Electrochemical Removal of Brown HT using Solar Cell as a Source of Electric Energy

G.O.El-Sayed, S.M.Reda and A.E.Fahmy
Chemistry Depart., Faculty of Science, Benha Univ., Benha, Egypt
E-Mail: gamaloelsayed@yahoo.com

Abstract

The removal of Brown HT dye from aqueous media by two electrochemical methods: electro oxidation and electrocoagulation. A photovoltaic cell producing about 6.3 V was used as an electric power source to minimize the process cost. Two graphite electrodes were used for electro oxidation, while iron electrodes were used for electrocoagulation. Different parameters affecting decolorization process were examined and evaluated. The optimum pH for maximum dye removal was about 10.0 for the two techniques. The two methods applied were fast and causing complete decolorization within about 30 min. The rate of decolorization depends on initial dye concentration, pH and salinity of the working solution.

Keywords: Brown HT, Electro oxidation, Electrocoagulation, Photovoltaic Cell .

1. Introduction

One of the major challenges facing mankind today is to provide clean water to a vast majority of the population around the world. The need for clean water is particularly critical in Third-World Countries. Natural water supplies as rivers, canals, estuaries and other water-bodies are being constantly polluted due to the discharge of industrial effluents as well as other anthropogenic activities and natural processes.

Among several chemical polluting materials, dyes are an important class of pollutants that are consisted of two main components; chromophores and auxochromes. Dyes have different structures according to their type, among of them azo dyes are the most important category of synthetic dyes. They are characterized by the presence of azo bonds (-N=N-) with one or more aromatic systems, which may also have another functional group. These dyes are widely used in a variety of industries like textile, plastic, leather, cosmetics and food industries. Recently, the use of edible dyes in the food industry has a significant increase because one of the most important qualities of food is color. Natural or synthetic food colorants are often added to foodstuffs and soft drinks in order to keep. The complex aromatic molecular structures of dyes make them highly stable and difficult to biodegrade [1]. The appearance of color is the most obvious indicator of water pollution which interferes with transmission of sunlight into water streams and therefore reduces the photosynthetic activity.

Many researches have been done on color removal from the colored waste waters considering various techniques, such as sedimentation [2], biological treatments [3], ozonation [4], ion-exchange [5], membrane technology [6], electrochemical coagulation and flocculation [7,8] sonochemical degradation [9], photochemical degradation [10], electrochemical removal [11], chemical oxidation [12] and adsorption [13] have been generally employed for color removal.

The electrochemical oxidation (EO) is widely used to remove colors from industrial effluents [14-16]. These methods involve the application of electrical current to the effluent to convert chloride to chlorine/hypochlorite. The produced chlorine and hypochlorite oxidize the pollutants and are then reduced to chloride ions. Different anodes were used successfully to treat various industrial effluents [17-19]. The following reactions may take place during electrolysis of the effluent. Chlorine gas is formed at the anode according to:
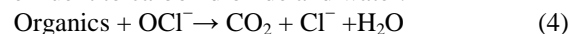
$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

At the cathode:

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

in the electrochemical cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorite.

$$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^- \tag{3}$$
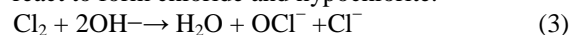
both hypochlorite and free chlorine are chemically reactive and oxidize organics in the effluent to carbon dioxide and water.

$$Organics + OCl^- \rightarrow CO_2 + Cl^- + H_2O \tag{4}$$

Electrocoagulation (EC) is another electrochemical method which applies the basic precepts of traditional water treatment [6]. In contrast to chemical coagulation method in which particles known as coagulants are added to aggregate the pollutant, EC uses electrodes to release coagulants. EC has been applied for removal of pollutants from wastewater. It includes the advantages like huge sludge production, process inefficiency, and necessity of further treatment mechanism. EC was successfully conducted for wastewater treatment. [20-22].

