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Removal of reactive azo dye using platinum-coated titanium electrodes with the electro-oxidation process

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ABSTRACT

The removal of Drimaren Orange HF 2GL (DOHF2GL) azo dye from aqueous solutions was researched using platinum-coated titanium electrodes with the electro-oxidation process. The effects of electrolyte type, NaCl concentration, current density, initial dye concentration, pH, and solution temperature on dye removal were investigated. The maximum removal efficiency was determined as 98.7% at the end of 120 min for electrolyte concentration 4 g/L NaCl, current density 1.74 mA/cm^2, temperature 20°C, pH 7, and dye concentration of 100 mg/L. When NaCl was used as an electrolyte, there was lower energy consumption and higher dye removal compared to $NaNO_3$ and Na_2SO_4. With the increase in NaCl concentration, the cell potential reduced, and the treatment efficiency was determined to increase. The current density was the most important parameter affecting dye removal rate and energy consumption was determined to be largely linked to the current density applied. The dye removal efficiencies increased with the applied current density and electrolyte concentration and decreased with the increase in initial dye concentration. Experimental data under different reaction conditions were used to determine that the dye removal kinetics followed pseudo-first-order kinetics. Fourier transform infrared spectroscopy (FTIR) studies were performed to assess the degradation of dye with the electro-oxidation process.

Keywords: Electro-oxidation; Dye removal; Ti/Pt anode; Kinetic study; IR spectroscopy

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1. Introduction

With the increase in demand for textile products, the wastewater amounts sourced in the textile industry are increasing. Wastewater from the textile industry is classified based on color (weak, moderate, and strong) and structure (anionic and cationic). The molecular structures of reactive dyes with strong color comprised a functional group formed by covalent bonds between a chromophore group (azo, anthraquinone, phthalocyanine, and triarylmethane) and cellulose fibers [1]. Azo dyes are the most commonly used synthetic dyes in the textile industry and comprise nearly 50% of dyes used in traditional textile industries [2]. It was reported that raw effluent originating from the textile industry has cytogenetic and mutagenic effects, whereas no toxicity was observed in the treated wastewater [3,4]. As a result, many researchers have completed studies on the removal of mainly azo dyes from wastewater [5–7]. Azo dyes and their degradation products may produce different by-products with mutagenic and carcinogenic effects [8]. Colored wastewater discharged into the receiving environment without treatment or with insufficient treatment prevents the passage of sunlight, slows the photosynthesis rate, and as a result reduces the dissolved oxygen value causing negative

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effects on the ecosystem [9,10]. Hence, it is very important to effectively remove azo dyes from wastewater.

For the removal of azo dyes from wastewater, physical, chemical, and biological processes can be used [11–13]. These methods are not sufficient to treat azo dyes, because using these processes does not fully remove azo dyes or produces secondary waste material as a result of degradation of azo dyes [14]. Biological treatment methods are the most commonly used techniques; however, the use of this method only limits the toxicity of azo dyes [15]. Coagulation/flocculation methods are commonly used; however, they have disadvantages due to requiring significant amounts of chemical materials and creating high amounts of sludge [16]. Active carbon adsorption is a commonly used and accepted method for the removal of dyes; however, treatment costs are high [17]. The use of advanced oxidation processes for the treatment of wastewater including azo dyes is becoming increasingly popular. Of these processes, the electro-oxidation process is a developing and promising technology. This process is commonly used due to versatility, strong oxidation ability, environmental compatibility, energy efficiency, cost-effectiveness, appropriateness for automation, and easy application ability [18]. The main disadvantages of this process are the operating costs due to energy consumption and the high cost of some anode materials used [19].

The electro-oxidation process is becoming more popular for the removal of organic material and color from wastewater. Electro-oxidation is based on using an insoluble anode material (Ti, Ti/Pt, Ti/RuO$_2$, Ti/IrO$_2$, graphite, stainless steel, and boron-doped diamond) to directly or indirectly oxidize organic material [20]. In the direct electro-oxidation process oxidants are produced by the electrode surface, while in the indirect electro-oxidation process different oxidants (like persulfate anion and active chlorine species) are produced linked to other salts dissolved in the wastewater [21,22]. The anode material used and experimental conditions play important roles in both the selectivity and efficiency of the oxidation process [23].

