Degradation of Direct Blue from Synthetic Wastewater using Electrochemical Oxidation Method

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Abstract: This study is concerning the decolorization of direct blue dye by electrochemical oxidation technique. Laboratory testing was performed using graphite and stainless steel plates as the anode and cathode, respectively. The tests were performed using synthetic wastewater instead of real textile wastewater. The effect of operational factors (pH, dye initial concentration, the concentration of electrolyte, electrical supply voltage and run duration) were determined to study the efficiency of electrochemical oxidation for the removal of direct blue dye. The results have revealed that the maximum efficiency of direct blue removal was 98% under the optimum factors (pH of 2, dye initial concentration of 100 mg/L, NaCl of 500 mg/L and 5 V voltage).

1. Introduction
It is clear that textile industries need a huge amount of water and chemicals during processing steps [1]. Dyes are the major chemical substance used during the coloring process. Despite their toxicity, a significant amount of dye goes with the industrial water effluence causing color and chemical pollution in water resources because dyes prevent the sunlight to penetrate through water and the chemicals are toxic, therefore, the aquatic live could be affected [2]. The electrochemical technique is one of the best methods that has been used for dyes decolorization. Many types of electrochemical methods were suggested to treat textile wastewater and remove dyes such as electrocoagulation [3,4], electrochemical oxidation [5,6], electrochemical coagulation and oxidation [7]. The electrochemical method has become a known technology to treat water and wastewater from organic and inorganic pollutants. Accordingly, many studies have been aimed to use electrochemical methods for treating industrial wastewater and removing not only dyes but also all other polluted loads [8, 9]. For instance, excellent results were obtained when Maxilon red dye was decolorized using electrooxidation (graphite plates) in serial with electrocoagulation (graphite plate as cathode and anode and stainless steel as an anode) [10]. Textile wastewater containing indigo carmine dye was treated with three types of electrochemical methods and as follows: electrocoagulation, electrooxidation and advanced electrochemical oxidation using the electro-Fenton process, and significant results were got, however, treating by electro-Fenton was the most effective because it was the headmost in speed, efficiency and economically [11]. Indigo blue dye was removed from actual textile effluent using electrooxidation method, taking the wastewater from the first wash box of the treatment plant in order to reduce the pollution load on the next step in the plant [12]. Electrocoagulation cell was the best way to reduce textile effluent polluted with reactive and basic dyes using two various types of plates, aluminum and iron. The results varied between 96% for the aluminum and 86 % for iron [13]. Electrochemical oxidation was able to remove 86% of color from actual textile wastewater using variable current densities and the best result was at 0.1 amperce [14]. Recently, in novel researches, advanced
electrooxidation treatment was conducted using ozone, hydrogen peroxide, oxygen and chlorine as oxidizing agents by producing OH ions which attack dyes molecules [15,16].

This study is to assess the opportunity to the degradation of direct blue dye from synthetic wastewater by electrochemical oxidation method with a stainless steel plate as a cathode and graphite plate as an anode at different running factors.

2. Experimental work

The experiments were conducted in a beaker 0.5 L in capacity. The anode (graphite plate) and the cathode (stainless steel plate) were dipped vertically in an electrolyte solution. The plates dimensions were (6 cm × 3 cm × 0.3 cm). In order to supply power, a direct current power was used. The solution was stirred constantly at 200 rpm and a magnetic stirrer, model LMS-1003 Korea, was used to shake the solution well. Many experimental runs were performed under different operating parameters. One liter of synthetic wastewater was prepared, using 1000 mg/L direct blue dye 2-Amino-β benzenedisulfoacid, and stored to be ready for use by dissolving 1 gm of dye powder in 1 liter of distilled water. Before each experiment, an appropriate concentration was prepared by taking an exact amount from the preliminary solution and dilute it in exact amount of water. The color removal efficiency was calculated from the relative decrease of absorbance at 566 nm peaks. Experiments were carried out at room temperature. For the determination of color, a spectrophotometer Thermo electro corporation, Model GENSYS 10 UV, U.S.A, was used to measure the transmittance at wavelength of 566 nm. The experimental work was performed at the Sanitary laboratory, College of Engineering, Mustansiriyah University. Figure 1 shows direct blue dye structure while Figure 2 shows the experimental set up.