Electrocoagulation process involves the electro generation of coagulants by dissolving sacrificial electrode like iron to form iron ions. The in situ generation of iron cations during the EC process takes place at the anode, whiles at the cathode, typically H_2 gas production occurs. Various reactions take place in the EC process, where iron is used as the electrode [23]:
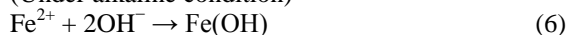
a) Anodic reactions

1) In acidic pH, the electrode is attacked by H^+ which enhances its dissolution by the following reaction:
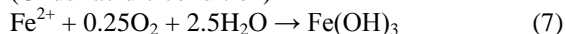
$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (5)$$

2) Other reactions taking place in the vicinity of the anode are:

(Under alkaline condition)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH) \qquad (6)$$

(Under acidic condition)

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 \qquad (7)$$

3) The generated ferrous ions are oxidized to ferric ions by oxygen in the aqueous phase:

$$Fe^{2+} + 0.25 O_2 + 0.5H_2O \rightarrow Fe^{3+} + OH^- \qquad (8)$$
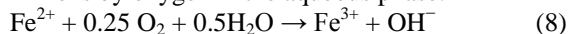
4) At the anode, oxygen evolution reaction may take place:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (9)$$

b) Cathodic reactions

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (10)$$

The resulting insoluble iron hydroxides can remove pollutants by electrostatic attraction or surface complexation. The EC process is fast and has an efficient rate of pollutant removal, compact size of the equipment, simple in operation, and has a low equipment costs.

The aim of this work is to evaluate the efficiency of electrochemical-oxidation and -coagulation techniques for the decolorization of aqueous solutions containing the food coloring agent Brown HT. Different parameters affecting the removal efficiency have been reported.

2. Materials and methods

The EC unit consists of a 50 mL electrochemical glass cell with two iron electrodes connected with a solar cell. The inter electrodes distance was 5 cm Fig (1). The average value potential difference was 6.3±1 V. Sodium chloride was added to the dye solution to accelerate the production of coagulant and consequently increase the decolorization rate. The pH of the working solution was measured by HANNA pH-meter (Italy). The dyestuff was used as a commercial salt supplied by the Al-Nasr Company Egypt. The chemical structure of Brown HT is shown in Fig (2).
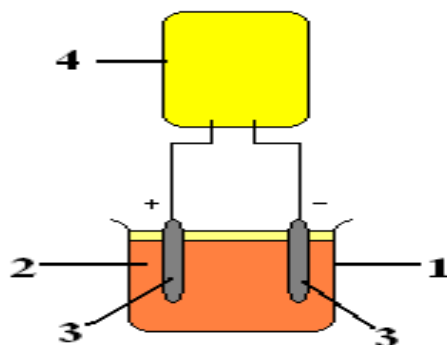
Fig(1) Electrocoagulation cell

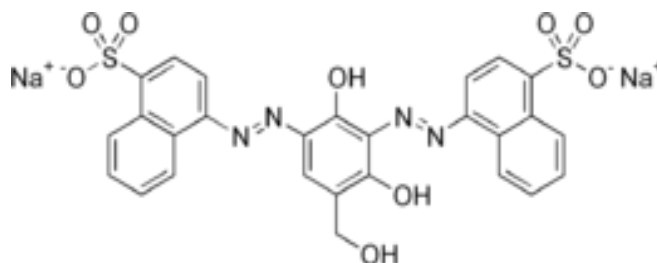1. Cell, 2. Dye solution, 3. Electrodes, 4. Photovoltaic cell

Fig (2) Chemical structure of Brown HT

The dye removal efficiency, Removal%, was expressed as a percentage as follows (Eq. (7)):

$$Removal(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (11)$$

Where C_0 and C_e are the initial and final dye concentration, respectively.