The aim of this study is to determine the optimum conditions for experimental parameters to treat synthetically prepared colored wastewater with appropriate cost using the electro-oxidation process. The effects of current density, electrolyte species, NaCl concentration, initial dye concentration, temperature, and initial pH on degradation of Drimaren Orange HF 2GL (DOHF2GL) in aqueous solutions with the electro-oxidation process were researched. After testing for compliance with some kinetic models using experimental data, an attempt was made to determine changes in the structure of the dye using Fourier transform infrared spectroscopy (FTIR) analysis.

2. Materials and methods

2.1. Chemicals

DOHF2GL dye was obtained from a textile factory located in Kayseri (Turkey) and used without any purification processes. Sodium chloride (≥99.0%), sodium nitrate (≥99.0%), sodium sulfate (≥99.0%), sulfuric acid (95.0–98.0%), and sodium hydroxide (≥97.0%) were obtained from Sigma-Aldrich (Germany) at analytical purity. Deionized water was used to prepare solutions.

2.2. Experimental procedure

Pt-coated Ti sieve-type electrodes were used as anode and cathode material (Umicore brand, Germany). The total electrode surface area was 576 cm^2 and the distance between the electrodes (anode–cathode) was 3 mm. The anodes and cathodes used in experimental studies were placed parallel to each other. Each experimental study had electrolyte and dye diluted to 600 mL with deionized water and then were set to the desired pH value using 0.5 M sulfuric acid and sodium hydroxide with a pH meter (WTW MultiLine, Multi 3620 IDS, Germany). The reactor used in the experiments was double-walled and operated in batch mode. The temperature of the solution was fixed to the desired temperature with a temperature-controlled heating-cooling circulator (LABO, C200-H13, Turkey). To ensure homogeneity of the solution, a magnetic stirrer was used (IKA, RCT basic, Germany) and the mixing rate was fixed to 600 rpm during the reactions. Later electricity was supplied to the system with a direct current power source (GW Instek, PSW 80-40.5, Taiwan). During each experiment, samples were taken from the reactor at regular intervals and immediately analyzed.

2.3. Analytical techniques

Dye concentration was determined with absorbance values using a UV-vis spectrophotometer (Hack Lange, DR6000) at the maximum wavelength ($\lambda_{\max}$ = 416 nm) from a prepared calibration curve. The efficiency and energy consumption (W) of dye removal were calculated from Eqs. (1) and (2), respectively:

$$\text{Removal efficiency, } (\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \tag{1}$$

$$W, \left(\text{kWh/m}^3\right) = \frac{V \times I \times t}{V_S} \tag{2}$$

where C_0 is the initial dye concentration (mg/L), C_t is the dye concentration at time t (mg/L), V is mean cell voltage (V), I is electrolysis current (A), t is electrolysis duration (h), and V_s is solution volume (m^3).

Variations in dye structure after electro-oxidation were assessed using an infrared spectrophotometer (Bruker, Alpha, Germany) in the spectral interval 500–4,000 cm^{-1} (resolution 4 cm^{-1}, scans 24). For this analysis, the solution was dried at the end of 120 min and the remaining solid residue was analyzed.

3. Results and discussion

3.1. Effect of current density

Current density has a significant effect on electrochemical treatment because it is the driving force for migration of ions [24]. Current density is the most important parameter controlling the reaction rate. If the excessive current density is used, costs increase and the life of the anode material may be reduced [25]. With the aim of determining the effect of current density, experiments were completed

