Environ Res Tec, Vol. 8, Issue. 2, pp. 382-398, June 2025

Environmental Research and Technology
https://dergipark.org.tr/en/pub/ert
DOI: https://10.35208/ert.1501290

Research Article

Central composite experimental design for Indigo Carmine dye removal from solutions by applying electrocoagulation and electrooxidation processes

Mustafa KORKMAZ*

Balıkesir University, Engineering Faculty, Environmental Engineering Department, 10145 Çağış Campus, Balıkesir City, Türkiye

ARTICLE INFO

Article history
Received: 14 June 2024
Revised: 17 Sep 2024
Accepted: 19 Sep 2024

Key words:
Batch and continuous reactor, central composite design, electrocoagulation, electrooxidation, Indigo carmine dye removal

ABSTRACT

Indigo Carmine dye is a textile and food coloring dye reporting as toxic and harmfull for living creatures in the case of entrance to food chain above toxic levels. Sometimes textile and food industries produce toxic and harmfull dye-containing wastewaters that should be treated for safely discharge. The electrocoagulation (EC) and the electrooxidation (EO) methods for removal of dyes from wastewaters are being investigated for the last two decades. In this study, the Indigo Carmine dye removal was investigated by applying the EC and the EO methods. For this purpose, aluminum electrodes for EC and graphite plates for EO were used. The central composite experimental design was applied as the optimization method for the EC and the EO processes. The optimization parameters were selected as time (10-30 minutes), current density (0.4-2 Ampere/500 mL) and concentration (50-250 mg/L), natural pH (5.78-6.90) and room temperature (20-26.2 °C). The EO process was determined to be effective than the EC process. Statistically important parameters were concentration and time-current density interaction for the EC, but all the parameters were statistically unimportant for the EO. Dye removal percentages by the EC were calculated between 82.75% and 98.38%, and dye removal percentages by the EO were calculated between 46.88% and 100% for the experimental matrix. Electrical consumptions were a bit high for the EO than the EC. A column ion exchange process (Selion SBA 2000 resin) was applied to the dye residue after the EO treatment. From the oxidation reduction measurements, the treated solutions were determined as dischargeable.

Cite this article as: Korkmaz M. Central composite experimental design for Indigo Carmine dye removal from solutions by applying electrocoagulation and electrooxidation processes. Environ Res Tec 2025;8(2) 382-398.

INTRODUCTION

The dye pollution risk of the surface waters is a big concern throughout the world due to the textile and the food coloring industries. Dye usage in the food and the textile products causes to discharge dye-containing process waters. Dyes are visible even at 1 mg/L concentration in water body. The wastewaters of the textile and the food coloring industries contain color from the used dye [1]. Also, textile dye-containing wastewaters include heavy metals, high COD and BOI, suspended solid materials, and high salt concentration [1]. The textile dye types are reactive dyes, direct dyes, acid dyes, all-purpose dyes, nat-

---

***Corresponding author.**
*E-mail address: korkmazm@balikesir.edu.tr

ural dyes, VAT dyes, disperse dyes and azoic dyes [2]. The Indigo Carmine dye is an acid dye. This dye is reported as toxic for humans [3] and it is used as food and textile coloring agent. The Indigo Carmine dye may cause to skin and eye irritations, cancer, permanent damage to cornea and reproductive system [3]. The dyes that are mixed to the surface waters reduce the photosynthetic activity in the aqueous mediums by impeding the sun light penetration to the water [1,4,5]. Some of dyes and pigments cause to death of the soil microorganisms. Hence, toxic dye containing effluents are not appropriate for irrigation of soil [1]. There are several technologies for removal of dyes from wastewaters. Adsorption, coagulation, electrocoagulation, electrooxidation and biosorption methods are being applied for dye removal at laboratory scale nowadays [1, 6, 7, 8, 9]. The adsorption of dyes has been widely investigated by various materials [1, 4]. But, the more clean technologies are needed. The EC technology has advantages due to its low sludge production, low energy consuming, high removal performance for dyes and easy operation [10]. The EO technology has the same advantages for dye removal and also it does not produce sludge [11].

An EC process works by the electrical current that dissolves the metal electrode (anode) for coagulation and adsorption of dye molecules. In the EC process, the harmless electrodes like as iron and aluminum for removal of dyes can be used. In the EC treatment of anions, cations or organics, the sacrificed electrode (anode) cations play a neutralization role for the charged pollutants and the cations coagulates the pollutants. At the end, the filtration or sedimentation of sludge can be applied. Also, in the EC of organic matters like as dyes, the process oxidizes the organic matter to CO_2 and H2O, or the intermediate products at the anode side a bit degree and most of the removal occurs by coagulation and flotation [12]. The reactions in the EC process are as follows [13]: Firstly, the anode electrodes like as iron or aluminum are dissolved by the electrical current flow from a cathode to an anode. The electrons of the anode plate are transferred from the anode to the cathode. The organic matters are also destroyed at the anode surface by the direct oxidation or indirect oxidation in the reactor body. The reactions for aluminum electrode used in EC can be given as follows [14]:

In the EO, the electrons from the anode pass to the cathode and the electrical current moves to the anode from the cathode [13]. But, electrical dissolution of the anode plates like as graphite or boron doped diamonds do not realize strongly. There are four oxidation mechanisms of the organics in the EO like as anodic oxidation, active hydroxyl oxidation, chlorine based oxidant oxidation and hydrogen peroxide [15]. In this study, magnesium chloride hegza hydrate was used as electrolyte salt for adjustment of the current density or voltage and forms the source of the oxidizing chloride radicals. Its chloride content was the reason for selection of this salt. The oxidizing molecules like as chlorine (Cl2), hypochlorous acid (HOCl), hypochlorite (OCl-) are generated at reactor of the EC or EO in the presence of chloride anions and hydrogen peroxide is produced at cathode side. The EO and the EC chloride based oxidants are produced by the following reactions [15]:

Hypochlorous acid dissociates to produce the hypochlorite ions, which are generally present at higher pH (pH>6) [15]. These extremely vigorous oxidizing molecules (HOCl, OCl- and Cl2) can deteriorate the surface of the organic substance and can

$$\text{Anode: Al} \rightarrow \text{Al}^{3+} + 3e^{-} \qquad \text{(Eq.1)}$$

$$\text{Cathode: } 3H_2O + 3e^{-} \rightarrow 3/2H_2 + 3OH^{-} \qquad \text{(Eq.2)}$$

General reactions in the reactor body:

$$3Al^{+3} + 9H_2O + 3OH^{-} \rightarrow 3Al(OH)_4^{\ -} + 9/2H_2 \qquad \text{(Eq.3)}$$

$$Al(OH\ )_3 + OH\ = Al(OH)_4^{\ -} \qquad \text{(Eq.4)}$$

$$\text{Anode: } 2Cl^{-} \rightarrow Cl_2 + 2e^{-} \qquad \text{(Eq.5)}$$

$$Cl_2 + H_2O \rightarrow H^{+} + Cl^{-} + HOCl \qquad \text{(Eq.6)}$$

$$HOCl \rightarrow OCl^{-} + H^{+} \qquad \text{(Eq.7)}$$

$$OCl^{-} + \text{Dye} \rightarrow H_2O + CO_2 + Cl^{-} \qquad \text{(Eq.8)}$$

shred. An EO process works by passing electrons from cathode through anode The conversion of the organic molecules to CO_2, H2O or intermediate products realizes at the surface of an anode by electrons and by the indirect oxidizing molecules (HOCl, OCl, and Cl2) [15]. Also, the direct oxidation occurs by the produced active hydroxyl radicals at the anode. The EO technology is an ecofriendly method for treating dye wastewater, because of the following advantages [16]: (i) The absence of extra redox or oxidizing chemicals, (ii) close control of the desired reaction conditions like as reaction rate and oxidant source addition, and (iii) the increased possibility of on-site treatment. In this study, the EO technology was applied using an insoluble graphite plate and EC was applied using an aluminum electrode. The central composite experimental design was applied to data of the EC and the EO for comparison of removal percentage of the dye and the electrical consumption values.

In a study, the electrochemical treatment of Basic Blue 3 dye from the textile wastewaters was reported. It was achieved more than 97% color removal with pH (8) after 10 minutes. 92-95% and 72-60% dye removal efficiencies were obtained in 6 minutes for 50-400 mg/L and 500-600 mg/L initial dye concentrations, respectively [17].

It was reported that dye with larger molecular weights were more affected by the increase in pH for removal. In dye removal with pH increase, Reactive Black 39 (1021.16 g/mol) is affected by the pH increase by decreasing removal from 100% to 74.83. Remazol Red 3B (674.10 g/mol) is affected with pH increase with a removal decrease from 96.54% to 83.01 [18].

It was observed that the color removal and COD removal efficiencies increased with the increase of mixing speed. A significant value of 99.5% was reached for the removal efficiency of Acid Red 20 from aqueous solution. The results obtained showed that the EO method is an usable method for removing light azo dyes from water [19].

It was reported that within 20 min of electrochemical treatment, about 99.94% of the color was removed from the KCl and 39.90% from the Na2SO4 solutions. This degradation efficiency in the KCl solutions can be attributed to indirect electrochemical oxidation, where, in the presence of chlorides, the electrolyte generates strongly oxidizing species, which enhance the efficiency of the treatment at the Pt electrode [20].

