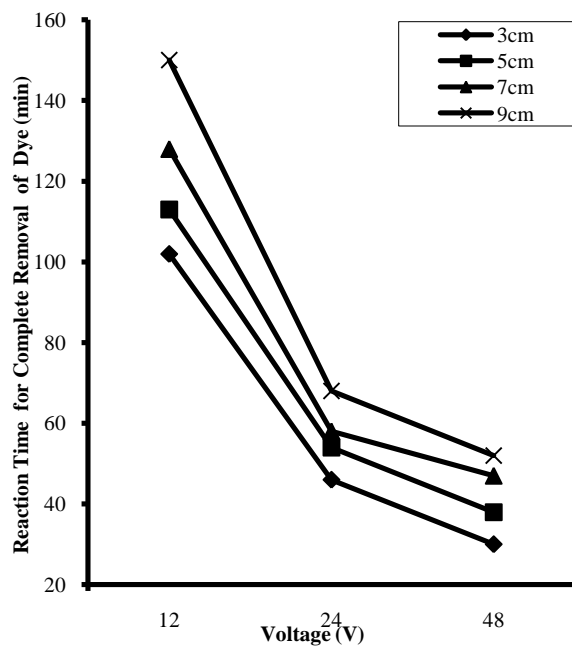


Fig. 3. The effect of electric power voltage on phenol red removal efficiency at various inter electrode distances of 3, 5, 7 and 9 cm

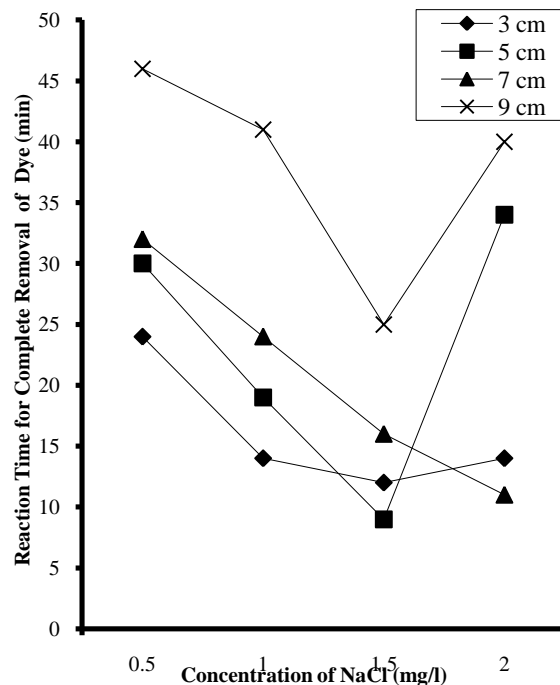


Fig. 4. The effect of NaCl concentration on phenolphthalein removal efficiency at various inter electrode distances of 3, 5, 7 and 9 cm and constant electric power voltage of 48 Volt.

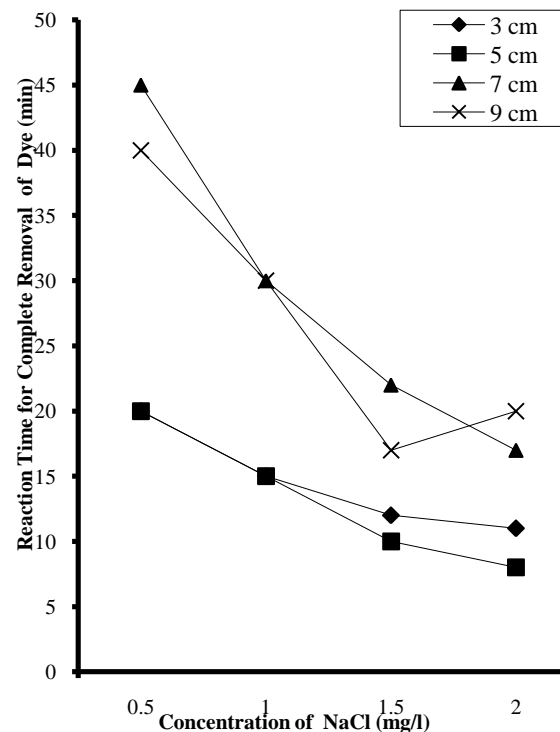


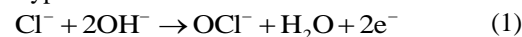
Fig. 5. The effect of NaCl concentration on phenol red removal efficiency at various inter electrode distance of 3, 5, 7 and 9 cm and constant electric power voltage of 48 Volt.

the results, with increasing NaCl concentration, a decrease in the removal time of dyes was observed. At a fixed inter electrode distance of 3 cm, the time required for 100% dyes removal decreased significantly (42% and 45% for phenolphthalein and phenol red, respectively) when the NaCl concentration was increased from 0.5 to 2 g/l. The time required for 100% phenol red removal reached minimum (8 min) at NaCl concentration of 2 g/l and inter electrode distance of 5 cm. According to the results, this time was 9 min at NaCl concentration of 1.5 g/l and inter electrode distance of 5cm for 100% phenolphthalein removal. It was stated that the conductivity of the solution and the current density increases when the concentration of salt in solution increases. In addition, NaCl would increase conductivity and the end, decrease power consumptions [32].