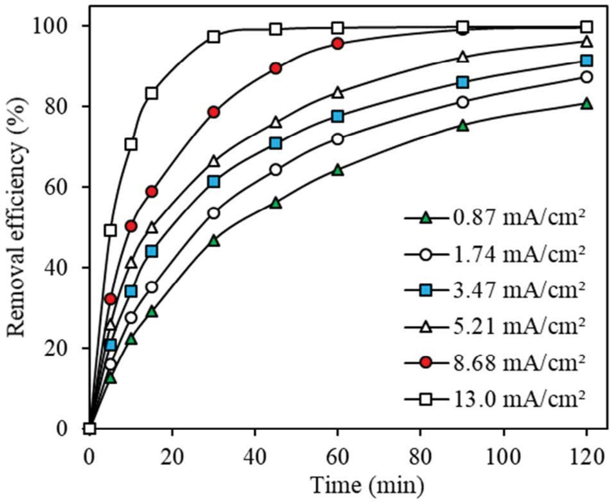

Fig. 1. Effect of current density on dye removal (C_0 = 100 mg/L; pH = 7; T = 20°C; Electrolyte = 0.5 g/L NaCl).

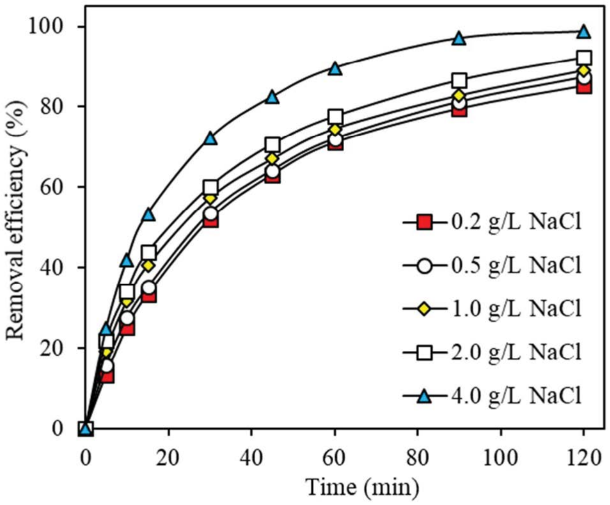

Fig. 2. Effect of NaCl concentration on dye removal (C_0 = 100 mg/L; pH = 7; T = 20°C; J = 1.74 mA/cm²).

with dye material concentration 100 mg/L, initial pH 7, electrolyte concentration 0.5 g/L NaCl and temperature 20°C fixed and current density varied to 0.87, 1.74, 3.47, 5.21, 8.68, and 13.0 mA/cm^2. In Fig. 1, the variation in current density had a significant effect on dye removal. As current density increased, the dye removal was 80.7%, 87.3%, 91.3%, 96.3%, 99.7%, and 99.8%, respectively, at the end of 120 min. When the high current density is applied, more rapid dye removal is ensured. With the current density of 8.68 mA/cm^2, the dye is nearly completely removed in nearly 90 min, while at 13.0 mA/cm^2 current density, 45 min are sufficient to ensure the same removal efficiency. The dye removal efficiency was realized in shorter times at high current density. Energy consumption must not be disregarded at the same time. While the energy consumption was 97.7 kWh/m^3 with 8.68 mA/cm^2 and 90 min treatment duration, it increased to 104.6 kWh/m^3 at the highest current density of 13.0 mA/cm^2 and 45 min treatment duration. At high current density, the electrical energy consumption increases, and the operating costs increase. From the experimental results, the optimum current density was 8.68 mA/cm^2. However, in order to examine the removal efficiency of other parameters and to reduce the energy cost, the current density was chosen as 1.74 mA/cm^2 in subsequent experiments.