In a study where the EC process equipped with iron and aluminum electrodes was used, the effects of initial pH, current density, conductivity and electrolysis time on the removal of Reactive Yellow 160 (RY160) dye were examined. High color removal efficiency was achieved in EC, regardless of the electrode material [21].

The central composite design tool of the response surface method in Minitab 16.0 software was used in data analysis. Firstly, Box and Wilson defined the response surface optimization (RSM) method [22]. They determined the experimental matrix giving the maximum output with the least number of runs. The model obtained from the central composite design method is formed with the help of regression analysis [22]. The importance of the main and their interactions in the model is determined by the regression coefficients and the confidence constants (p) [22]. The central composite design method is used in many areas of science and industry. In the central composite design method, the effects of two or more factors (up to ten factors) on output can be determined. The results obtained can be analyzed with three-dimensional and the counter graphics. The model obtained by the central composite design method is used to calculation of output of selected parameter levels for estimation of experimental data. The effectiveness of the model can be understood by the coefficient of determination values like as R-Sq, R-Sq(adj) and R-Sq(pred) [22].

In this study, the EO and the EC methods were compared in a batch reactor applying central composite design for Indigo Carmine dye removal. The reasons of selection of the EC and the EO processes were that these technologies are clean, rapid, effective and easily handable [10,11]. The Indigo Carmine dye was selected because this dye is toxic and widely used in the food and textile industries. Although Indigo Carmine dye is considered toxic and has many adverse effects, it is found in many foods, and the maximum permitted level is 500 mg/kg in foods [23]. The EC and EO methods removed the dye at high degree and these technologies were clean and very practical. The dye removal approaches by these technologies have been studied in litherature too, but every dye has own moleculer size, structure, structural bond and end by-products after treatment, therefore their behaviour under treatment give interesting and promising results, if the dye can be removed completely for high concentrations. Removal of dyes by EC occured by coagulation way as a result of coagulating aluminum cation and aluminum hydroxide and produced oxidizing chemicals like as chlorine gas, hypochlorous acid, reactive hydroxly ions and hydrogen peroxide [10,11]. The EO enables to remove dyes from waters without any sludge after treatment. On the other hand, EC sludge amount after treatment of dyes is very low. Similar to EC, EO runs by electron, chlorine gas, hypochlorous acid, reactive hydroxyl oxidations and hydrogen peroxide [20]. In addition to these, optimization of these technologies gives opportinuity for operation of real reactors by scale-up of miniaturized reactor to big reactor. The operation pHs, temperatures, the state of oxidizing species for dye removal and operability of these reactors is very important. In these respects, this study is important and complexity of the solution chemistries during removal is one of the important points that should be understand. Sometimes, coagulation, adsorption and especially ion exchange, biosorption materials can become ineffective for anionic dye removal from waters. For this purpose, EC and EO technologies show good performance for anionic dyes like Indigo Carmine [10,11].

In the literature, Huangfu et al. (2021) reported that the Indigo Carmine dye removal by graphite-graphite (C-C, anode-cathode), aluminum-graphite (Al-C, anode-cathode) and steinless steel-graphite (SS-C, anode-cathode) electrodes by the classical single parameter experiments [24]. In the present study, it was investigated the aluminum and graphite electrodes performances for Indigo Carmine dye removal in detail by investigating time, concentration and current density for central composite experimental design for upgrading the miniaturized reactor to real big reactor. The energy consumptions were optimized for both the electrodes. Also, discharge potentiels of the treated solutions were evaluated by oxidation reduction potentiel analysises. Continuous reactor application for EO process were determined as the most effective than EC. Advanced treatment of dye residue after EO process treatment was done by anion exchange resin (Selion SBA 2000). Dye removal mechanisms, removal costs and literature comparision were described.

MATERIAL AND METHODS

Properties of Indigo Carmine Dye

The Indigo Carmine dye is an indigo-5,5'-disulfonic acid disodium salt and has formula of C16H8N2Na2O8S2. The dye solution has blue color at pHs up to 13 and above pHs 13, the dye solution has yellow color. It is a food and textile coloring agent. The stock dye solutions were prepared at per four days. During these four days, the color absorbance of the Indigo Carmine dye solution did not change.

EC and EO Experiments for Central Composite Experimental Design in a Batch Reactor

Two aluminum electrodes (anode and cathode) for EC and two graphite plates (anode and cathode) for EO were used for the Indigo Carmine dye removal from waters. The effective dimensions of one graphite plate had 50×70×10 mm (Width×Height×Thickness) and effective dimensions of one aluminum electrode had 50×70×2 mm (Width×Height×Thickness). The electrode total areas were 89 cm2 for EO and 73.8 cm2 for EC. The distance between the aluminum electrodes were 5.2 cm and the distance between the graphite plates were 4 cm in the batch reactors. One plate for anode and one plate for cathode were used for both of the EC and the EO processes. The low and high levels of the parameters in the EC and the EO for central composite design are given in Table 1. The stock dye solution was prepared as 2,000 mg/L concentration and the working solutions were prepared freshly from the stock solution. The central composite experimental design was studied for Indigo Carmine dye removal as a function of time (10-30 min), current density (0.4-2 A/500 mL) and concentration (50-250 mg/L) at natural pHs (5.78-6.9) and room temperature (20-26.2 °C). A batch reactor with 750 mL volume was filled with 500 mL dye solution and stirred at 1,000 rpm speed.

An amount of 3 or 6 g MgCl2.6H2O (Merck product) was added to the dye solution as supporting electrolyte. The 3 g salt was enough for all the experiments, but for only 2 ampere study, 3 gram salt did not provide 2 amper value, therefore 6 gram salt was added. Its chloride content was the reason for selection of this salt. The DC-power supply was switched on while the reactor content was being stirred. At the end of the reaction, 4 mL treated wastewater was pipetted and filtered with Whatman filter paper for the EC. The treated wastewater was taken directly for the EO. The spectrophotometers are very useable devices for color measurements and Indigo Carmine dye measurements were done after filtration of treated solution of EC by Whatman fitler paper which does not adsorb the Indigo Carmine dye. Measurement in spectrofotometer was done at 610 nm wavelengt by using one light road applying quartz cell. Measurements were done after dilution of supernatant solution. The calibraion curve was used for calculation of concentration and it was plotted between 0-10 mg/L concentration. After filtration of Whatman filter paper, there is any flock for EC and for bare dye solution, the filter paper was seen that it did not adsorb the dye.

The experiments were carried out according to the optimization experimental matrix established by Minitab 16.0 software. The reaction products and experimental setups are given in Figure 1, Figure 2 (EC) and Figure 3 (EO), respectively. The dye chemical structure is given in Figure 4. The initial solution temperatures were between 20 and 26.2 °C throughout the experiments at room conditions. The pure water was used in preparation of the working solutions. A vacuum filtration device was used for filtration of the treated dye solutions after the EC by using a special filtration tube. The Indigo Carmine dye has dense blue color. The dye removal percentage was calculated using the following equation.

$$\eta = \frac{(C_0 - C) \times 100}{C_0} \qquad \text{(Eq.9)}$$

Here, is the removal percentage (%). C0 and C are the initial and the treated water dye concentrations (mg/L).

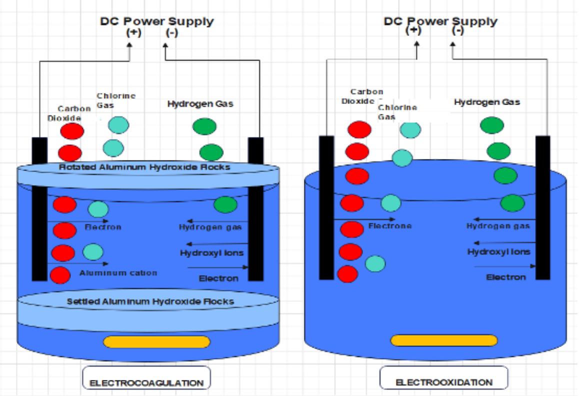


Figure 1. Reaction products in EC and EO processes

Ion Exchange Treatment of Persistent Dye Residue after EO by Selion SBA 2000 Resin

The dye residue after the EO treatment of the Indigo Carmine dye had yellow color. The dye residue after the EO process was treated with Selion SBA 2000 basic resin in a column reactor filled with 25 g resin. The resin was dried at ambient room temperature. The treatment parameters for the batch EO process was initial 100 mg/L Indigo Carmine dye concentration, current density 1.5 A, solution volume 500 mL, 2,500 rpm stirring speed, room temperature, and natural pH. Ion exchange treatment for the dye residue was applied after the batch EO process. Ion exchange column had 1.78 cm inner diameter and 25 cm height. The ion exchange experiments were carried out for only 100% removal (i.e. treated sample was taken for initial durations

Table 1. The low and high values of parameters for EC and EO processes

Parameter and levels	-2	-1	0	1	2
Time (min)	10	15	20	25	30
Current Density (A)	0.4	0.8	1.2	1.6	2
Concentration (mg/L)	50	100	150	200	250

of outlet solutions of column reactor) and these are not kinetic studies. The dye residue was the inert side of the dye after the EO treatment.