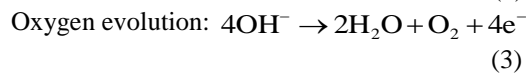
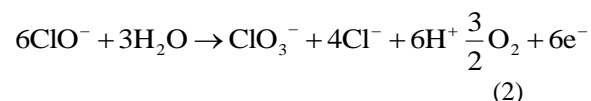
In addition, the higher NaCl concentration will generally cause an increase in generated hypochlorite ions that act as the main oxidizing agent in the dye degradation. The main reactions occurring during the anodic oxidation of organic compounds in the presence of NaCl are [27] (Eqs. 1-4):

- **Anode**

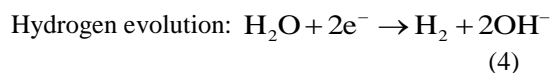
Hypochlorite formation:



Chlorate formation:



- **Cathode**



- In Solution and/or near the anode surface Indirect oxidation of organic compound and its oxidation intermediate with hypochlorite:



Moreover, the presence of chlorine in the effluent might cause indirect pollutant oxidation. Because, producing of Cl_2 , ClO_2 , $\text{OH}\cdot$, $\text{O}\cdot$, $\text{ClOH}\cdot$, H_2O_2 , O_2 , H_2 , CO_2 products during the brine solution electrolysis. Therefore, increasing in NaCl concentration increases the oxidative radicals, which favor the rate of oxidation of organic material [25]. The progress of the destruction of the organic dyes studied has been evaluated by COD measurement at optimum conditions (electric power voltage of 48 V; inter electrode distance of 5 cm; and NaCl concentration of 2 g/l for phenol red and 1.5 g/l for phenolphthalein). The results show a COD

decreasing of 85% and 80% for phenol red and phenolphthalein, respectively, at optimum conditions.

CONCLUSION

In this study, the electrolysis process was used to oxidation of phenol red and phenolphthalein organic dyes in wastewater under various operational conditions to investigate the color removal efficiency. It was observed from the result that the time required for 100% dye removal decreased with increasing electric power voltage and NaCl concentration; and decreasing inter electrode distance. In this way, the time required for 100% phenol red removal reached a minimum (8 min) at NaCl concentration of 2 g/l and inter electrode distance of 5 cm. According to the results, this time was obtained 9 min at NaCl concentration of 1.5 g/l and inter electrode distance of 5 cm for phenolphthalein. In this condition, the COD removal efficiency reached maximum (85 and 80 percent for phenolphthalein and phenol red, respectively).

ETHICAL ISSUES

Ethical issues have been completely observed by the authors.

CONFLICT OF INTERESTS

Authors have no conflict of interests.

AUTHORS' CONTRIBUTIONS

All authors participated in design, conduct of the study, and have contributed in drafting, revising and approving of the manuscript.

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REFERENCES

- [1] Zin, N. Decolorization of dye solution containing azo acid orange 7 by electricity [dissertation]. Malaysia: Faculty of Civil Engineering University Technology Malaysia. 2005; 7-10.
- [2] Daneshvar N, Vatanpour V, Khataee AR, Rasoulifard MH, Rastegar M. Decolorization of mixture of dyes containing malachite green and orange II by fenton-like reagent. Journal of Color Science and Technology. 2008; 1: 83-89.
- [3] Politiv D, Sidiras D. Wastewater treatment for dyes and heavy metals using modified pine sawdust