3. Results and discussion
3.1 Electro oxidation [EO]
3.1.1 Effect of chloride dose

This set of experiments were performed by changing sodium chloride dose from 0.5 to 5.0 g/L

for a dye solution (50 mL) containing 50 mg/L At pH 8. As shown in Fig (3), increase of NaCl content causes an increase in the decolorization efficiency.

The presence of chloride ions plays an important role in the electro oxidation process by i) increase in the concentration of the supporting electrolyte increases the hypochlorite ions production and the cell conductivity [24] and ii) enhancement of the destruction of organics present in the solution which results in a rise of current density at the same voltage which provides more chance for the production of chlorine in the relatively higher current densities [25].
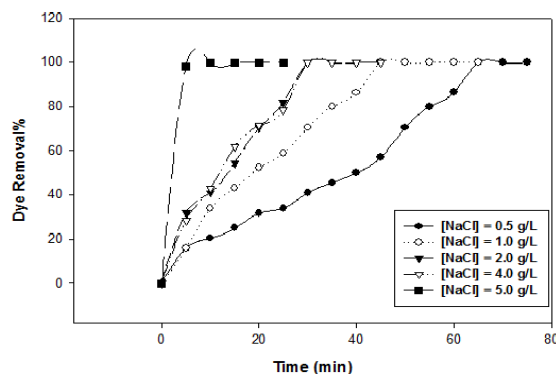

Fig (3) Effect of chloride concentration on electrooxidation process using graphite electrodes

3.1.2 Effect of pH

The effect of initial pH was carried out from pH 3.4 – 10.1 at electrode distance (ED) 50 mm and time 30 min. The results Fig (4) show that about 44% of color can be removed in 10 min in case of pH 3.4, while about 98% and 100% color removal were observed at pH values 7.0 and 10.1, respectively. So, the efficiency of color removal was better in the alkaline solution than those in the neutral solution and acidic solution. . The lowest color removal rate was observed at an initial pH of 3.4. At 30 min of electrolysis, color was removed completely at all media used.
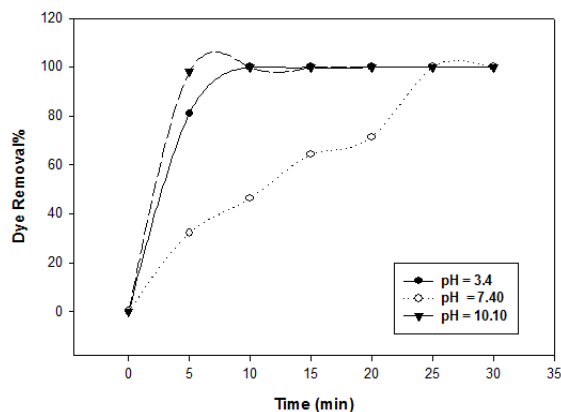
Fig(4) Effect of pH on electro oxidation process using graphite electrodes

These results obtained re in agreement with previous researches [26,27]. In acidic conditions, hypochlorous acid was predicted to be the most species in the solution. Higher rate of decolorization in acidic condition may be due to higher oxidation potential of hypochlorous acid rather than hypochlorite. At neutral and basic pHs, the rate of reaction was lowest which can be attributed to undesirable side reactions such as oxidation of free chlorine to chlorate and perchlorate, formation of chlorate by chemical combination of HOCl and hypochlorite ions which are at equilibrium in water, electrolysis of water and cathodic reactions involving loss of hypochlorite [28].