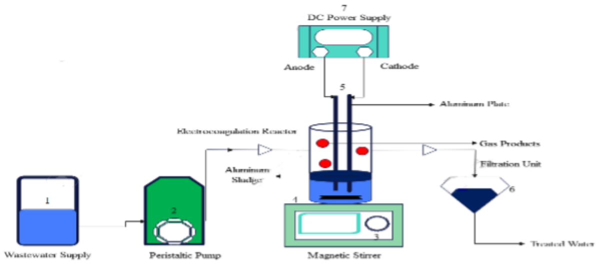


Figure 2. Experimental setup for EC process (The general experiments conducted in batch mode and continuous mode was applied only for comparision with EO, Data are not given for continuous reactor)

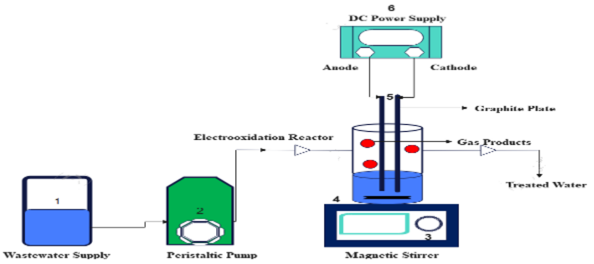


Figure 3. Experimental setup for EO process (The general experiments conducted in batch mode and continuous mode was applied only for comparision with EC)

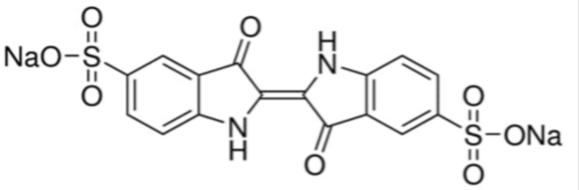


Figure 4. Open formula of Indigo Carmine dye

The central composite design is a tool in the response surface optimization method of Minitab 16.0 software. This optimization method is widely used for industry, science and other areas. It analyzes an experimental matrix determined by the software. The central composite experimental design is formed from an experimental matrix established by conducting the preliminary experiments for maximum concentration removal from wastewater. The central composite design may consist of a factorial or fractional factorial designs. The factorial design can be upgraded to the central composite design by adding the center and a group of axial points that allow estimation of optimum conditions [25]. Generally, the central composite design statistical analysis is formed from the following stages.

i-) Determination of the experimental matrix conditions from the preliminary studies conducting a series of the classical single parameter experiments for completely pollutant removal. Anova analysis of the parameters for whether one parameter is at statistically significant level or not, for instance 95% (i.e. $p<0.05$),

ii-) Development of the regression model such as linear, linear-square, linear-interaction or full quadratic,

iii-) Calculation of the model response by the regression model for true operation of the reactor and estimation of the experimental data by regression model. The regression model is useful to relate the factor and the response in a mathematical model by following equation.

$$\text{Dye removal (\%)} = b + b1X1 + b2X2 + b3X3 + b4X1X1 + b5X2X2 + b6X3X3 + b7X1X2 + b8X1X3 + b9X2X3 + \acute{\varepsilon} \quad \text{(Eq.10)}$$

Here, b, b1, b2, b3, b4, b5, b6, b7, b8, b9 are model constants and X1, X2, X3, X1X1, X2X2, X3X3, X1X2, X1X3, X2X3 are the coded factors and their interactions representing to time, current density, concentration and interactions of these parameters. $\acute{\varepsilon}$ is error. In this study, the uncoded values of the parameters were used for data analysis, that is, real values of the factors were used in the statistical analysis. Full quadratic model eqauation was used for model development.

RESULTS AND DISCUSSION

Central Composite Design of Removal of the Dye by EC and EO Processes

The parameters (current density, time and concentration) were studied for removal of the Indigo Carmine dye from water in a batch reactor. For this purpose, the EC and the EO processes were applied. The low and high level of parameters for the EC and the EO were time (10-30 min), current density (0.4-2 A), and concentration (50-250 mg/L). The experimental matrix for the EC and the EO is given in Table 2. The Anova analysis showing the statistically importance of the parameters is given in Table 3. The EC maximum dye removal percentage was obtained as 98.38% (10 minutes, 1.2 A, 150 mg/L) and the EO maximum dye removal percentage was obtained as about 100% (20 minutes, 1.2 A, 50 mg/L). The confidence level of Anova analysis was selected as 95% ($p<0.05$) of which above the confidence constants show the statistically unimportance of the parameter. The statistically important parameters or interactions were model constant and time-current density interaction for the EC; however, all the parameters for the EO were determined as unimportant. In the optimization, currect density, concentration and time was studied. Natural pH, room temperature, current density, time and concentration are real operation parameters. Therefore, there is no necessitate for extending parameter number like as temperature and pH. The developed regression model could be estimate well the data. The estimation of the model to data is very meaningfull from statistically importance of parameter value change (p). R-Sq(adj) values show the enough number of parameters for modelling. R-Sq(pred) values show the low estimation of model the removal data. But, it was thought that the real estimated values of the removal percentages were enough for operation of reactors. The avarage error values between real and estimated data were around 6%. The full quadratic model was used in development of regression models. The regression models for the EC and the EO are obtained as follows:

$$\text{EC Dye removal (\%)} = 76.8437 + 0.2136*T + 13.2956*CD + 0.0976*C + 0.0177*T*T + 0.3223*CD*CD - 0.0006*C*C - 1.2461*T*CD + 0.0027*T*C + 0.0531*CD*C \quad \text{(Eq.11)}$$

$$\text{EO Dye removal (\%)} = 66.5666 + 2.2818*T + 45.2960*CD - 0.4266*C - 0.0622*T*T - 30.1970*C*CD - 0.0003*C*C + 0.4756*T*CD + 0.0022*T*C + 0.2743*CD*C \quad \text{(Eq.12)}$$

Here, T is time (min), CD is current density (A), C is concentration (mg/L).

The prediction of data by regression models is given in Table 2. The surface plots of the EC and the EO are given in Figure 5. The end point pHs and voltages are given in Table 2.

Time-Current Density Effect for the EC Process

Time effect on the Indigo Carmine dye removal from solution by the EC process was studied at time interval of 10 and 30 minutes. Results are given in Figure 5. From Figure 5, dye removal increased at high time-low current density interaction. Dye removal leaved as low at high current density studies. The increasing time and current density produced high amount of aluminum hydroxide and aluminum cation in the reactor and resulted in a high coagulant amount which was expected the more Indigo Carmine dye removal. But, high aluminum hydroxide and aluminum cations decreased the removal. It was thought that there was equilibrium between the dye and aluminum species interaction for high current density. For instance, boron adsorption on alunite [26], Dowex 2×8 ion exchange resin [27] and zinc hydroxide [28] remained as steady at high adsorbent amounts. Also, the removal percentage high from 95% in the Indigo Carmine dye removal can cause to this situation due to rapidly decreasing of concentration gradient at high current density. Because, as can be seen in Section 3.3 (concentration-time effect for the EC), dye removal increased at high concentrations. Removal percentages changed between 95-100%. Also, a desorption could be occurred at high current densities. Above pH 5.5, aluminum cations are at aluminum hydroxide form and at pHs (4-5.5), aluminum cations and aluminum hydroxides are present. High time and high current density cause to production of high aluminum species due to high electrolysis amount. In the reported studies, dye removal percentages in EC and EO processes were increased by current density increase for Basic Blue 3 and Acid Red 20 dyes, respectively [17,19]. In this study, the decreasing effect of high current can be related by solid-to-dye ratio relation, desorption and rapidly decrease in concentration of dye. Dye removal was determined as concentration dependent.

Concentration-Time Effect for the EC

The dye concentrations for the Indigo Carmine dye removal were studied at 50 and 250 mg/L concentration interval. Results are given in Figure 5. The figure indicates that the maximum dye removal was obtained at high concentration-stable time interaction. Time was ineffective at high concentrations. Due to driving force of high dye concentration [1], the dye removal increased at high concentrations. The ineffectiveness of time at high concentrations can be attributed to rapidly decrease of the dye concentration. Removal percentages were between 85 and 95%. On contrast to these results, Basic Blue 3 dye removal percentages decreased by concentration increase for EC process [17]. These results showed that the removal of the Indigo Carmine dye was concentration depended for aluminum electrodes.

Current Density-Concentration Effect for the EC Process

The current density is an important parameter in dissolution of metal electrodes for coagulation of dyes from waters. Also, high current density provides the high oxidation ratio of dye molecules due to raising electron transfer. Results are given in Figure 5. The current density raise generally increases the coagulant dosage and thus the removal yield is expected to increase. In the EC experiments, the dye concentration had raising effect on removal at high concentration-stable current density interaction conditions. The current density was ineffective at high concentrations. These results can be related with the solid-dye equilibrium conditions, because dye adsorption on low coagulant and high coagulant was same [29]. Removal percentages changed between 85-95%. Reactive Yellow 160 dye removal increased by current density increase and reached to steady at high current densities for aluminum and iron electrodes [21]. This situation in the present study can also be related by rapidly removal of dye because low concentrations decrease the removal (Figure 5).