- as adsorbent. *Procedia Engineering*. 2012; 42: 1969–82.
- [4] Chen X, Chen G, Yue PL. Investigation on the electrolysis voltage of electrocoagulation. *Journal of Chemical Engineering Science*. 2002; 57: 2449–55.
- [5] Daneshvar N, Ashassi-Sorkhabi H, Tizpar A. Decolorization of orange II by electrocoagulation method. *Journal of Separation and Purification Technology*. 2003; 31: 153–62.
- [6] Sathian S, Rajasimman M, Radha G, Shanmugapriya V, Karthikeyan C. Performance of SBR for the treatment of textile dye wastewater: Optimization and kinetic studies. *Alexandria Engineering Journal*. 2014; 53: 417–26.
- [7] De Jager D, Sheldon MS, Edwards W. Color Removal from Textile Wastewater Using a Pilot-Scale Dual-Stage MBR and Sequent RO System. *Separation and Purification Technology*. 2014; 135: 135–44.
- [8] Diez MC, Mora ML, Videla S. Adsorption of phenolic compounds and color from bleached Kraft mill effluent allophonic compounds. *Journal of Water Research*. 1999; 33(1): 125–30.
- [9] Clark T, Bruce M, Anderson S. Decolorization of extraction stage bleach plant effluent by combined hypochlorite oxidation and anaerobic treatment. *Journal of Water Science Technology*. 1994; 29(5-6): 421–32.
- [10] Kobya M, Can OT, Bayramoglu M. Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *Journal of Hazardous materials*. 2003; B100: 163–78.
- [11] Zaroual Z, Azzi M, Saib N, Chaint E. Contribution to the study of electrocoagulation mechanism in basic textile effluent. *Journal of Hazardous materials*. 2005; 131: 73–78.
- [12] Rajeshwar K, Ibanez J G, Swain G M. Electrochemistry and environment. *Journal of applied electrochemistry*. 1994; 24: 1077–91.
- [13] Radha KV, Sridevi V, Kalaivani K. Electrochemical oxidation for the treatment of textile industry wastewater. *Journal of Bioresource Technology*. 2009; 100: 987–90.
- [14] Jia J, Yang J, Liao J, Wang W, Wang Z. Treatment of dyeing wastewater with ACF electrodes. *Journal of Water Research*. 1999; 33(3): 881–84.
- [15] Chandra mouli P, Venkata Mohn S, Jayarama Reedy S. Electrochemical processes for remediation of wastewater and contaminated soil: emerging technology. *Journal of Scientific & Industrial research*. 2004; 63: 11–19.
- [16] Daneshvar N, Ashassi-Sorkhabi H, Tizpar A. Decolorization of orange II by electrocoagulation method. *Separation and Purification Technology*. 2003; 31: 153–62.
- [17] Panizza M, Cerisola G. Removal of color and COD from wastewater containing acid blue 22 by electrochemical oxidation. *Journal of Hazardous Materials*. 2008; 153: 83–88.
- [18] Kobya M, Senturk E, Bayramoglu M. Treatment of poultry slaughterhouse wastewaters by electrocoagulation. *Journal of Hazardous Materials*. 2006; 133: 172–76.
- [19] Wijannarong S, Aroonsrimorakot S, Thavipoke P, Kumsop A, Sangjan S. Removal of Reactive Dyes from Textile Dyeing Industrial Effluent by Ozonation Process. *APCBEE Procedia*. 2013; 5: 279–82.
- [20] Tichonovas M, Krugly E, Racys V, Hippler R, Kauneliene V, Stasiulaitiene I, Martuzevicius D. Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment. *Chemical Engineering Journal*. 2013; 229: 9–19.
- [21] Daneshvar N, jafarzadeh N. Treatment of textile wastewater containing basic dyes by electrocoagulation process. *Journal of Water and wastewater*. 2009; 57: 22–29.
- [22] Gattrell M, Kirk D. The electrochemical oxidation of aqueous phenol at a glassy carbon electrode. *Journal of Chemistry Engineering*. 1990; 68: 997–03.
- [23] Comninellis C, Pulgarin C. Anodic oxidation of phenol for waste water treatment. *Journal of Applied Electrochemistry*. 1991; 21: 703–08.
- [24] Comninellis C. Electrocatalysis in the electrochemical conversion/ combustion of organic pollutants for waste water treatment. *Electrochimica Acta*. 1994; 39: 1857–62.
- [25] Vlysside AG, Papaioannou D, Loizidou M, Karlis PK, Zorpas AA. Testing an electrochemical method for treatment of textile dye wastewater. *Waste Management*. 2000; 20: 569–57.
- [26] Ashtoukhy E.S.Z.EI, Amin NK, Abdelwahab O. Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor. *Journal of Chemical Engineering*. 2009; 146: 205–10.
- [27] Ugurlu M, Karaoglu MH, Kula I. Experimental investigation of chemical oxygen demand, lignin and phenol removal from paper mill effluents using three-phase three-dimensional electrode reactor. *Journal of Environ. Stud*. 2006; 15: 647–54.
- [28] Piya-arehtam P, Shenchunthichai K, Hunsom M. Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode. *Water Research*. 2006; 54: 1–8.

[29] Dalvand A, Gholami M, Joneidi A, Mahmoodi NM. Investigation of electrochemical coagulation process efficiency for removal of reactive red 198 from colored wastewater. *Journal of Color science and technology*. 2009; 3: 97-05.

[30] Aoudj S, Khelif A, Drouichea N, Hecini M, Hamitouche H. Electrocoagulation process applied to wastewater containing dyes from textile industry. *Chemical Engineering and Processing*. 2010; 49: 1176–82.

[31] Xu L, Wang W, Wang M, Cai Y. Electrochemical degradation of tridecane dicarboxylic acid wastewater with tantalum-based diamond film electrode. *Desalination*. 2008; 222: 388–93.

[32] Sengil IA, Ozacar M. The Decolorization of C.I reactive blak 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes. *Journal of Hazardous materials*. 2009; 161: 1369-76.