3.2. Effect of NaCl concentration

Electrolyte concentration (NaCl concentration) is one of the most important parameters affecting electro-oxidation [26]. With the aim of determining the effect of different concentrations of NaCl, chosen due to low cost, the relatively high solubility of active chlorine species produced, and strong oxidant properties, a range of experiments were completed and the results obtained are given in Fig. 2. The initial dye concentration was fixed to 100 mg/L, with a current density of 1.74 mA/cm^2, initial pH 7, and temperature of 20°C for the experiments. The NaCl concentrations were 0.2, 0.5, 1.0, 2.0, and 4.0 g/L with electrochemical treatment for 120 min. When Fig. 2 is investigated, the dye removal efficiency for 0.2, 0.5, 1.0, 2.0, and 4.0 g/L NaCl was 85.2%, 87.3%, 89.0%, 92.2%, and 98.7%, respectively. Based on these results, it is understood that the amount of NaCl is one of the most important parameters affecting the electro-oxidation of dye. As the NaCl concentration increases, larger amounts of active chlorine are produced due to the increase in the mass transfer of chlorine to the anode surface and as a result, there is an increase in dye removal reported in some studies [27,28]. As the NaCl amount increases, conductivity will increase, the potential of the electrochemical cell will reduce and energy consumption will fall [29]. Here the energy consumption with 0.2 g/L NaCl was 17.7 kWh/m^3 while increasing the NaCl concentration to 4.0 g/L caused the energy consumption to fall to 10.1 kWh/m^3. Studies may be performed about higher electrolyte concentrations for lower energy consumption. However, the addition of high amounts of NaCl may increase the efficiency of oxidation but may also cause the formation of more dangerous chlorine organic compounds so higher NaCl amounts were not trialed [30]. For these reasons, the 4.0 g/L NaCl concentration was chosen as the optimum parameter for the following experiments.

3.3. Effect of different electrolytes

For electrochemical treatment to occur, the solution needs to be electrically conductive [31]. The electrolyte type and concentration added to the solution with the aim of ensuring electrical conductivity determines the performance of the electro-oxidation process. As a result, with the aim of increasing the electrical conductivity of the synthetic solution with an initial dye concentration of 100 mg/L, three different electrolytes (NaCl, $NaNO_3$, and Na_2SO_4) were used. The concentration of each electrolyte in solution was 4 g/L, with results obtained at current density of 1.74 mA/cm^2 (J), initial pH 7, and temperature 20°C shown in Fig. 3. The dye removal efficiency for NaCl, $NaNO_3$ and Na_2SO_4, respectively, were determined as 98.7%, 87.7%, and 86.4%. Dye removal was observed to be more rapid

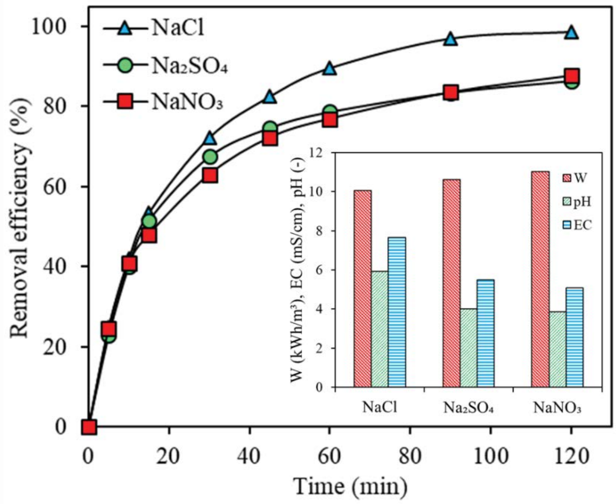

Fig. 3. Effect of electrolyte type on dye removal (C_0 = 100 mg/L; pH = 7; T = 20°C; J = 1.74 mA/cm^2; Electrolyte = 4 g/L).

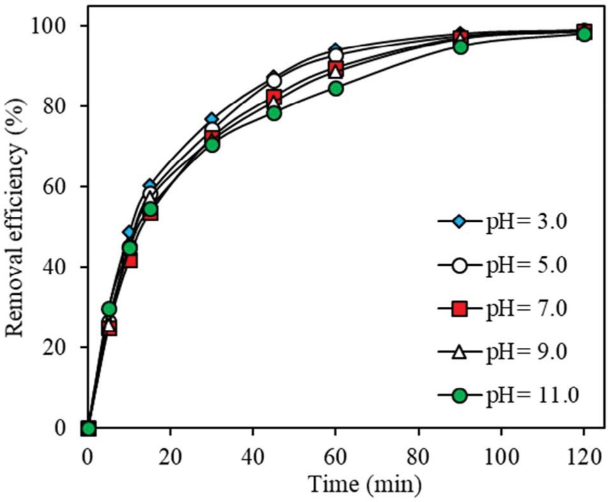

Fig. 4. Effect of pH on dye removal (C_0 = 100 mg/L; T = 20°C; Electrolyte = 4 g/L NaCl; J = 1.74 mA/cm^2).