Time-Current Density Effect for the EO Process

Time is a key parameter for dye removal from water by the EO process and operation time was studied at 10-30 time intervals by the central composite design. Results are given in Figure 5. The Figure 5 showed to increase of removal at high value of time and moderate current density. The effects of the parameters can be attributed the high interaction time and thus high interaction opportunity of electrons with dye molecules [30]. Removal percentages changed between 40 and 95%. Moderate current density effect on removal may be due to operation solution temperature, pH and amounts of the produced oxidants like as active hydroxyl, hypochlorous acid, chlorine gas and hydrogen peroxide. The removal of Acid Red 20 dye by EO process increased with current density increase and moderate current provided enough removal percentage for about 100% extent [19].

Concentration-Time Effect for the EO Process

Results are given in Figure 5. High time and low concentration increased the removal yield. Removal percentages changed between 60 and 95%. High time increased the interaction opportunity of the dye and oxidants. Low concentration effect can be related with sufficient oxidant amounts like as electron, hypochlorous acid, hydrogen peroxide and active hydroxyl ions against low dye concentration. The removal of Reactive Blue 21 dye removal was reported to reach the maximum value at 10 minutes and high current by EO process [20].

Current Density-Concentration Effect for the EO Process

Current density controls the deterioration amount and rate of organics like as dyes by the EO process as the electron amount in the reactor body increases with the current density increase. The results are given in Figure 5. The Figure 5 indicated the increasing removal yield at high value of current density and low dye concentration. This increasing electron amount increased the removal. Removal percentages changed between 40 and 95%. The reason of low concentration can be attributed to high oxidizing opportunity between dye and chlorine gas, electron, hypochlorous acid, hydrogen peroxide and active hydroxyl ion amount. Manisha and coworkers reported to increase of Rhodamine B dye removal by current density and electrolyte concentration increase [31].

Comparison of the Batch and the Continuous Reactors for Dye Removal

Dye removal from wastewaters can be realized by batch and continuous reactors. For this purpose, this study provides two reactor types. EC and EO processes should be study for real operation conditions and their performances should be optimized for real operation of these two reactors. The batch reactor data comparison of yield of the EC and the EO processes are given in Figure 6. The most effective results were obtained for the EO process. The continuous reactor was, therefore, applied for the EO process. The experimental parameters for the EO process at the continuous mode were 100 mg/L dye concentration, 1,000 rpm stirring speed, 3 g/500 mL MgCl2.6H2O backround electrolyte amount, natural pH (6.85), initial temperature 26.2 °C, 1.6 Ampere, 500 mL reactor starting volume, 11.76 mL/min volumetric flow rate. The removal percentage change during the removal in the continuous process is given Figure 7. The dye could be treated as about 100% by continuous EO process although after passing 2.46 fold hydraulic retention time (HRT). The residence time was calculated as 42.5 minutes and it was measured that the reactor reached to steady state and removal percentage was about 100% during the removal in continuous reactor. The reactor was taken to continuous mode after operation of the batch reactor at 15 minutes for 500 mL dye solution. Although the dye removal was at about 100% extent, a bit yellow color as end residue was observed. The starting color of the dye was dense blue. Thus, dye removal extent was measured as a bit below 100% extent. Therefore, the dye residue from outlet water of the EO process should be removed. Therefore, an ion exchange process was applied to the persistent dye-containing solution after the batch EO process. The oxidation reduction potential (ORP) of aluminum coagulation for the dye was measured as - 448 mV after 4 g MgCl2.6H2O, 100 mg/L dye, 1.6 Ampere, 15 minute operation time, 500 mL. The oxidation reduction potential (ORP) of graphite treatment for the dye was measured as 670 mV after 3 g MgCl2.6H2O, 100 mg/L dye, 1.6 Ampere, 15 minute operation time, 500 mL. The oxidation reduction potential (ORP) of the used pure water was measured as 580 mV. As can be seen from these results, the treated solutions can be discharged directly. The negative value of aluminum coagulated solution shows the unoxidant property of the solution. The ORP values of some foods as examples are given in Figure 8 [32].

Persistent Dye Residue Treatment after the Batch EO by Applying Ion Exchange

The Indigo Carmine dye has dense blue color. The yellow dye residue after EO process treatment could be refined by ion exchange resin (Selion SBA 2000 basic resin) at 100% efficiency and photographs of dye residue and its refined outlet water from ion exchange column are given in Figure 9. It is clear from Figure 9 that dye residue could be treated at 100% extent. The used resin was an anionic material and removed completely dye residue. Dyes are generally visiable in the surface waters even at 1 mg/L concentration, therefore, a removal extent of 100% was selected as discharge standart. A neutralization operation can be proposed for discharge of acidic treated dye water after EO process and ion exchange process

Table 2. Experimental matrix for dye removal by EC and EO (20-26.2 oC, 1,000 rpm, 500 mL, Natural pH=5.78-6.90) (*6 g/500 mL MgCl2.6H2O was used and in other experiments 3 g/500 mL MgCl2.6H2O was used)

Parameters				Response (%)							
Run	T(min)	CD (A)	C (mg/L)	EC (%)	Predicted (%)	End pHs	Voltage (V)	EO (%)	Predicted (%)	End pHs	Voltage (V)
1	15	0.8	200	92.88	98.04	4.40	13.1-12.5	71.48	62.58	2.98	17.4-14.7
2	30	1.2	150	94.63	89.09	4.21	20.5-17.2	99.21	95.57	2.63	20.4-15.1
3	25	0.8	200	96.81	102.68	4.34	12.4-11.5	69.92	68.73	2.69	15.9-13.4
4	20	1.2	150	95.25	98.01	4.24	19-14.3	89.58	94.84	2.61	23.7-15.8
5	25	0.8	100	95.56	93.92	4.24	13.2-12.3	98.50	92.94	2.60	16.2-12.8
6	15	0.8	100	92.81	85.98	4.35	11.7-11.1	99.41	89.00	2.52	16.5-13.4
7	15	1.6	200	95.78	102.83	4.16	24.6-20.9	90.63	90.44	2.77	25.1-23.7
8	20	0.4	150	96.08	96.02	4.54	7-7.1	46.88	56.73	2.68	8.9-8.6
9	10	1.2	150	98.38	101.46	4.34	17.3-16.1	72.92	81.68	2.32	23.2-18.4
10*	15*	1.6*	100*	92.94	89.53	4.08	27.6-22.4	99.44	94.91	2.22	28.7-20.2
11	20	2	150	93.79	86.90	3.94	28.8-24.2	99.04	94.30	2.27	21.7-15.9
12	25	1.6	200	91.22	109.51	3.96	25.7-20.2	95.70	100.39	2.19	30.4-19.1
13	20	1.2	50	82.75	82.47	4.16	21-18	100.31	106.19	2.33	22.2-16.9
14	25	1.6	100	84.25	75.51	3.96	23.5-20.5	99.50	102.66	2.07	29.5-18.1
15	20	1.2	250	95.46	128.54	4.27	18-16.1	78.44	77.50	2.57	19.1-16.6

Table 3. Anova analysis of dye removal by EC and EO processes

Parameters	EC R-Sq=90.91%, R-Sq(pred)=14.21%, R-Sq(adj)=74.54%		EO R-Sq=84.78%, R-Sq(pred)=0.00%, R-Sq(adj)=57.38%	
	Constant	p	Constant	p
Constant	76.8437	0.023	66.5666	0.578
T	0.2136	0.871	2.2818	0.716
CD	13.2956	0.384	45.2960	0.524
C	0.0976	0.422	-0.4266	0.457
T*T	0.0177	0.533	-0.0622	0.641
CD*CD	0.3223	0.941	-30.1970	0.184
C*C	-0.0006	0.086	-0.0003	0.826
T*CD	-1.2461	0.024	0.4756	0.807
T*C	0.0027	0.432	0.0022	0.888
CD*C	0.0531	0.230	0.2743	0.197

