Application of Electrocoagulation Process for the Removal of Acid Orange 5 in Synthetic Wastewater

Shokri, Aref *⁺

Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, I.R. IRAN

ABSTRACT: *In this study, the Electro Coagulation (EC) was used for the removal of acid orange 5 from synthetic wastewater in a batch electrochemical reactor. The impact of the operational variables such as current density, initial pH, time of electrolysis, and initial concentration of the dye was investigated. The results showed that the optimum conditions was obtained at initial pH of 7, current density at 2 mA/cm², 60 mg/lit of Acid orange 5 and time of reaction at 60 min. At optimum conditions, the removal efficiency of acid orange 5 and Chemical oxygen Demand (COD) were 99.3 and 85.5%, respectively. The kinetic study showed that the removal reaction was first order and the rate constant and half-life of reaction were obtained.*
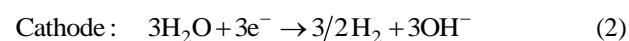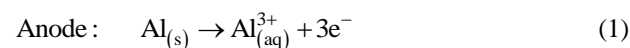
INTRODUCTION

The synthetic dyes have influenced on environment during recent decades. Many industries such as textile, paper, leather, pharmaceutical and food generate a huge amount of wastewater polluted with dyes throughout the world [1]. The application of azo dyes in industries is more important than other dyes. The existence of dyes even at very low concentration is greatly visible and undesirable. The Azo dyes are toxic, mutagenic and carcinogenic, thus their release into the environment would be dangerous to aquatic life and human health [2]. Therefore, the degradation of wastewater polluted with Azo dyes has stimulated universal interest [3].

As the traditional approaches cannot degrade Azo dyes efficiently, Advanced Oxidation Processes (AOPs) are considered as one of the most operative procedures for degradation of Azo dyes [3–4]. The Electro Coagulation (EC) method is more economic than other treatment methods used for dyeing wastewater such as, biological treatment, activated carbon adsorption, ultrafiltration, and ozonation [5]. The EC involves no addition of chemicals and provides better removal abilities for the same species than chemical coagulation. The coagulant in this case is produced by dissolution of a sacrificial anode. The EC uses an electrical current to produce several metal ions in solution. The contaminants present in wastewater are maintained in solution by electrical charges. The advantages of EC are simple equipment and easy operation, short-term reactive retention period, production of less sludge and consequently dropping the sludge disposal cost [6].

In this project, aluminum was used as an electrode material in EC process and the main reactions are as follows:
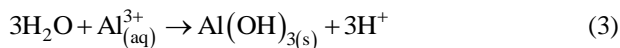
$$\text{Anode}: \quad Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \tag{1}$$

$$\text{Cathode}: \quad 3H_2O + 3e^{-} \rightarrow 3/2\,H_2 + 3OH^{-} \tag{2}$$

* To whom correspondence should be addressed.
+ E-mail aref.shokri3@gmail.com

Al^{3+} and OH^- ions were produced by electrode reactions (Eqs.(1) and (2)) to form different monomeric types, which finally converted to $Al(OH)_{3(s)}$ based on the Eq. (3).

$$3H_2O + Al^{3+}_{(aq)} \rightarrow Al(OH)_{3(s)} + 3H^+ \qquad (3)$$

The produced species, $Al(OH)_{3(s)}$, has large surface areas that can adsorb soluble organic pollutants and trapping the colloidal particles. Lastly, these flocks are separated simply from aqueous solution by electro floatation or sedimentation [7–8]. In addition, the gas bubble can transfer the contaminant to the top of the solution that it can be more simply concentrated, collected and removed. The metallic ions can react with hydroxide ions produced at cathode during the evolution of H_2 gas, this phenomenon results in the formation of insoluble hydroxides that will transfer pollutants out of the solution. It also donates the coagulation by neutralizing of negatively charged colloidal particles which have been stated to be more compressed than sludge acquired by chemical methods [9–10].