in the presence of NaCl. This situation may be associated with the production of a variety of oxidant types linked to the type of salt [31]. The addition of chlorine encourages the electrochemical formation of active chlorine species like strong oxidants Cl_2 (Eq. (3)), HOCl (Eq. (4)), and OCl^- (Eq. (5)) linked to the current density and solution pH value [32] and lead to the more rapid removal of dye. Farizoğlu et al. [33] observed similar effects for electro-oxidation of Reactive Black 5 dye in the presence of NaCl. In conclusion, NaCl is chosen more often as it provides higher dye removal and is also easy to obtain, and has relatively high solubility [24]. The energy consumption (W), solution pH, and electrical conductivity (EC) values at the end of 120 min linked to electrolyte type are given in the inset in Fig. 3. When energy consumption is compared, the lowest energy consumption of 10.1 kWh/m^3 was obtained using NaCl. When equal amounts of electrolyte are used, NaCl ensures higher electrical conductivity so the electrical resistance of the solution reduces and energy consumption reduces. When final pH values are examined, the electrolyte type closest to neutral pH value is NaCl.

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad (3)$$

$$Cl_{2(aq)} + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (4)$$

$$HClO \leftrightarrow H^+ + OCl^- \quad (5)$$

3.4. Effect of initial pH

With the aim of determining the effect of initial pH on dye removal, experiments were completed with initial pH of 3, 5, 7, 9, and 11, and the results obtained are shown in Fig. 4. The experiments used dye concentration 100 mg/L, current density 1.74 mA/cm^2, electrolyte concentration 4 g/L, and temperature 20°C. To set the initial pH, 0.5 M NaOH, and H_2SO_4 were used. For all pH values, the mean dye removal was 98.8% ± 0.33% at the end of 120 min, with no notable variation observed. However, when the rate constant (k_1) is investigated, it was calculated as 0.0576, 0.0516, 0.0466, 0.0483, and 0.0453 min^{-1}, respectively, linked to the increase in pH (Table 1). As NaCl is used with the aim of ensuring electrical conductivity, the effect of active chlorine species is important here. Among active chlorine species, the dominant type is Cl_2 up to pH 3, with HOCl dominant from pH 3 to 8 and ClO^- dominant at pH > 8 [5]. For oxidation of dye with active chlorine species, Cl_2, and HOCl have higher standard electrode potentials compared to ClO^- [31], so higher rate constants are obtained in acidic environments. At the end of the electrolysis duration, the mean energy consumption was 10.2 ± 0.2 kWh/m^3, with no notable variation observed. In the present study, the effect of pH on the electro-oxidation process of dye can be said to be limited with small differences in the removal efficiencies. In order to avoid additional costs generated by adjusting pH, neutral pH was chosen as the optimum condition.

3.5. Effect of initial dye concentration

With the aim of determining the effect of initial dye concentration on dye removal, a broad range of dye concentrations (50–800 mg/L) were studied in the presence of 4 g/L NaCl. Experiments were completed with a current density of 1.74 mA/cm^2, initial pH 7, and temperature 20°C. Fig. 5 shows that with increasing dye concentration, the dye removal efficiency reduced, with a dye removal efficiency of 98.8%, 98.7%, 95.5%, 92.6%, and 85.5% at the end of 120 min linked to dye concentration. Additionally, the initial pH values were determined to have reduced at the end of 120 min linked to increasing concentration. The final pH values were measured as 5.93, 5.64, 4.08, 3.56, and 3.41, respectively. Similar results were shown by researchers to be due to the formation of acidic by-products causing a fall in pH values in studies about the removal of organic material with electro-oxidation [34,35]. At the end