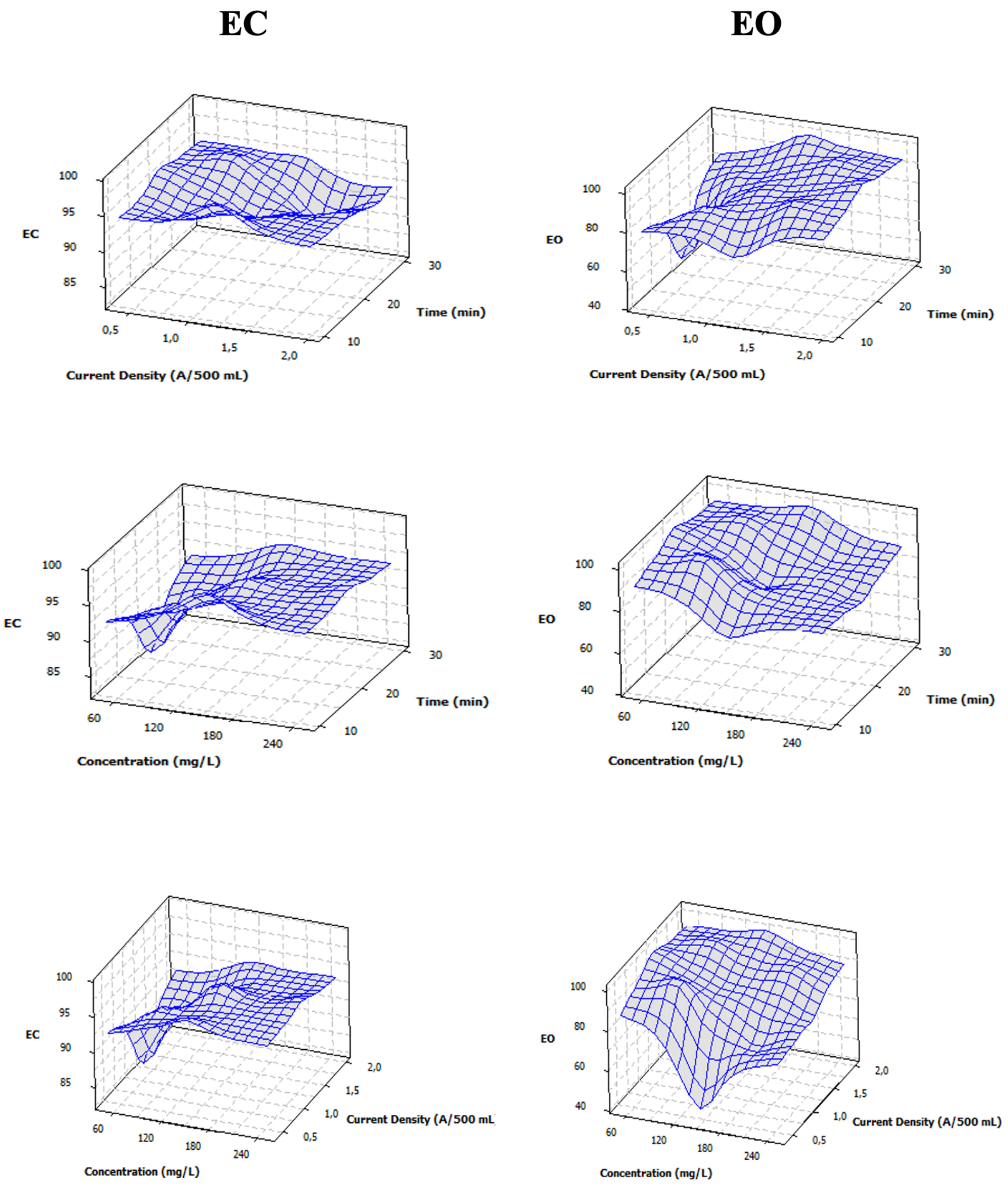
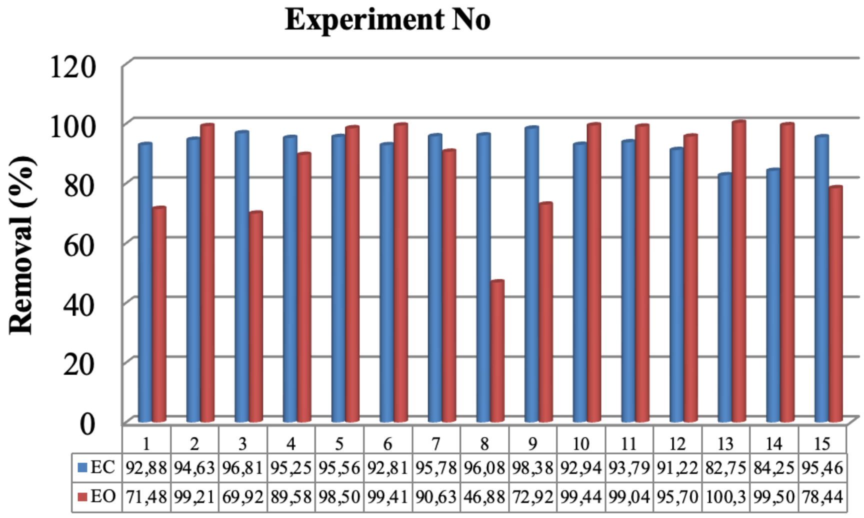
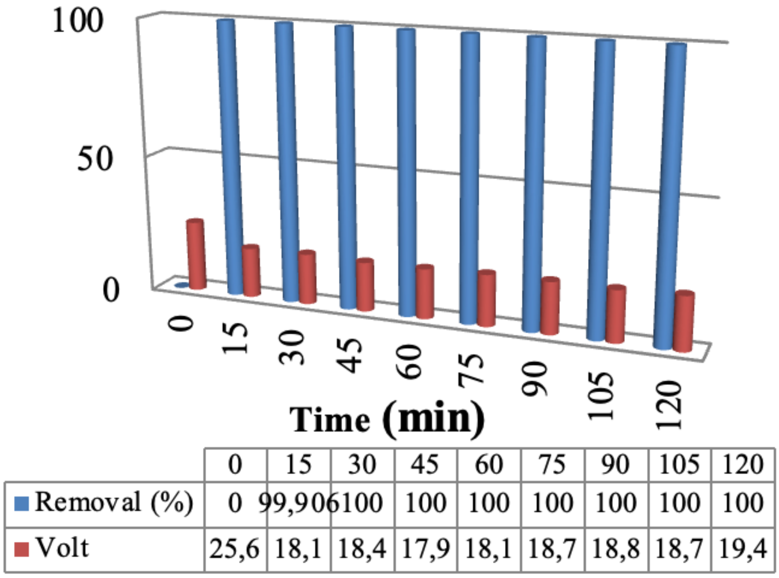


Figure 5. Removal percentage of dye as a function of parameters



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
🟦 EC	92,88	94,63	96,81	95,25	95,56	92,81	95,78	96,08	98,38	92,94	93,79	91,22	82,75	84,25	95,46
🟥 EO	71,48	99,21	69,92	89,58	98,50	99,41	90,63	46,88	72,92	99,44	99,04	95,70	100,3	99,50	78,44

Figure 6. Removal percentage of dye for EC and EO processes



	0	15	30	45	60	75	90	105	120
🟦 Removal (%)	0	99,906	100	100	100	100	100	100	100
🟥 Volt	25,6	18,1	18,4	17,9	18,1	18,7	18,8	18,7	19,4

Figure 7. Removal percentage of dye for EO in the continuous system

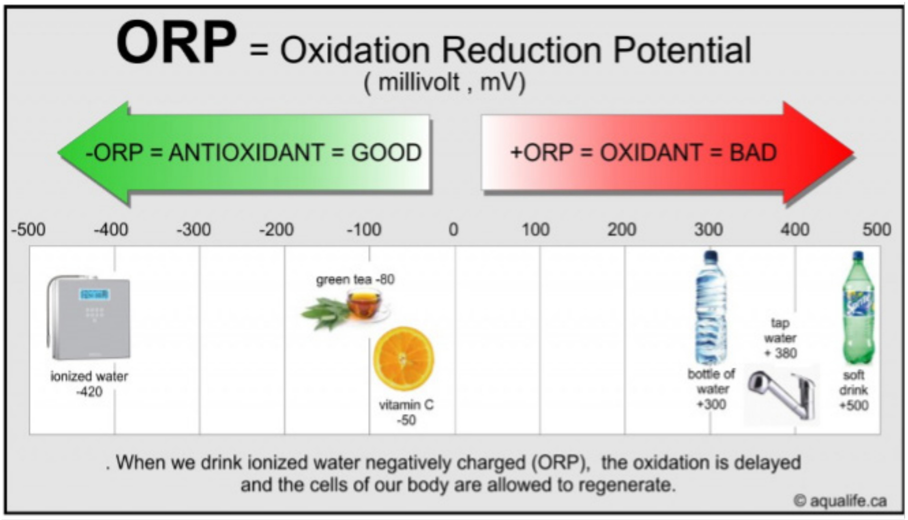


Figure 8. ORP values of some foods [32]

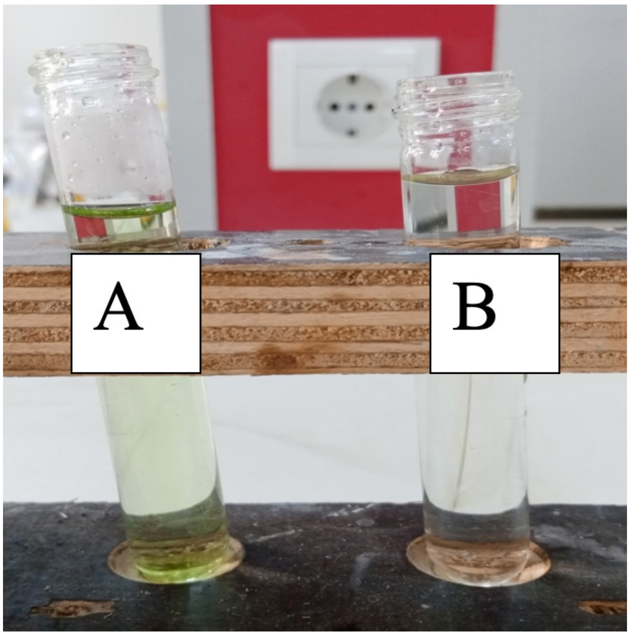


Figure 9. Treatment dye residue by Selion SBA 2000 anionic ion exchange resin after EO (A: Dye residue, B: Treated dye residue, 200 mg/L dye, constant 1.4 A, Natural pH, Room temperature (21.2 °C), 500 mL, 3 g MgCl.6H2O, 45 minutes oxidation time)

Energy consumption for the EC and the EO processes

The energy consumptions for the EC and the EO were calculated by the following equation [33].