In spite of the large amount of scientific research on the remediation of Azo dyes in wastewaters by EC, no study has been performed in the treatment of Acid orange 5 in aqueous environment using EC or other processes as far as research is concerned. In the present work, the removal of Acid orange 5 from aqueous solutions was investigated by electrocoagulation method. The effects of the operating parameters, such as current density, initial pH, initial concentration of the dye, and time of reaction on color removal efficiency in a synthetic wastewater containing Acid orange 5 were explored.

EXPERIMENTAL SECTION
Materials

Acid Orange 5 (99.5% purity, CAS Number:554–73–4), was purchased from the Merck Company of Germany. The dye was used without further purification. Desired concentrations of dye solution were created by diluting proper amounts of stock solution with distillate water. H_2SO_4 and NaOH are all supplied from Merck. Distilled water was used throughout the experiment.

Electrochemical reactor

The experiments were accomplished in a glass cylindrical batch reactor containing 1 liter of solution.

The system was equipped with a sampling system (Fig. 1). The water bath, BW 20G model from Korean company, was applied for fixing temperature at 25 °C through circulating a flow of water in the jacket of the reactor. The two anodes and two cathodes were made from aluminum plates (99.5% purity), with dimensions of 4.6 cm×5.5 cm×0.3 cm and connected to a digital DC power supply (Topward 6306D, 30 V and 6 A) in mono polar mode. The total immersed and effective surface area of each electrode was 45 cm^2 and the spacing between the electrodes was 1.5 cm.
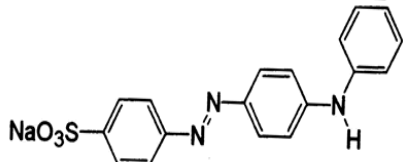
General procedure

The synthetic wastewater is composed of distillate water and Acid Orange 5 with a definite concentration in each run. The volume of the solution for experiment in each batch was 1000 ml. The pH was adjusted by adding NaOH or HCl (0.1 M) and measured by pH Meter PT-10P Sartorius Instrument Germany. In all experiments, about 1.5 g/L of NaCl was added to the solution to keep the solution to be conductive, and a Jenway Conductivity Meter (Model 4200) was employed to control the conductivity of the solution. The samples were withdrawn at 10 min intervals for up to 60 min. The concentration of dye in the solutions was analyzed by a UV–Vis spectrophotometer (Agilent, 5453, American) at a wavelength of 448 nm. The solution was stirred at 150 rpm by a magnetic stirrer to let the chemical to be precipitated and grow large enough for separation. The electrodes were washed completely before and after each run, by dipping in HCl solution (5% v/v) for at least 15 min and rinsing again with distilled water.

The COD of samples were measured by the HACH's COD method by COD reactor with direct monitoring spectrophotometer (DR/5000U) from HACH Company. It was measured by the standard closed reflux and Colorimetric method and the absorbance of samples was estimated by at 600 nm [11]. The suitable efficiencies were estimated with respect to its initial values and the removal percent for Acid orange 5 and COD were obtained as in Eqs. (4) and (5):

$$\text{Re moval of Acid organe } 5(\%) = \left(\frac{[C]_0 - [C]}{[C]_0}\right) \times 100 \quad (4)$$

$$\text{Re moval of COD}(\%) = \left(\frac{[COD]_0 - [COD]}{[COD]_0}\right) \times 100 \quad (5)$$

Table 1: The Chemical structure and characteristics of Acid Orange 5.