3.1.3 Effect of initial dye concentration

It was of a particular interest to investigate the maximum loaded dye concentration on the effectiveness of the graphite electrode in treating MxR dye from wastewater. Fig (5) displays the effect of different initial dye concentrations (20-80 mg/L) on the rate of dye degradation and corresponding color removal. Total color removal of the dyes can be achieved in the presence of initial dye load up to 80 mg/L. The highest removal

rate of color removal was observed at dye concentration 20 mg/L. However, above that concentration of MxR dye the color removal rate did not changed. The results can be explained in

terms of diffusion control, assuming that mineralization occurred on the electrode surface mediated by OCl^- ions.
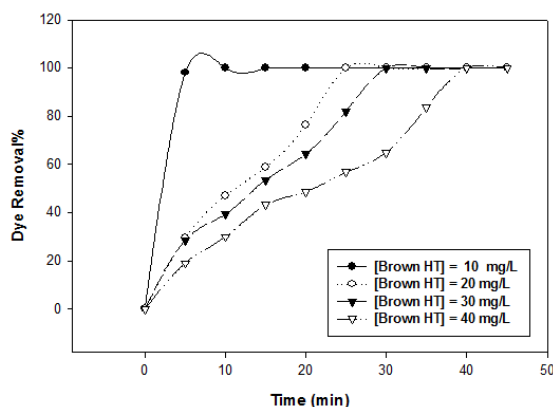

Fig (5) Effect of initial dye on electro oxidation process using graphite electrodes

At low initial concentrations, the electrochemical reaction is faster than the diffusion. When the initial concentration increases, more organic molecules are transferred to the surface of electrode and the amount of dye reduction is increased. The OCl^- ions that are generated are limiting in this case, and the degradation efficiency would decrease with increased initial concentration of the dye [29].

3.2.1 Electrocoagulation [EC]
3.2.1 Effect of chloride dose

It is important to investigate the effect of electrolyte since actual wastewater usually contains certain amount of salts [30]. The effect of background electrolyte, NaCl was investigated for a solution containing 50 mg/L Brown HT dye at different concentrations of NaCl (1 - 5 g/L). For each concentration of background electrolyte, the decolorization rate was followed for 30 min. As shown in Fig (6), with the increase of NaCl

concentration from 1 to 5 mg/L, the rate of decolorization significantly increases. At the end of electrolysis, the removal of dye color reached 100%. The supporting electrolyte increases solution conductivity; hence it influences the generated current and energy consumption of the removal process. The increase in the conductivity allowed by the addition of sodium chloride is known also to reduce the cell voltage V at constant current density due to the decrease of the ohmic resistance of wastewater [31]. Many researchers have found NaCl as the best supporting electrolyte [32,33]. Chloride ions could significantly reduce the adverse effects of other anions, such as HCO_3^- and SO_4^{2-}, by avoiding the precipitation of calcium carbonate in hard water that could form an insulating layer on the surface of the electrodes and increase the ohmic resistance of the electrochemical cell [34]. In conclusion, it may be said that higher conductivity is more desirable for high process performance.
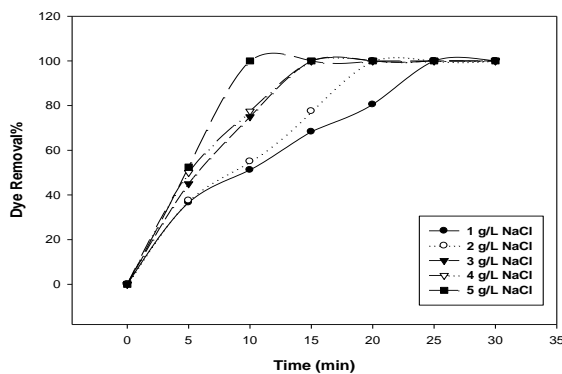

Fig (6) Effect of chloride concentration on electrocoagulation process using iron electrodes.