Table 1
Rate constants calculated under different conditions for dye removal

J (mA/cm^2)	NaCl (mg/L)	C_0 (mg/L)	T (°C)	Initial pH (–)	k (min^{-1})	R^2
0.87	0.5	100	20	7	0.0181	0.9689
1.74	0.5	100	20	7	0.0233	0.9722
3.47	0.5	100	20	7	0.0290	0.09686
5.21	0.5	100	20	7	0.0378	0.9702
8.68	0.5	100	20	7	0.0597	0.9905
13.0	0.5	100	20	7	0.1252	0.9989
1.74	**0.2**	100	20	7	0.0219	0.9745
1.74	**0.5**	100	20	7	0.0233	0.9722
1.74	**1.0**	100	20	7	0.0261	0.9607
1.74	**2.0**	100	20	7	0.0299	0.9646
1.74	**4.0**	100	20	7	0.0466	0.9889
1.74	4.0	100	20	**3**	0.0576	0.9886
1.74	4.0	100	20	**5**	0.0516	0.9913
1.74	4.0	100	20	**7**	0.0466	0.9889
1.74	4.0	100	20	**9**	0.0483	0.9782
1.74	4.0	100	20	**11**	0.0453	0.9606
1.74	4.0	**50**	20	7	0.0694	0.9856
1.74	4.0	**100**	20	7	0.0466	0.9889
1.74	4.0	**200**	20	7	0.0364	0.9867
1.74	4.0	**400**	20	7	0.0276	0.9892
1.74	4.0	**800**	20	7	0.0178	0.9906
1.74	4.0	200	**10**	7	0.0356	0.9879
1.74	4.0	200	**20**	7	0.0364	0.9867
1.74	4.0	200	**30**	7	0.0405	0.9808
1.74	4.0	200	**40**	7	0.0490	0.9818
1.74	4.0	200	**50**	7	0.0565	0.9803

Values shown in bold indicate the levels of experimental parameters tested.

of the electrolysis duration, the mean energy consumption was 10.5 ± 0.2 kWh/m^3, with no notable variation observed.

3.6. Effect of temperature

In electrochemical treatment applications, the temperature is an important parameter. The role of temperature in the electro-oxidation process is not easily understood because more than one reaction occurs simultaneously [24]. One study reported the removal efficiency reduced [27] with the increase in temperature, another study found not much effect [24] while another study reported it increased [36]. With the aim of determining the effect of temperature on dye removal, a range of experiments were completed at different temperatures (10°C, 20°C, 30°C, 40°C, and 50°C). In the experiments, the initial dye concentration was 200 mg/L, NaCl concentration 4 g/L, current density 1.74 mA/cm^2, and initial pH 7. With the temperature increase, the variation in dye removal is illustrated in Fig. 6. The dye removal increased with the increase in temperature and was found to be 94.8%, 95.5%, 96.8%, 97.2%, and 97.6%, respectively. The increase in temperature increases the activity of molecules in the solution. As a result, electrical conductivity and electrolytic current solution temperature are increased and this causes an increase in the dye removal rate [37,38]. Additionally, with the increase in temperature, cell potential reduces, and energy consumption falls. Linked to the temperature increase, the energy consumption was calculated as 11.5, 10.6, 10.1, 9.8, and 9.5 kWh/m^3, respectively. Therefore, based on the above analysis, 50°C was chosen as the optimal temperature.

3.7. Kinetics

The kinetics of the electro-oxidation process are very complicated due to multiple reactions occurring simultaneously [39]. To test experimental data obtained for dye removal, the pseudo-first-order kinetic model was used. The nonlinear form of this kinetic model is given in Eq. (6):

$$C_t = C_0 e^{-k_1 t} \tag{6}$$

where C_0 is initial dye concentration (mg/L), C_t is dye concentration at time t (mg/L), k_1 is the pseudo-first-order reaction rate constant (min^{-1}), and t is the time of reaction (min). Under different reaction conditions, the rate constant value for the pseudo-first-order kinetic model was calculated using nonlinear regression analysis. The nonlinear least square technique via “solver add-in” in Microsoft