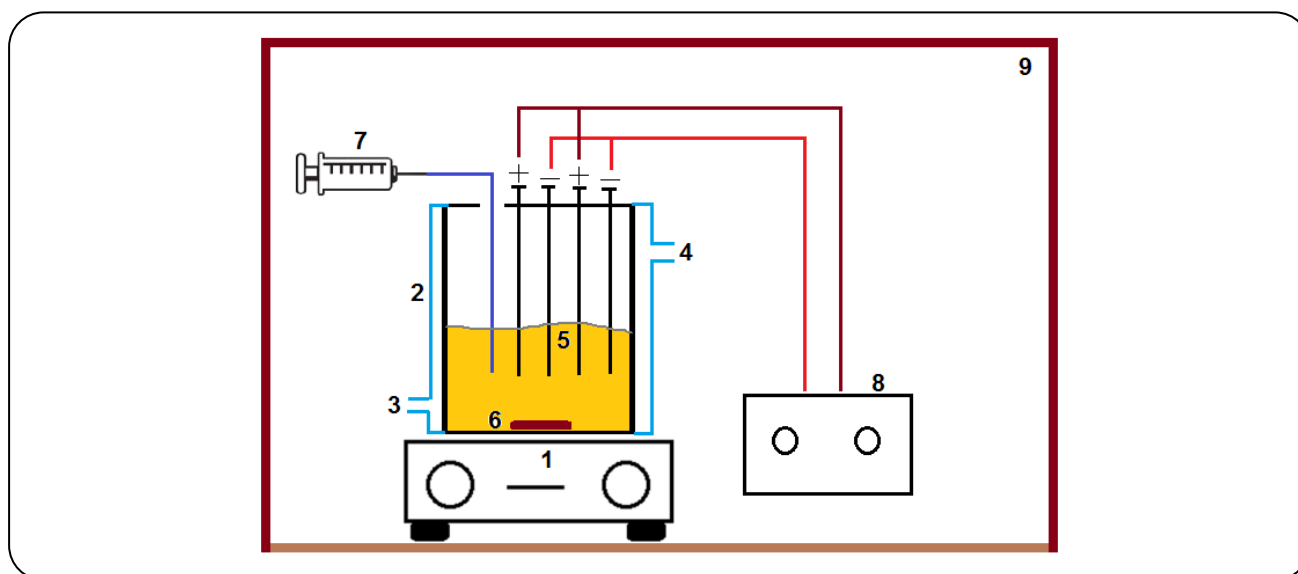| Pollutant	Molecular structure	λ_{max}(nm)	Molecular Mass
Acid orange 5 $(C_{18}H_{14}N_3NaSO_3)$		448	375.38

Fig. 1: Schematic diagram of the experimental set up used. Notes: (1) Magnetic stirrer, (2) Batch Electrochemical reactor, (3) Cooling water inlet, (4) Cooling water outlet, (5) Aluminium Electrodes, (6) Magnetic Bar, (7) Sampling Port, (8) DC power supply, (9) Wooden Box.

Where $[C]_0$ and $[COD]_0$ are the concentration of the dye and amounts of COD at the start of the reaction, and $[C]$ and $[COD]$ are the concentration of the Acid orange 5 and extents of COD at time t, respectively. In this project, it is not essential to use Design Expert software to determine the optimum variables so One Factor at a Tme (OFAT) method was used because of the fewer variables and the number of levels in various factors was not the same.

RESULTS AND DISCUSSION

Influence of current density on the dye removal efficiency

In all electrochemical processes, current density is the most significant parameter for controlling the reaction rate in the electrochemical reactor. It has been proven that current density determines the coagulant production rate, and hence affects the growth of created flocks which cause the pollutant to be treated in the EC process [12]. Different current densities from 0.5 to 4 mA/cm^2, were selected to investigate the influence of current density on the removal of Acid orange 5. As it can be seen from Fig. 2, an increase in current density from 0.5 to 2 mA/cm^2 leads to the improvement in the removal efficiency from 64.7% to 96.5% at pH of 6. When the current density was increased, the number of Al^{3+} cations and consequently the particles of Al(OH)$_3$ were enhanced. Therefore, the amounts of anodic dissolution of aluminum were increased and larger extent of precipitate was formed for the removal of dyes. Furthermore, the bubble generation rate was enhanced and the bubble size reduced with increasing current density, so a large extent of dye was removed by H$_2$ floatation [13–14].

In fact, as the current density was increased, the required time for the treatment decreased.