3.2.2 Effect of pH

To explore the effect of the pH on EC efficiency with iron electrode, the initial pH was examined at pH 3.0, 7.0 and 10.0 by addition of 0.1 (N) HNO_3 and/or NaOH. A typical progress of pH change is shown in Fig (7). During the electrocoagulation process which was performed for 30 min, it can be seen that dye removal was increased with increase in pH. Maximum removal (100%) was reached after 10 min for dye solution of pH 10. The solubility of iron hydroxide species strongly depends on the chemistry of the electrolysis media. So, removal of dye by EC is significantly affected by solution pH. Both initial pH and the elevation of

pH during EC affect dye solubility and hence its removal. Electrocoagulation favors the formation of ferric hydroxide flocs instead of ferrous hydroxides to remove organic and metal pollutants [35]. During EC, the cathode produces OH^- (eq. 3) and the solution pH increases. The high local pH areas around the anode can enhance the production of Fe^{3+}, resulting in improved dye removal [36]. The factors influencing the distribution of iron species during EC has been studied and it was reported [37] that solution pHs above 8.5 favor the oxidation of Fe^{2+} to Fe^{3+} by dissolved oxygen during EC process.
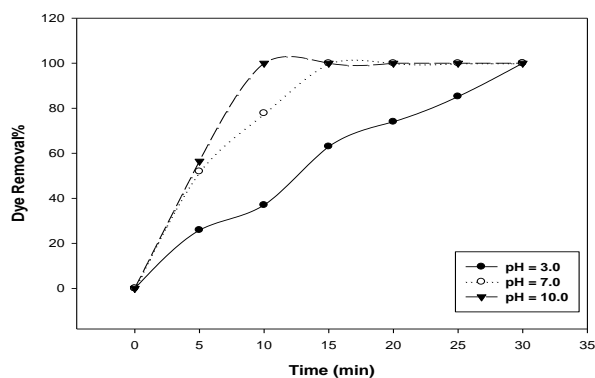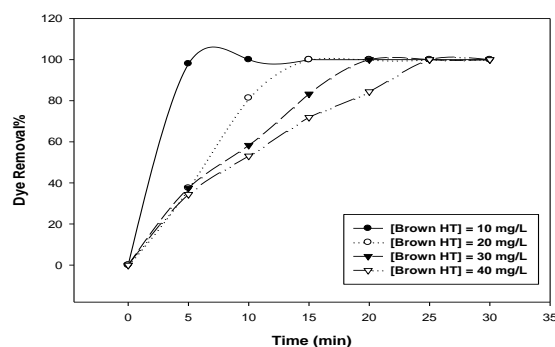

Fig (7) Effect of pH on electrocoagulation process using iron electrodes

3.2.3 Effect of dye concentration

A set of experiments was performed with different initial concentrations of Brown HT dye (10 – 40 mg/L) at pH 10 to determine the time required for color removal under optimum condition of electrocoagulation process. The results

obtained Fig (8) indicates that at higher concentrations, longer time is needed for removal of dye. The adsorption capacity of the flocs formed became exhausted with increasing dye content. Similar results were reported for the decolorization of different dyes by EC process [38-40].

Fig(8) Effect of initial dye on electrocoagulation process using iron electrodes

4. Conclusion

It was found that the best electrodes for removal of Brown HT is iron electrodes compared to graphite electrodes. Both electro oxidation and electrocoagulation techniques are effective for dye removal from aqueous media. The best pH for effective operation is about 10. Mximum removal of dye was completed after about 5 min at optimum pH. The two methods are cost-effective, especially

when a photovoltaic cell is used as a source of energy.

References

[1]   S.Wang, H.T.Li, Kinetic modeling and mechanism of dye adsorption on unburned carbon, Dyes Pigments, vol.72, pp.308–314, 2007.

[2] N.P.Cheremisinoff, Handbook of water and wastewater treatment technologies, Butterworth-Heinemann, Boston, 2002.

[3] I.K.Kapdan, R.Ozturk, Effect of operating parameters on color and COD removal performance of SBR : sludge age and initial dyestuff concentration, J. Hazrd. Mater. Vol. B123, pp. 217–222, 2005.

[4] Y.M.Slokar, A.M.Le Marechal, Methods od decoloration of textile wastewaters, Dyes Pigments, vol .37, pp. 335–356, 1997.