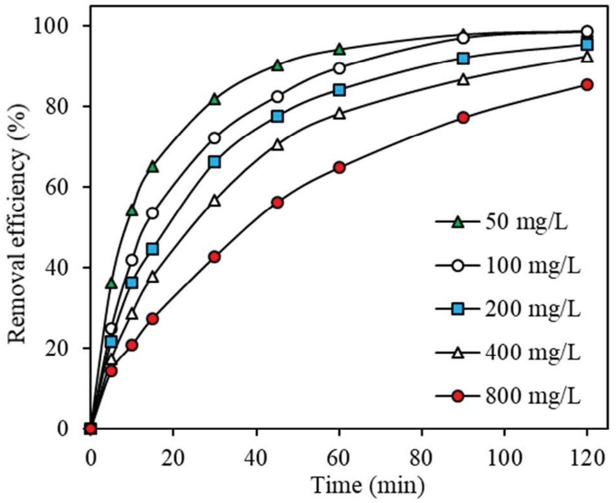

Fig. 5. Effect of initial dye concentration on dye removal (pH = 7; $T = 20°C$; Electrolyte = 4 g/L NaCl; $J = 1.74$ mA/cm^2).

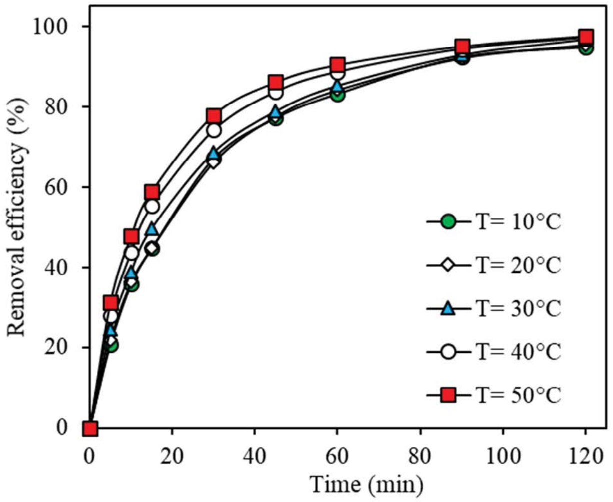

Fig. 6. Effect of temperature on dye removal (pH = 7; $C_0 = 200$ mg/L; Electrolyte = 4 g/L NaCl; $J = 1.74$ mA/cm^2).

Excel was used to fit the experimental data to the selected model. The reaction rate constants are given in Table 1. The removal kinetics for electro-oxidation of dye were investigated and determined to follow pseudo-first-order reaction kinetics.

The best criterion for how well experimental data fit is the determination coefficient (R^2) calculated with the regression analysis procedure. If this coefficient is equal to 1, it is proof the experimental data fit perfectly [40]. Results show experimental data fit the pseudo-first-order kinetic model. This kinetic model was used to describe dye removal kinetics in different studies [41]. In the experiments performed, the highest calculated reaction rate constant was for electrolyte concentration 0.5 g/L NaCl, current density 13.00 mA/cm^2, initial dye concentration 100 mg/L, temperature of 20°C, and pH 7 with 0.1252 min^{-1}. Pseudo-first-order reaction rate constants increased as current density, NaCl concentration and temperature increased and decreased with increases in initial dye concentration and initial pH.

3.8. FTIR study

FTIR spectra are used for the characterization of organic compounds in water or wastewater [42]. FTIR analysis was performed because the molecular structure of the dye was not found in a literature search. Comparing FTIR spectra before and after degradation of dye with the electro-oxidation method, a variety of changes occurred in the dye molecules (Fig. 7). When the FTIR spectra are investigated, the peaks observed in the broad band from 3,600 to 3,000 cm^{-1} are O–H strain vibrations, N–H strain