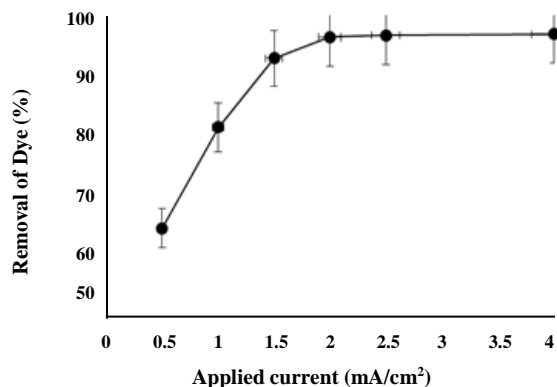*Fig. 2: Influence of current density on the removal efficiency of Acid orange 5(initial pH at 6, [Acid Orange 5]= 60 mg/L, time of reaction at 60 min).*

So, for a distinct time, the removal efficiency increases considerably with an increase in current density. Outside 2 mA/cm^2 of current density, no noticeable progress in removal efficiency is occurred. Therefore, the value at 2 mA/cm^2 was introduced as optimum in this study.

Effect of initial pH on the removal efficiency of dye

In order to explore the influence of pH on the removal of Acid orange 5, a series of tests were performed by adjusting the initial pH in the range from 4 to 10. The influence of pH on electro coagulation is presented in Fig. 3. The distribution and stability of Aluminum species in the solution is different in various pH. The results showed that the maximum removal of dye was obtained at pH of 7, because the solid flakes of Al(OH)$_{3(s)}$ were formed at this pH. The flocks of Al (OH)$_{3(s)}$ are valuable for adsorption of soluble organic pollutants and trapping of colloidal particles [15–16]. The efficiency of dye removal was less at low and high pH. When the pH increased from 4 to 7, the removal of dye was enhanced from 51.3 to 99.3%. This trend was related to the amphoteric behavior of aluminum hydroxide, which cannot precipitate at low pH [17], because at pH of 4, the soluble cations such as Al^{3+} and Al(OH)$^{2+}$ are major. The more increase in the pH to 8 and 10 can result in the decrease in dye removal efficiency to 81.2 and 56.4%, respectively. The concentration of soluble anion, Al(OH)$_4^-$, was enhanced at pH of 10.

In addition, the pH was changed during the treatment process and it was increased at low initial pH. *Vik et al.,* recognized that this phenomenon is related to H$_2$
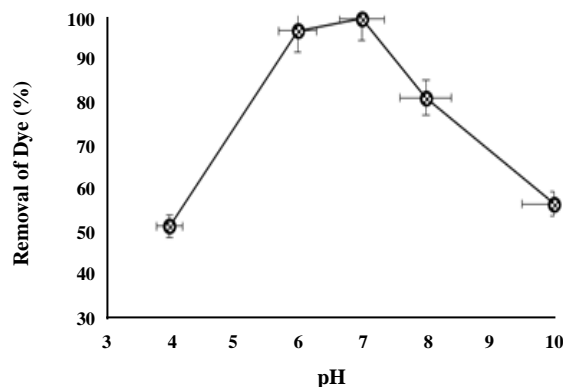

Fig. 3: Effect of initial pH on the removal efficiency of Acid orange 5 (current density at 2 mA/cm^2, [Acid Orange 5] = 60 mg/L, electrolysis time at 60 min).

evolution at Cathodes [18]. The final pH cannot vary very much in alkaline pH, and a slight descent was observed. But, when the solution pH is above 9, the pH was decreased, so the electro coagulation process can act as pH buffer [19–20].

Influence of the dye concentration

The degradation efficiency of Acid orange 5 in different initial concentrations from 30 to 120 mg/lit is presented in Fig. 4. The amount of degradation was reduced from 99.0 to 68.5% with an increase in the concentration of Acid orange 5 from 30 to 120 mg/lit. It may be related to the fact that at a constant current density, the same amount of aluminum ions passes to the solution at different dye concentrations. Thus, the production of aluminum hydroxide complexes was inadequate to coagulate the large number of dye molecules at high concentration [21–22].

This phenomenon proposes the requisite of additional treatment time when the concentration of dye is high in the reactor. The energy consumption and the costs of the process were increased, obviously.