Here, V, I and t are average voltage of the system (V), electrical current density (A) and reaction time (h), respectively.

The energy consumption in the EC and the EO processes is vital for applicability of the treatment to the dye-containing wastewaters. The energy consumption values are given in Figure 10. As can be seen in Figure 10, the energy consumption for the EC increased with high current-high time, constant concentration-high time and middle concentration-high current. The energy consumption for the EO increased with high current-high time, constant concentration-high time and middle concentration-high current. It is a general role for the electrochemical treatment processes that the energy consumption increases with time and current increase (Eq. 13 shows the evidence). The electrical consumption of the EO was generally a bit high from EC processes, and EO process is assumed as advantageous due to zero sludge production. The comparison of the EC and the EO processes was given in Figure 10 and 11.

Here, T is time (min), CD is current density (A), C is concentration (mg/L). WEC is energy consumption for electrocoagulation and WEO is energy consumption for electrooxidation.

The experimental matrix for the energy consumption by the EC and the EO processes is given in Table 4. The Anova analysis for the energy consumption by the EC and the EO processes is given in Table 5. The Anova analysis of the EC process showed that current density-current density interaction and time-current density interaction were statistically important, however, for the EO process, all the parameters were statistically unimportant. The uncoded factors were used in the development of regression models for the energy consumptions. As can be seen in Table 4, energy consumptions in EO process were a bit high from EC process but it was not so important. R-Sq(adj) values show the enough number of parameters for modelling. R-Sq(pred) values show the good estimation of model the energy consumptions.

$$W\left(\frac{kW \times h}{m^3}\right) = \frac{V \times I \times t}{Volume} \qquad \text{(Eq.13)}$$

$$WEC\left(\frac{kW \times h}{m^3}\right) = 12.6073 - 0.7623*T - 13.6215*CD - 0.0388*C + 0.0062*T*T + 7.1522*CD*CD + 0.0001*C*C + 0.9342*T*CD + 0.001*T*C - 0.0035*CD*C \qquad \text{(Eq.14)}$$

$$WEO\left(\frac{kW \times h}{m^3}\right) = -7.30407 + 0.04023*T + 5.87118*CD + 0.03770*C - 0.01940*T*T - 4.76620*C*CD - 0.00018*C*C + 1.16375*T*CD + 0.00048*T*C + 0.00429*CD*C \qquad \text{(Eq.15)}$$

Table 4. Experimental matrix for energy consumption by EC and EO (20 oC, 1000 rpm, 500 mL)

Parameters				Response			
Run	**T(min)**	**CD (A)**	**C (mg/L)**	**WEC**	**Predicted**	**WEO**	**Predicted**
1	15	0.8	200	5.12	6.14	6.42	7.01
2	30	1.2	150	22.62	23.20	21.30	23.06
3	25	0.8	200	7.97	10.47	9.77	9.92
4	20	1.2	150	14.00	15.02	15.80	17.67
5	25	0.8	100	8.50	9.13	9.67	10.01
6	15	0.8	100	4.56	5.80	5.98	7.58
7	15	1.6	200	18.20	19.62	19.52	17.21
8	20	0.4	150	1.88	2.23	2.33	-0.06
9	10	1.2	150	6.68	8.07	8.32	8.40
10	15	1.6	100	20.00	19.56	19.56	17.43
11	20	2	150	35.33	36.96	25.07	29.30
12	25	1.6	200	30.60	31.43	33.00	29.43
13	20	1.2	50	15.60	15.32	15.64	16.03
14	25	1.6	100	29.33	30.37	31.73	29.18
15	20	1.2	250	13.64	16.72	14.28	15.71

Table 5. Anova analysis of energy consumption by EC and EO

Parameters	EC R-Sq=99.65%, R-Sq(pred)=97.07%, R-Sq(adj)=99.02%		EO R-Sq=94.58%, R-Sq(pred)=47.85%, R-Sq(adj)=84.82%	
	Constant	**p**	**Constant**	**p**
Constant	12.6073	0.303	-7.30407	0.857
T	-0.7623	0.247	0.04023	0.985
CD	-13.6215	0.090	5.87118	0.807
C	-0.0388	0.488	0.03770	0.844
T*T	0.0062	0.635	-0.01940	0.672
CD*CD	7.1522	0.014	-4.76620	0.512
C*C	0.0001	0.651	-0.00018	0.696
T*CD	0.9342	0.004	1.16375	0.127
T*C	0.001	0.525	0.00048	0.928
CD*C	-0.0035	0.854	0.00429	0.949

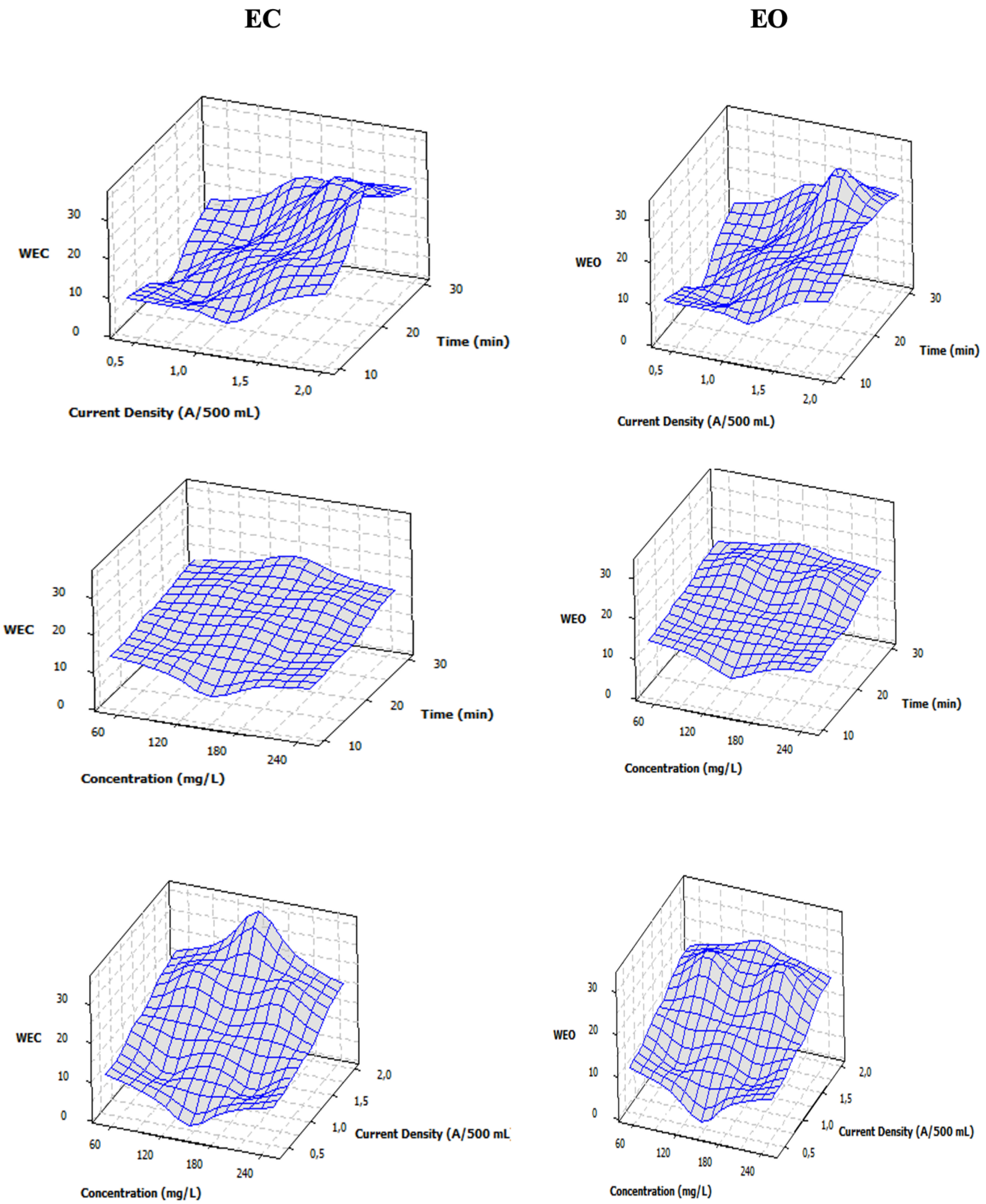
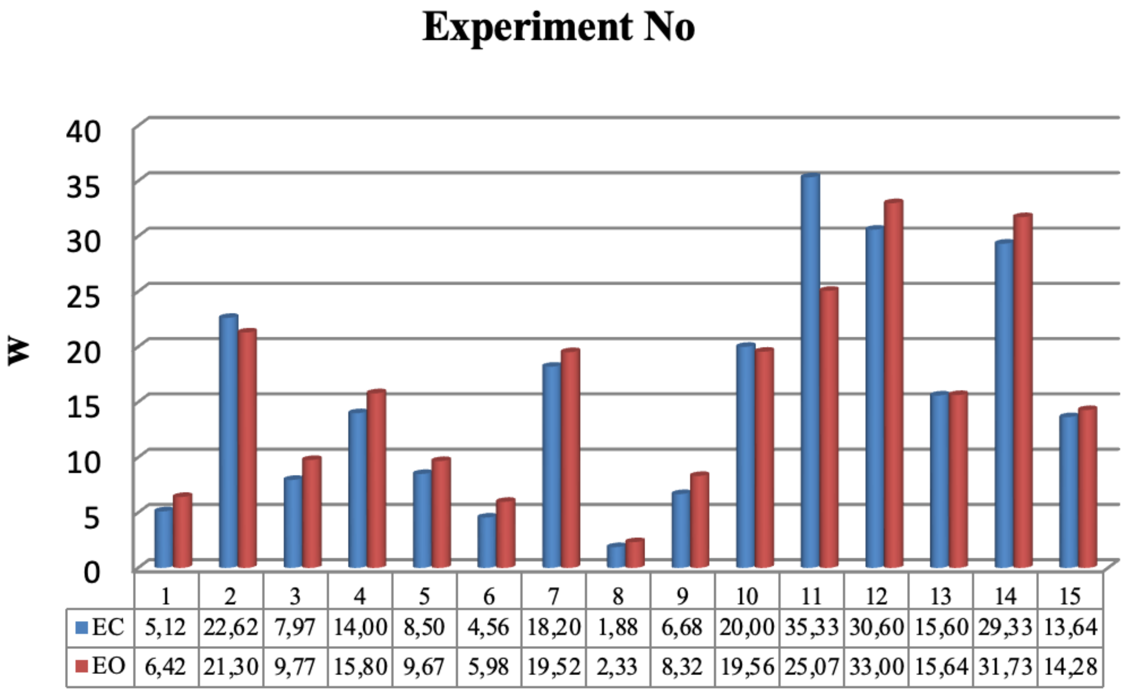