![Figure 1. Direct blue dye structure](image)

![Figure 2. Scheme diagram of the experimental set up](image)

3. Results and discussions:

3.1. pH effect

Different pH values were considered (2, 4, 6, 8, 10, 12) to calculate pH e during the experiments. The solution was adjusted with sodium hydroxide or sulfuric acid 0.1 M NaOH and 0.1 M H₂SO₄, at two electrolyte concentrations NaCl (500, 1000 mg/L) and voltage of 5 volt. The observations are as illustrated in Figure 3, where the removal of color increases with the decreasing of the pH of the solution. In acidic solutions, hypochlorous acid, generally is the most type in the electrolyte, therefore,
it has higher oxidation potential, more than hypochlorite ion. On the other hand, at the natural and alkaline conditions, the oxidation of free chlorine produces chlorate by the reaction between hypochlorous acid and hypochlorite ions, then the electrolysis of water loses hypochlorite [10]. It can be obtained from Figure 3 that the percentage of color reduction had changed from 98 % at pH 2 to 48% at pH 12 for NaCl concentration of 500 mg/L and voltage of 5 V after about 50 minutes reaction time. The maximum removal percentages was 98 % for direct blue as shown in Figure 3. Dogan et al.2012 have gained the same pH degree when electrochemical treatment was used to remove blue 1 indigo dye, and dye was removed from textile wastewater at low pH [14].

![Figure 3. pH variation effect on the removal efficiency](image)

3.2. Initial dye concentration effect:
Special attention was given to examine the effect of dye initial concentration on the removal efficiency and dye degradation. Figure 4 represents the curve of the initial dye concentrations (50, 100, 200 mg/L) versus the percentage removal of dye. The maximum loaded dye concentration was 100 mg/L with removal efficiency of 98%, but in case of initial concentration more than 100 mg/L, the rate of color removal was lower. To explain these results, the relation between OCl\(^{-}\) ions and dye molecules is going inversely. When the concentration was lower, more OCl\(^{-}\) ions were able to take possession of the reaction, therefore the degradation occurred at high rate. On the other hand, when the initial concentration increased, i.e more dye molecules, but still have the same number of OCl\(^{-}\) ions, the degradation process decreased [17].

![Figure 4. Initial dye concentration effect on the removal efficiency.](image)
3.3. NaCl concentration effect:
The general chloride reactions involved in the electrochemical oxidation are as follows[18]:

| Equation left side | Equation right side |
|--------------------|---------------------|
| 2Cl⁻               | Cl₂⁺ 2e⁻            |
| H₂O + Cl₂          | H⁺ + HOCl + Cl⁻     |
| HOCl               | H⁺ + ClO⁻           |
| 6HOCl + 3 H₂O      | 2ClO⁻³ + 14Cl⁻ + 12H⁺ + 3O₂ + 6e⁻ |
| 2e⁻ + 2H₂O + ClO⁻  | Cl⁺ + 2OH⁻          |
| 6ClO⁻ + 3H₂O       | 2ClO⁻³ + 4Cl⁻ + 6H⁺ + 1.5O₂ + 6e⁻ |
| 2e⁻ + 2H₂O         | 2OH⁻ + H₂           |
| R + HOCl           | P + Cl⁻             |

Where R = dye and P = product
Experiments were done using different NaCl concentrations 250, 500 and 1000 mg/L. As a result, color blue was decreasing due to the reaction between the hypochlorite ion (OCl⁻) and the dye. The hydrolysis reaction for the chlorine molecules produces the hypochlorite ions. The effect of changing the electrolyte concentration (250, 500 and 1000 mg/L) on color is illustrated in Figure 5. It is clear from the figure that the maximum color removal was achieved at NaCl concentration of 500 mg/L and pH = 2. No effects or decolorization were detected when NaCl solution concentration was increased to be more than 500 mg/L, as it was decreased to be 95% at 1000 mg/L concentration. The same conclusion was achieved by Lathea et al. 2017, where it was found that 0.1 mg/L NaCl concentration is satisfactory to treat textile effluent with removal efficiency more than 90% [19]. Miled et al. 2010 used 0.1, 0.5 and 1mg/L NaCl concentrations for the removal of indigo dye in acidic and neutral synthetic wastewater (pH 4). Time color removal was increasing with the increasing of NaCl concentrations, but not higher than 0.5 mg/L [20].

![Figure 5. NaCl concentration effect on the removal efficiency](image)

3.4. Voltage effect
The effect of varying the voltage in the range of 3, 4, 5 and 10 V at different operational conditions was investigated. As it appears in Figure 6, the removal of color was greatly increased with increase voltage, reaching to 5 V then decreased at 10 V. There was no significant difference in results at 4 and 10 V. Color removal efficiency also was in the maximum of 98%. This could be due to the increased oxidation reaction occurred on the anode plate, i.e, produce oxygen molecules in the solution, so, Cl⁻ ions would oxidized to OCl⁻. OCl⁻ is responsible for removing color from solution [10].
3.5. Running duration effect

To study the effect of time on the electrochemical process, each run continued for three hours at NaCl=500mg/L, pH=2 and 5 V. After 50 minutes of electrochemical treatment, color removal was achieved 98%. In general, at the first 30 minutes of the experimental run, high removal of color was obtained and then the removal became small, and this is clear in Figures 7, 8 and 9. Therefore, it is enough to treat the wastewater for 50 minutes at pH 2, dye concentration of 100 mg/L, NaCl concentration 500 mg/L and 5 volt electrical supply. Almost, similar duration time was gained to remove methylene blue from textile effluent [6]. However, color has been removed from textile and carwash effluent by the electrochemical method after 180 min. [7,14].