Effect of electrolysis time on the removal of Acid Orange 5 and COD

The time of reaction is affected on the treatment efficiency in EC process. The influence of electrolysis time was considered at a constant current density of 2.0 mA/cm^2 and initial pH of 7. The removal percent of Acid orange 5 versus time is shown in Fig. 5 and it was improved from 36.5 to 99.3%, with an increase in electrolysis time from 10 to 60 min.
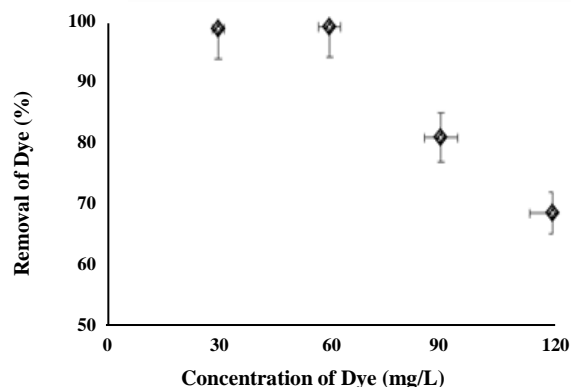
Fig. 4: Effect of initial dye concentration on the removal efficiency of Acid Orange 5(initial pH at 7, current density in 2 mA/cm², electrolysis time at 60 min).
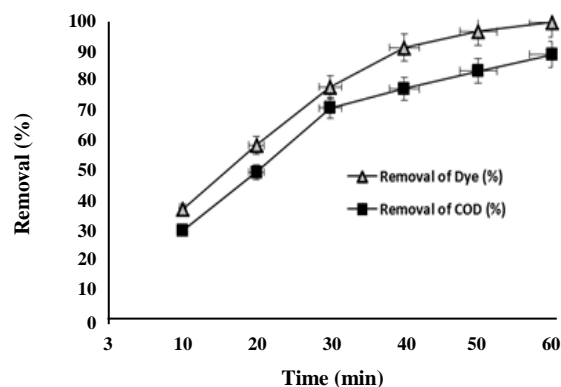

Fig. 5: Effect of electrolysis time on the removal of Acid Orange 5 and COD at optimum conditions ([Acid Orange 5]= 60 mg/L, initial pH at 7, current density at 2 mA/cm²).

The release of coagulating species was originated from anodic electro dissolution during electrolysis. The dye removal efficiency depends on the concentration of Al ions formed on the electrodes. When the electrolysis time increases, the concentration of Al^{+3} ions and their hydroxide flakes enhances, so the removal of dye was improved [23–24].

As it can be deducted from Fig. 5, at optimum condition the removal of COD (85.5%) was lower than the removal of Acid Orange 5 (99.3%). The differences between the removal of COD and Dye was low because of the less formation of intermediate products.

Kinetic study

In the removal of Acid Orange 5 by EC process a kinetic study was performed at optimum conditions. The kinetic relation in the removal of Acid Orange 5 by the EC process can be introduced as the following nth order reaction kinetics:

$$\frac{-d[\text{Acid Orange 5}]}{dt} = k[\text{Acid Orange 5}]^n \qquad (6)$$

Where [Acid Orange 5] represents the concentration of the dye, k the reaction rate coefficient, n the order of reaction, and t is the time. In this study the experimental data was fitted with the first order kinetics. Through integration from Eq. (6) and in the case that it is a first-order reaction, the mentioned equation becomes:

$$-\ln\frac{[\text{Acid Orange 5}]}{[\text{Acid Orange 5}]_0} = kt \qquad (7)$$

In which $[\text{Acid Orange 5}]_0$ is the initial concentration of dye. Based on the Eq.7, a term $\ln\dfrac{[\text{Acid Orange 5}]_0}{[\text{Acid Orange 5}]_t}$ versus reaction time was plotted and after linear regression analysis, the first order rate constants ($k=87.8\times10^{-3}$ min^{-1}) and half-life of removal reaction ($t_{1/2}$= 7.9 min) were determined [25]. The correlation coefficient (R^2) of 0.9518 validates the first order kinetic model. A good fit of first-order kinetic model to the observed data is displayed in Fig. 6.