Figure 10. Energy consumption for EC and EO processes as a function of parameters



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
🟦 EC	5,12	22,62	7,97	14,00	8,50	4,56	18,20	1,88	6,68	20,00	35,33	30,60	15,60	29,33	13,64
🟥 EO	6,42	21,30	9,77	15,80	9,67	5,98	19,52	2,33	8,32	19,56	25,07	33,00	15,64	31,73	14,28

Figure 11. Energy consumption for EC and EO processes as a function of experiment no

Dye Removal Mechanisms, Removal Costs and Literature Comparision

The amount of released aluminum cation from aluminum electrode (anode) was calculated using following equation and given in Table 6. The cost of energy consumption was given in Figure 12 per cubic meter treated wastewater. As can be seen in Figure 12, the cost of EO was found as a bit high from EC but EO process gave the best removal percentages for the dye. Also, graphite is not soluble in water and therefore, its cost is advantageous from soluble aluminum electrode. Salt cost for both the process is equal.

Here, I is current (A), t is time (second), M is molecular weight (g/mole), n is electron valence, F is Faraday constant (96,500 C/mole) [34].

Dye removal mechanisms for EO process was realized by direct oxidation with active hydroxyl radicals, indirect oxidation by hypochlorite anion, chlorine gas, hydrogen peroxide. The reactions for chlorine gas and hypochlorite anion were given in Eq (5-8). The generation of hydrogen peroxide at cathode is given in the following equations [35].

The active oxygens in the hydrogen peroxide is oxidized the organic matter or hydrogen peroxide is dissociated to active hydroxyl radicals to oxidize the organic matter like dyes. Similar to EO process, these oxidizing reactions occur in EC process but the general removal of dye occurs by coagulation and flotation.

$$Al^{3+}(g) = \frac{I \times t \times M}{n \times F} \qquad \text{(Eq. 16)}$$

$$\begin{aligned} &Acidic-medium: O_2 + H_2 + 2e^- \rightarrow H_2O_2 \\ &Alkaline-medium: O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \end{aligned} \qquad \text{(Eq. 17)}$$

$$OH^- + OH^- \rightarrow H_2O_2 \qquad \text{(Eq. 18)}$$

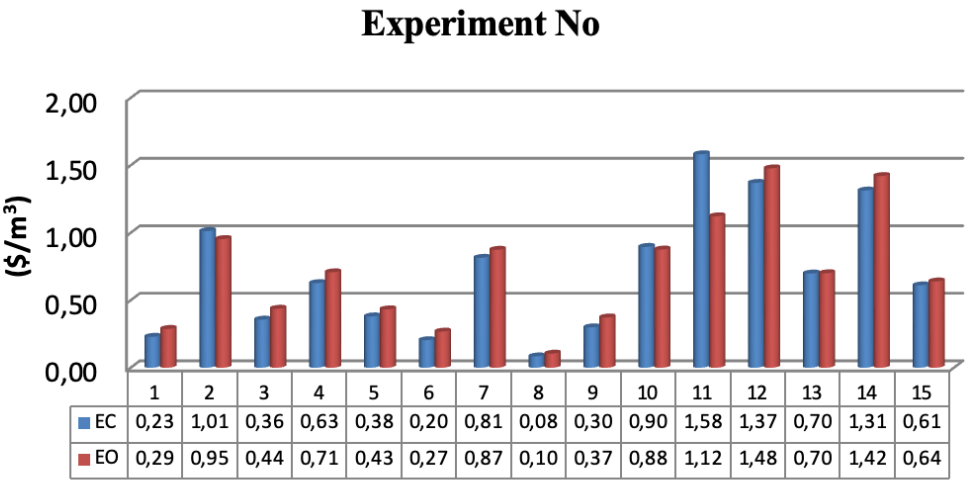


Figure 12. Energy consumption costs for EC and EO processes as a function of experiment no

Table 6. Al^{3+} amount release from anode to the solution phase for EC process

Experiment No	Amount (g)
1	0.067
2	0.201
3	0.112
4	0.134
5	0.112
6	0.067
7	0.134
8	0.045
9	0.067
10	0.134
11	0.224
12	0.224
13	0.134
14	0.224
15	0.134

In a reported study, energy consumption values were evaluated for textile dye decolorization (t=15 min) and COD removal (t=120 min) as 2.7-18.9 kWh/kg dye decolorization and 51.0-190.7 kWh/kg COD removal, respectively [36]. In an other study, for certain concentrations of 2.5 mM, 5.0 mM, 7.5 mM, and 10 mM NaCl, energy consumption values can be reported as follows: 4.21 kW-h/m3, 3.10 kW-h/m3, 2.96 kW-h/m3, and 2.60 kW-h/m3, respectively [37]. In this study, the energy consumptions showed to values of 1.88-35.33 kW-h/m3 for EC and 2.33-33.0 kW-h/m3 for EO. Dalvand and coworkers reported that electrode consumption, energy consumption and operating cost were 0.052kg/m3, 1.303kWh/m3 and 0.256US$/m3 for Reactive Red 198, respectively [38].

CONCLUSION

The Indigo Carmine dye removal from synthetically prepared solutions was investigated using the EC and the EO processes as a function of current density, concentration and time. The central composite design was applied for these two processes and the EO was found more effective than EC and 100% dye removal was achieved by the EO process followed the ion exchange. The batch and the continuous flow reactors were applied and the continuous flow reactor was determined as large time applicable for the EO method. Even after 2.46 fold hydraulic retention time, the dye removal performance of the continuous reactor was good. As a result, the removal of this dye could be achieved successfully in the batch and the continuous EO reactors for safely discharge. The electrical consumption of the EO was high a bit from the EC processes and due to sludge production of EC, EO process was determined to be advantageous. The persistent dye residue was removed at 100% yield from the outlet water of the batch EO reactor by ion exchange treatment. The experimental and the statistical analysis results of the dye removal can be summarized as follows. The statistically important parameters or interactions for dye removal were model constant and time-current density interaction for the EC; however, all the parameters for the EO were determined as unimportant. In the energy consumption analysis, the EC process showed that current density-current density interaction and time-current density interaction were statistically important, however, for the EO process, all the parameters were statistically unimportant.

•In the EC process: Dye removal increased at high time-low current density interaction. Dye removal increased at high concentration-stable time interaction. Dye concentration had raising effect on removal at high concentration-stable current density interaction conditions.

•In the EO process: The time-current density interaction effect showed to increase of removal at high value of time and moderate current density. High time and low concentration increased the removal yield. The concentration-current density interaction indicated the increasing removal yield at high value of current density and low dye concentration.

•In EC process, the sludge production was low and therefore, EO process was found as advantageous. pH change in EC for

0.8 A and 200 mg/L concentration at 0, 2, 5, 10 and 15 minutes were 5.60, 4.19, 3.92, 3.84 and 3.70 ± 0.1. pH change in EO for 0.8 A and 200 mg/L concentration at 0, 2, 5, 10 and 15 minutes were 5.60, 2.48, 2.32, 2.14 and 2.23 ± 0.1.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the cor responding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

REFERENCES

[1]. M. Korkmaz, C. Özmetin, BA. Fil, E. Özmetin, and Y. Yaşar, “Methyl violet dye adsorption onto clinoptilolite (Natural Zeolite): Isotherm and kinetic study,” Fresenius Environmental Bulletin, Vol. 22(5), pp. 1523-1533, 2013.