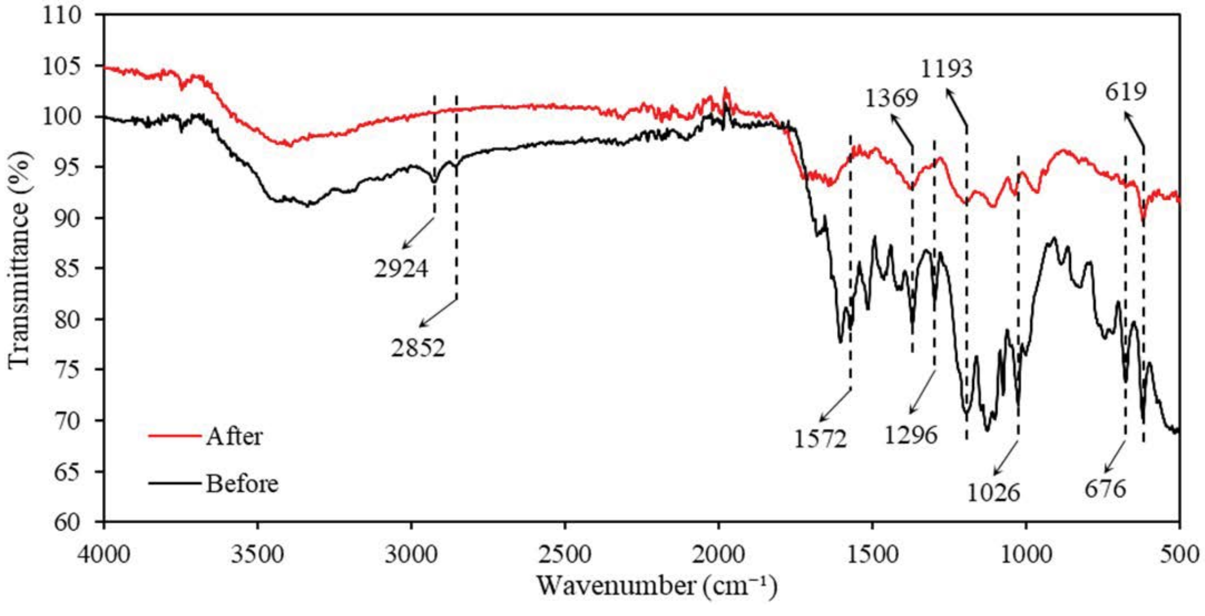

Fig. 7. FTIR spectra of dye before and after treatment.

vibration intramolecular and intermolecular hydrogen bonds [43,44]. The peaks belonging to $-CH_2$ strain vibrations are at 2,924 and 2,852 cm^{-1}, with bending vibrations observed in the interval 1,465–1,460 cm^{-1} [45]. Peaks at 1,572; 1,296; and 1,026 cm^{-1} are N=N, C–N, and C–H strain vibrations [46–49]. Peaks at 1,369 and 1,193 cm^{-1} indicate the presence of S=O strain vibrations [50]. Peaks at 676 and 619 cm^{-1} are probably two bands due to C–Cl strain present in all dye molecules [51]. After removal of dye with the electro-oxidation process, the strength of some peaks reduced, while others disappeared. As a result, it may be concluded the dye underwent degradation.

4. Conclusions

Removal of DOHF2GL was completed with the electro-oxidation method using Pt-coated Ti electrodes. The use of NaCl as an electrolyte ensured higher dye removal. With the increase in NaCl concentration, the cell potential reduces, and treatment efficiency increases. With initial dye concentration 100 mg/L, current density 1.74 mA/cm^2, initial pH 7, temperature 20°C, electrolysis duration 120 min, and NaCl concentration 4 g/L, there was 98.7% dye removal with 10.1 kWh/m^3 energy consumption. The current density was the most important parameter affecting dye removal rate and energy consumption was determined to be largely linked to the current density applied. Additionally, the temperature was determined to have an effect, though low, on dye removal efficiency, and energy consumption. With the increase in initial dye concentration and initial pH, dye removal efficiency was reduced; however, and energy consumption was not affected. Dye removal kinetics were determined to follow pseudo-first-order kinetics.

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