CONCLUSIONS

The EC system can remove Acid orange 5, successfully. The impacts of the main operating parameters on dye removal efficiency have been investigated. The high efficiency is acquired with a current density at 2 mA/cm², beyond which no notable progress may be attained. The process is extremely reliant on the pH of the solution. The treatment efficiency was very low either at acidic or alkaline pH. The finest pH is revealed to be at 7. The high removal of dye was happened at low concentration of Acid Orange 5.

The results showed that the optimum conditions was obtained at initial pH of 7, current density of 2 mA/cm², 60 mg/L of Acid orange 5 and 60 min of reaction. The first order rate constants (k= 87.8 × 10^{-3} min^{-1}) and half-life of removal reaction were determined for the removal of dye. At optimum conditions, the removal efficiency of dye and COD were 99.3 and 85.5%, respectively.
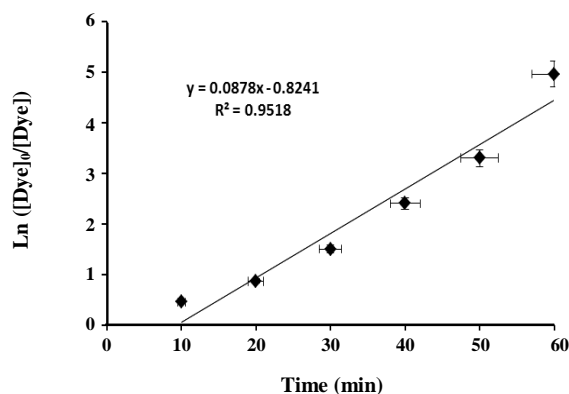
Fig. 6: Plot of the first-order equation in the removal kinetic of Acid Orange 5 at optimum conditions.

REFERENCES

[1] Eren Z., Ultrasound as a Basic and Auxiliary Process for Dye Remediation: A Review, *J. Environ. Manage.,* **104**: 127–141(2012).

[2] Wu J., Liu F., Zhang H., Zhang J.H., Li L., Decolorization of CI Reactive Black 8 by Electrochemical Process with/without Ultrasonic Irradiation, *Desalin. Water Treat.,* **44**: 36–43(2012).

[3] Shokri A., Employing electrocoagulation for the removal of Acid Red 182 in aqueous environment by using Box-Behenken design method, *Desal. Water Treat.,* **115**:281-287(2018).

[4] Shokri A., Removal of Acid red 33 from aqueous solution by Fenton and photo Fenton processes, *J. Chem. Health Risks,* **7**: 119–131(2017).

[5] Khandegar V., Saroha Anil K., Electrocoagulation for the Treatment of Textile Industry Effluent–A Review, *J. Environ. Manage.*, **128**: 949–963(2013).

[6] Mollah M.Y.A., Gomes J.A.G., Dasc K.K., Cocke D.L., Electrochemical Treatment of Orange II Dye Solution-Use of Aluminum Sacrificial Electrodes and Floc Characterization. *J. Hazard. Mater.,* **174**: 851–858 (2010).

[7] Gourich B.A., Sekki K., Madani M., Chibane, Removal Turbidity and Separation of Heavy Metals Using Electrocoagulation–Electroflotation Technique: A Case Study, *J. Hazard. Mater.,* **164**: 215–222 (2009).

[8] Khosravi R., Hossini H., Heidari M., Fazlzadeh M., Biglari H., Taghizadeh, A., Barikbin B., Electrochemical Decolorization of Reactive Dye from Synthetic Wastewater by Mono-Polar Aluminum Electrodes System, *Int. J. Electrochem. Sci.,* **12**: 4745–4755(2017).

[9] Shokri A., The treatment of spent caustic in the wastewater of olefin units by ozonation followed by electrocoagulation process, *Desainl. Water Trea.,* **111**: 173-182(2018).