[2]. https://textilelearner.net/different-types-of-dyes-with-chemical-structure/ [Online]. Available: (2024)

[3]. S.S. Bala, A.J. Alkhatib, S.S. Bashir, and M. Abdulhadi, “Photocatalytic degradation of Indigo Carmine in aqueous solutions by the antibacterial agent pefloxacin and UVA,” Biomedical Journal of Scientific & Technical Research, Vol. 5, pp. 4903-4909, 2018.

[4]. B.L. Cíntia, Z.F.P. João, A.P. Julio, C. Polonio, “Effects of textile dyes on health and the environment and bioremediation potential of living organisms,” Biotechnology Research & Innovation, Vol. 3(2), pp. 275-290, 2019.

[5]. M. Berradi, R. Hsissou, M. Khudhair, M. Assouag, O. Cherkaoui, A.E. Bachiri, and A.E. Harfi, “Textile finishing dyes and their impact on aquatic environs,” Heliyon, Vol. 5(11), pp. 02711, 2019.

[6]. B. Shi, G. Li, D. Wang, C. Feng, H. Tang, “Removal of direct dyes by coagulation: the performance of preformed polymeric aluminum species,” Journal of Hazardous Materials, Vol. 143(1-2), pp. 567-574, 2007.

[7]. F. Silva, L. Nascimento, M. Brito, K. Silva, W. Paschoal, and R. Fujiyama, “Biosorption of methylene blue dye using natural biosorbents made from weed,” Materials (Basel), Vol. 12(15), pp. 2486, 2007.

[8]. N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, “Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters,” Journal of Hazardous Materials, Vol. 129(1-3), pp. 116-122, 2006.

[9]. A. Demir Delil, N. Gören, “Investigation of electrocoagulation and electrooxidation methods of real textile wastewater treatment,” Eskişehir Techical University Journal of Science Techical Applied Science and Engineering, Vol. 20(1), pp. 80 – 91, 2019.

[10] Z. Yılmaz, M.B. Karagözoğlu, “Atıksuların arıtılmasında elektrokoagülasyon uygulamaları,” BEÜ Fen Bilimleri Dergisi, Cilt 8 (1), s. 319-334, 2019.

[11] M.S. Najafinejad, S. Chianese, A. Fenti, P. Lovino, D. Musmarra, “Application of electrochemical oxidation for water and wastewater treatment: An overview,” Molecules, Vol. 28, pp. 4208, 2023.

[12]. D.R. Ryan, “Electrocoagulation-electrooxidation for mitigating trace organic compounds in model source waters”, Degree of Master of Science and Engineering, Marquette University, Milwaukee, Wisconsin 2019.

[13] T. Arslan, “Kompleks olarak bağlı ağır metal içerikli atık suların elektrokoagülasyon ile arıtımı,” Yüksek Lisans Tezi, İstanbul Teknik Üniversitesi, İstanbul, Türkiye, 2008.

[14] M.A. Sadik, “Removal of reactive dye from textile mill wastewater by leading electrocoagulation process using aluminum as a sacrificial anode,” Advances in Chemical Engineering and Science, Vol. 9, pp. 182-193, 2019.

[15] A.A. Beddai, B.A. Badday, A.M. Al-Yaqoobi, M.K. Mejbel, Z.S. Hachim, and M.K.A. Mohammed, “Color removal of textile wastewater using electrochemical batch recirculation tubular upflow cell,” International Journal of Chemical Engineering, Vol. 2022, pp. 1-8, 2022.

[16] C. Wang, “Decolorization of congo red with three dimensional flow-by packed-bed electrodes,” Journal of Environmental Science and Health Part A, Vol. 38(2), pp. 399–413, 2003.

[17] E. Bulut, “Tekstil atık sularından C.I. Bazik Mavi 3 boyarmaddesinin elektrokimyasal uygulama ile giderilmesi,” SAÜ Fen Bilimleri Dergisi, Cilt. 20 (3), s. 521-531, 2016.

[18] L. Gazigil, O.T. Can, “Elektrokoagülasyon yöntemi ile sulardan boyarmadde gideriminde molekül büyüklüğü ve pH etkisi,” APJES, Citt 5, s. 113-122, 2017.

[19] J. Erkmen, M. Adıgüzel, “Acid red-20 sentetik endüstriyel boyar maddenin elektro-oksidasyon yöntemi ile sulu çözeltiden uzaklaştırılması,” NÖHÜ Mühendislik Bilimleri Dergisi, Cilt 11(2), s. 363-371, 2022.

[20] S.E. Aggadi, Z.E. Abbassi, A.E. Hourch, "Color removal from dye-containing aqueous solutions by electrooxidation," Desalination and Water Treatment, Vol. 215, pp. 232–236, 2021.

[21] A. Aygün, B. Eren, "Elektrokoagülayon yöntemiyle Reaktif Yellow 160 boyar maddesinin giderimi," APJES, Cit 5, s. 10-18, 2017.

[22] M. Korkmaz, E. Özmetin, Y. Süzen, E. Çalgan, C. Özmetin, "A new adsorbent (aluminum modified talc) for phosphate removal from alkaline solutions and optimization of data by central composite design," Desalination Water and Treatment, Vol. 245, pp. 178–190, 2022.

[23] M.E. Ristea, and O. Zarnescu, "Indigo Carmine: Between necessity and concern", Journal of Xenobiotics, Vol. 13(3), pp. 509–528, 2023.

[24] Z. Huangfu, and W. Zhang, S. Hao, M. Zhang, and J. Yao, "Construction of novel electrochemical treatment systems for indigo wastewaterand their performance," Pigment & Resin Technology, Vol. 50(3), pp. 264–270, 2021.

[25] Minitab 16.0 programme help tool description of central composite design

[26] D. Kavak, "Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design," Journal of Hazardous Materials, Vol. 163, pp. 308–314, 2009.

[27] N. Öztürk, and T.E. Köse, "Boron removal from aqueous solutions by ion-exchange resin: Batch studies," Desalination, Vol. 227, pp. 233–240, 2008.

[28] M. Korkmaz, C. Özmetin, E. Özmetin, E. Çalgan, Ö. Ziyanak, "Boron removal from colemanite mine wastewater by coagulation using zinc hydroxide—A factorial optimization study," Celal Bayar University Journal of Science, Vol. 18, pp. 77-83, 2022.

[29] Özmetin, C., Korkmaz, M., "Full factorial design of experiments for boron removal by iron hydroxide from colemanite mine wastewater", Journal of Balikesir University Institute of Science and Technology, 21(1):244-253, (2019).

[30] H.M.A. Asghar, T. Ahmad, S.N. Hussain, and H. Sattar, "Electrochemical oxidation of methylene blue in aqueous solution," International Journal of Chemical Engineering and Applications,Vol. 6(5), pp. 352-355, 2015.

[31] M.S. Kothari and K.A. Shah, "Electrochemical oxidation for decolorization of Rhodamine-B dye using mixed metal oxide electrode: modeling and optimization," Water Science & Technology, Vol. 81, pp. 720-731, 2020.

[32] https://aqualife.ca/orp-oxydation-reduction-potential/ [Online]. Available: (2024)

[33] A.E. Yilmaz, R. Boncukcuoglu, M.M. Kocakerim, M.T Yilmaz, C. Paluluoglu, "Boron removal from geothermal waters by electrocoagulation," Journal of Hazardous Materials, Vol. 153, pp. 146–151, 2008.

[34] A.E. Yılmaz, R. Boncukcuoğlu, M.M. Kocakerim, E. Kocadağistan, "An empirical model for kinetics of boron removal from boron containing wastewaters by the electrocoagulation method in a batch reactor," Desalination, Vol. 230, pp. 288–297, 2008.

[35] I. Dioufa, O. Diab, M.B. Diedhioua, P. Droguib, A.O. Tourea, S.M. Lo, M. Rumeaua, and C. Gueye Mar-Diop, "Electro-generation of hydrogen peroxide using a graphite cathode fromexhausted batteries: study of influential parameters on electro-Fenton process," Environmental Technology, Vol. 41, pp. 1434–1445, 2020.

[36] B.K. Körbahti and K. M. Turan, " Evaluation of energy consumption in electrochemical oxidation of Acid Violet 7 textile dye using Pt/Ir electrodes," JOTCSA, Vol. 3(3), pp. 75-92, 2016.

[37] O. Sözüdoğru, "Electrochemical oxidation of wastewater contaminated with Astrazon Red Violet 3RN Dye on Ti/IrO$_2$/RuO$_2$: Evaluation of process parameters, Kinetics, and energy consumption, Iranian Journal of Chemistry and Chemical Engineering, Vol. 42(11), pp. 3640-3658, 2023.

[38] A. Dalvand, M. Gholami, A. Joneidi, N. M. Mahmoodi, "Dye removal, energy consumption and operating cost of electrocoagulation of textile wastewater as a clean process," Clean– Soil, Air, Water, Vol. 39 (7), pp. 665–672, 2011.