Figure 6. Voltage variation effect on the removal efficiency

Figure 7. Running duration effect on the removal efficiency at various NaCl con. (pH=2, dye con. = 100 mg/L, volt=5 V)
Conclusions
The electrochemical method has high efficiency of removal of color for different operational conditions (different values for pH, initial dye concentrations, NaCl concentration, voltage and operation time). The optimum operating conditions for the treatment process were at pH=2, initial concentration of 100 mg/L, NaCl =500 mg/L, Voltage=5 V, for 50 minutes operation time, at which color removal percentage was 98%. The overall results indicate that the electrochemical method can be used as a preliminary treatment to remove direct blue color.

Reference
[1] Fatiha Z, Patrick D, Brahim L, Jalila B, Jean Fois B, Said B and Kacem K 2008 Decolourization of dye-containing effluent using mineral coagulants produced by electrocoagulation Journal of Hazardous Materials 155 153–163.
[2] M Joshi, R Bansal and R Purwar 2004 Color removal from textile effluent Indian Journal fiber & textile research 29 239-259.
[3] Khanittha C and Wichan C 2009 Reuse of dye wastewater through colour removal with electrocoagulation process As. J. Energy Env. 10 250-260.

[4] Erick B, Yung-Tse H, Ruth Y and Mohammed S 2011 Electrocoagulation in Wastewater Treatment, Water 3 495-525.

[5] Norazzizi N, Siti F M A and Riyanto M R O 2013 Textile Industries Wastewater Treatment by Electrochemical Oxidation Technique Using Metal Plate International Journal of Electrochemical Science 8 11403–11415.

[6] Yao X L, Zai Y L, Xiao Y W, Chun J Z, Yu X L and Dao B J 2014 Electrochemical degradation of methylene blue using electrodes stainless steel net coated with single-walled carbon 4nanotubes, Desalination and Water Treatment 1-8.

[7] Humberto R J, Carlos B D, Ivonne L, Cheikh F and Bilyeu B 2015 A Combined Electrocoagulation-Electrooxidation Process for Carwash Wastewater Reclamation International Journal of Electrochemical Science 10 6754–6767.

[8] Sachin K P, Kiran R P, Manoj H M 2015 A Review of Electrocoagulation Technique in Treatment of Textile Mill WasteWater Journal of Information, Knowledge and Research in Civil Engineering 3 203-207.

[9] A Review, Journal of Environmental Management,128 949-963.

[10] Gamal O El-Sayed, Mohamed S Awad and Zahraa A Ayad 2014 Electrochemical Decolorization of Maxilon Red GRL Textile Dye International Research Journal of Pure & Applied Chemistry 4 402-416.

[11] Stergiopoulos D, Dermentzis K, Nakoudakis P and Tropoulos S 2014 Electrochemical Decolorization and Removal of Indigo Carmine Textile Dye from Wastewater Global Nest Journal 16 499-506.

[12] Dogan D and Haluk T, Electrochemical Treatment of Actual Textile Indigo Dye Effluent 2012 Pol. J.Environ. Stud. 21 1185-1190.

[13] Khanittha C and Wichan C 2009 Reuse of dye wastewater through colour removal with electrocoagulation process Asian Journal on Energy and Environment 10 250-260.

[14] Usha N M, Rekha H B and Mahaveer D 2014 Contribution of Treating Textile Dye Wastewater International Journal of Environmental, Chemical, Ecological Geological and Geophysical Engineering 8 130-132.

[15] Mohamed A H and Ahmed N 2017 Advanced Oxidation Processes for Textile Wastewater, Treatment International Journal of Photochemistry and Photobiology 2 85-93.

[16] Hassaan M A and Madkour F F 2016 Application of Ozonation and UV assisted Ozonation for Decolorization of Direct Yellow 50 in Seawater The Pharmaceutical and Chemical Journal 3 131-138.

[17] Ali A N, Mojtaba D, Elham R S 2017 Journal of Environmental Health Science & Engineering 15 1-11.

[18] Parsa J B and Mahmood A 2007 Decolorization of Synthetic and Real Wastewater by Indirect Electrochemical Oxidation Process Acta Chim. Slov 54 792-796.

[19] Latha A, Partheeban P and Ganesan R 2017 Treatment of Textile Wastewater by Electrochemical Method International Journal of Earth Sciences and Engineering 10 146-149.

[20] Miled W, Haj S and Roudesli S 2010 Decolorization of High Polluted Textile Wastewater by Indirect Electrochemical Oxidation Process Journal of Textile and Apparel Technology and Management 6 1-6.

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