[5] B.S.Kaith, J. Dhiman, J.K.Bhatia, Preparation and application of grafted Holarrhena antidycentrica fiber as cation exchanger for adsorption of dye from aqueous solution. Journal of Environmental Chemical Engineering, vol.3, pp.1038-1046, 2015.

[6] K. Rambabu, S.Velu, Modified cellulose acetate ultrafiltration composite membrane for enhanced dye removal, International Journal of Chemical Sciences, vol.14, pp. 195-205, 2016.

[7] C.-L.Yang, J. McGarrahan, Electrochemical coagulation for textile effluent decolorization, Journal of Hazardous Materials, vol. 127 pp. 40-47, 2005.

[8] M.Elazzouzi, Kh.Haboubi, M.S.Elyoubi, Electrocoagulation flocculation as a low-cost process for pollutants removal from urban wastewater, Chemical Engineering Research and Design, vol. 117, pp. 614-626, 2017.

[9] H.Ferkous, O.Hamdaoui, S.Merouani, Sonochemical degradation of naphthol blue black in water: Effect of operating parameters, Ultrasonics Sonochemistry, vol. 26, pp. 40-47, 2015.

[10] M.Thabet, A.A.El-Zomrawy, Degradation of acid red 17 dye with ammonium persulphate in acidic solution using photoelectrocatalytic methods, Arabian Journal of Chemistry, vol. 9, pp. S204–S208, 2016.

[11] M.Sala, V.López-Grimau, C.Gutiérrez-Bouzán, Photo-Electrochemical Treatment of Reactive Dyes in Wastewater and Reuse of the Effluent: Method Optimization. Materials, vol. 7, pp. 7349-7365, 2014.

[12] S.A.Abo-Farha, Comparative Study of Oxidation of Some Azo Dyes by Different Advanced Oxidation Processes: Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like, Journal of American Science, vol. 6, pp. 128-142, 2010.

[13] M.Hema, S.Arivoli, Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon, Journal of Applied Science and Environmental Management, vol. 12, pp. 43 – 51, 2008.

[14] S.G.Segura, M. Maesia, S.G. Eiband, J. V. de Melo, C. A .Martínez-Huitle, Electrocoagulation and advanced electrocoagulation processes: A

general review about the fundamentals, emerging applications and its association with other technologies, Journal of Electro analytical Chemistry, Vol. 801, PP.267-299, 2017.

[15] E. Gengec, Treatment of highly toxic cardboard plant wastewater by a combination of electrocoagulation and electro oxidation processes, Ecotoxicology and Environmental Safety, vol. 145, pp. 184-192, 2017.

[16] A. Wang, J. Qu, H. Liu, J. Ge, Degradation of azo dye Acid Red 14 in aqueous solution by electro kinetic and electrooxidation process. Chemosphere, vol. 55, pp. 1189-1196, 2004.

[17] R.M. Farinos, L.A.M. Ruotolo, Comparison of the electro oxidation performance of three-dimensional RVC/PbO_2 and boron-doped diamond electrodes. Electrochimica Acta, vol. 224, pp. 32-39, 2017.

[18] C. Chen, E. Nurhayati, Y. Juang, C. Huang, Electrochemical decolorization of dye wastewater by surface-activated boron-doped nanocrystalline diamond electrode. Journal of Environmental Sciences, vol. 45, pp. 100-107, 2016.

[19] L. Fan, Y. Zhou, W. Yang, G. Chen, F. Yang, Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model, Dyes and Pigments, vol. 76, pp. 440-446, 2008.

[20] S. Garcia-Segura, M. Maesia S.G. Eiband, J.V. de Melo, C.A. Martínez-Huitle, Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies. Journal of Electro analytical Chemistry, vol. 801, pp. 267-299, 2017.

[21] L. Xu, G. Cao, X. Xu, S. Liu, Z. Duan, C.He, Y. Wang, Q.Huang Simultaneous removal of cadmium, zinc and manganese using electrocoagulation: Influence of operating parameters and electrolyte nature, Journal of Environmental Management, Vol. 204, PP. 394-403, 2017.