[10] Gengec E., Treatment of highly Toxic Cardboard Plant Wastewater by a Combination of Electrocoagulation and Electrooxidation Processes, *Ecotoxicol. Environ. Saf.,* **145**: 184–192(2017).

[11] Shokri A., Degradation of 2-Nitrophenol from Petrochemical Wastewater by Ozone, *Russ. J. Appl. Chem.,* **88**: 2038−2043 (2015).

[12] Yılmaz A.E., Boncukcuoglu R., Kocakerim M.M., Kocadagistan E, An Empirical Model for Kinetics of Boron Removal from Boron Containing Wastewaters by the Electrocoagulation Method in a Batch Reactor, *Desalination*, **230**: 288–297(2008).

[13] Bayramoglu M., Eyvaz M., Kobya M., Treatment of the Textile Wastewater by Electro Coagulation: Economical Evaluation, *Chem. Eng. J.,* **128**: 155–161 (2007).

[14] Adhoum N., Monser L., Decolourization and Removal of Phenolic Compounds from Olive Mill Wastewater by Electrocoagulation, *Chem. Eng. Process.,* **43**:1281–1287(2004).

[15] Hakizimana J.N., Gourich B., Chafi M., Stiriba Y., Vial C., Drogui P., Naja J., Electrocoagulation Process in Water Treatment: A Review of Electrocoagulation Modeling Approaches, *Desalination,* **404** (2017) 1–21(2017).

[16] Essadki A.H., Bennajah M., Gourich B., Vial C.h., Azzi M., Delmas H., Electrocoagulation/ Electrofloatation in an External-Loop Airlift Reactor—Application to the Decolorization of Textile Dye Wastewater: a Case Study, *Chem Eng. Process*, **47**:1211–1223(2008).

[17] Alizadeh M., Ghahramani E., Zarrabi M., Hashemi S., Efficient De-colorization of Methylene Blue by Electro-coagulation Method: Comparison of Iron and Aluminum Electrode, *Iran. J. Chem. Chem. Eng. (IJCCE),* **34**(1) 39-47 (2015).

[18] Vik E.A., Carlson D.A., Eikum A.S., Gjessing E.T., Electrocoagulation of Potable Water, *Water Res.,* **18**: 1355–1360(1984).

[19] Demirbas E., Kobya M., Operating cost and Treatment of Metalworking Fluid Wastewater by Chemical Coagulation and Electrocoagulation Processes, *Process Saf. Environ. Prot.,* **105**: 79–90(2017).

[20] Bazrafshan E., Biglari H., Mahvi A.H., Humic Acid Removal from Aqueous Environments by Electrocoagulation Process Using Iron Electrodes, *J. Chem.,* **9**: 2453–2461(2012).

[21] Kobya M., Hiz H., Senturk E., Aydiner C., Demirbas E., Treatment of Potato Chips Manufacturing Wastewater by Electrocoagulation, *Desalination,* **190**: 201–211 (2006).

[22] Modirshahla N., Behnajady M.A., Mohammadi-Aghdam S., Investigation of the Effect of Different Electrodes and Their Connections on the Removal Efficiency of 4-Nitrophenol from Aqueous Solution by Electrocoagulation, *J. Hazard. Mater.,* **154**: 778–786 (2008).

[23] Daneshvar N., Khataee A.R., Amani Ghadim A.R., Rasoulifard M.H., Decolorization of C.I. Acid Yellow 23 Solution by Electrocoagulation Process: Investigation of Operational Parameters and Evaluation of Specific Electrical Energy Consumption (SEEC), *J. Hazard. Mater.*, **148**: 566–572(2007).

[24] Shokri A., Mahanpoor K., Degradation of Ortho-Toluidine from aqueous solution by the TiO_2/O_3 process, *Int. J. Ind. Chem.,* **8**:101–108(2017).

[25] Shokri A., Investigation of UV/H_2O_2 Process for Removal of Ortho-Toluidine from Industrial Wastewater by Response Surface Methodology Based on the Central Composite Design, *Desalin. Water Treat.,* **58**: 258–266(2017).