[22] G.O.El-Sayed, M.S.Awad, Z.A.Ayad, Electrochemical Decolorization of Maxilon Red GRL Textile Dye. International Research Journal of Pure & Applied Chemistry, vol. 4, pp. 402-416, 2014.

[23] M.S. Mahmoud, J.Y. Farah, T.E. Farrag, Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes. Egyptian Journal of Petroleum, vol. 22, pp. 211–216, 2013.

[24] A. Maljaei, M. Arami, N.M. Mahmoodi, Decolorization and aromatic ring degradation of colored textile wastewater using indirect

electrochemical oxidation method. Desalination, vol. 249, pp. 1074–1078, 2009.

[25] C.C. Jara, D. Fino, V. Specchia, G. Saracco, P. Spinelli, Electrochemical removal of antibiotics from wastewaters. Applied Catalysis B: Environment, vol. 70, pp. 479–487, 2007.

[26] N. Huda, A.A.A. Raman, M.M. Bello, S. Ramesh, Electrocoagulati

.on treatment of raw landfill leachate using iron-based electrodes: Effects of process parameters and optimization. Journal of Cleaner Production, Vol. 167, PP. 432-446, 2017.

[27] P. Kariyajjanavar, N. Jogttappa, Y.A. Nayaka, Studies on degradation of reactive textile dyes solution by electrochemical method. Journal of Hazardous Materials, vol. 190, pp. 952–961, 2011.

[28] F. Yi, S. Chen, C.Yuan, Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater. Journal of Hazardous Materials, vol. 157, pp. 79–87, 2008.

[29] C.A. Martinez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. Applied Catalysis B: Environment, vol. 87, pp. 105–145, 2009.

[30] M.S. Secula, I. Crețescu, S. Petrescu, An experimental study of indigo carmine removal from aqueous solution by electrocoagulation. Chemical Engineering and Environmental Protection, Desalination, vol. 277, pp. 227–235, 2011.

[31] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, Journal of Hazardous Materials B, vol. 100, pp. 163–178, 2003.

[32] M. Chafi, B. Gourich, A.H. Essadki, C. Vial, A. Fabregat, Comparison of electrocoagulation using iron and aluminium electrodes with chemical coagulation for the removal of a

highly soluble acid dye, Desalination, vol. 281, pp. 285–292, 2011.

[33] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, Journal of Hazardous Materials, B133, pp. 172–176, 2006.

[34] J.B. Parsa, H.R. Vahidian, A.R. Soleymani, M. Abbasi, Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption, Desalination, vol. 278, pp. 295–302, 2011.

[35] Y. Gendel, O. Lahav, A new approach to increasing the efficiency of low-pH Fe-electrocoagulation applications, Journal of Hazardous Materials, vol. 183, pp. 596-601, 2010.

[36] Ö. Hanay, H. Hasar, Effect of anions on removing Cu^{2+}, Mn^{2+} and Zn^{2+} in electrocoagulation process using aluminum electrodes, Journal of Hazardous Materials, vol. 189, pp. 572-576, 2011.

[37] D. Lakshmanan, D.A. Clifford, G. Samanta, Ferrous and ferric ion generation during iron electrocoagulation, Environmental Science and Technology, vol. 43, pp. 3853–3859, 2009.

[38] N. Daneshvara, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters, Journal of Hazardous Materials, vol. B129, pp. 116–122, 2006.

[39] J.B. Parsa, H.R. Vahidian, A.R. Soleymani, M. Abbasi, Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption, Desalination, vol. 278, pp. 295–302, 2011.

[40] M. Ahmadi, J. Behin, A.R. Mahnam, Kinetics and thermodynamics of peroxydisulfate oxidation of Reactive Yellow 84, Journal of Saudi Chemical Society, vol. 20, pp. 644–650, 2016.