Optimization of material and energy consumption for removal of Acid Red 14 by simultaneous electrocoagulation and electroflotation

Amin Hooshmandfar, Bita Ayati and Ahmad Khodadadi Darban

ABSTRACT

Decolorization of wastewater of industries which consume dye is an environmental priority. Electrocoagulation and electroflotation methods are appropriate for treatment of these wastewaters. This study investigates the effect of four parameters, electrical conductivity, current density, initial dye concentration, and initial pH, on the performance of a simultaneous electrocoagulation/electroflotation system for removal of Acid Red 14. The optimum values of these parameters were determined based on the amount of electrical energy and aluminum consumption and the best performance of coagulation and bubble generation. The optimum condition was revealed to be electrical conductivity = 1,600 μS/cm, current density = 60 mA/cm², initial dye concentration = 185 mg/L and initial pH = 7. After less than 180 min of electrolysis, 90% dye removal was achieved with a specific energy consumption = 102 kWh/kg dye_removed, anode dissolution = 2.09 kg Al/kg dye_removed and sludge total suspended solids = 15,050 mg/L. Liquid chromatography–UV–mass spectroscopy analyses were conducted on samples of raw and treated wastewater. Results showed that intermediate compounds formed from the breaking of the dye molecules. The advantages of this method are a low material and energy consumption. The amount of produced sludge was low; consequently sludge disposal and management costs would be reduced. This method should be used cautiously for treatment of textile wastewater due to the formation of intermediate compounds.

Key words | Acid Red 14, aluminum, electrochemical treatment, sludge

INTRODUCTION

The textile industry significantly affects the environment, producing high volume of wastewater from water and chemicals used in processes including sizing, washing, bleaching, dyeing, printing, and finishing. The wastewater contains salts, acid, or alkali, washing solvents, other chemicals, intermediates, and residue dyes. In the presence of toxic, colored substances in water, light fails to penetrate the waters lower layers and consequently the photosynthesis of water plants and the level of dissolved oxygen decreases, and results in the death of aquatic life. Dyes are stable compounds that are not easily biodegradable, especially azo dyes, which are considered to be carcinogens that pollute the surface and groundwater (Merzouk et al. 2010; Khandegar & Saroha 2015).

Color removal is accomplished through various physical, chemical, or biological methods or a combination of them. Physical methods include absorption, membrane filtration, and ultrasonic waves; chemical methods are ion exchange, electrolysis, coagulation, and conventional, and advanced oxidation; biological methods use algae, fungi, and bacteria (Pajootan et al. 2012; Wang et al. 2014; Yahiaoui et al. 2014). Chemical coagulation is a common method for the treatment of wastewaters containing dye; however, its disadvantages include a high production of sludge and a high concentration of dissolved solids in treated wastewater. Chemical coagulation is effective for sulfur and disperse dyes. Acid, direct, vat, and reactive dyes coagulate, but do not settle, while cationic dyes do not even coagulate (Can et al. 2006).

Recently, electrochemical methods have been considered as appropriate techniques for the treatment of various industrial wastewaters due to their environmental versatility and compatibility. These methods have advantages over others, such as simpler equipment, higher
performance, and shorter retention time to remove contaminants, easier operation, and less need for chemicals (Yahiaoui et al. 2012; Yuksel et al. 2012). Electrochemical methods produce a lower amount of sludge which have high sedimentation or flotation rate and a lower amount of water (Khandegar & Saroha 2013).

In electrocoagulation, coagulants are produced in situ during anode dissolution by passing an electric current. Simultaneous production of hydrogen gas at the cathode aids the flotation of flocs. Electricity is supplied to the electrodes, one of which is the positive anode and the other one is the negative cathode. The solution’s electrical conductivity results in the establishment of an electric field. The electrolysis of water produces hydrogen bubbles that move upward, transporting suspended particles to the surface, and forming a sludge layer that is mechanically collected. According to reaction (3), alkalinity is produced in the form of \( \text{OH}^- \) at the cathode during the electrolysis. Produced gases are very active and alter their buoyancy properties when they attack the surface of the solids. These electrochemical effects do not exist in other flotation techniques (Matis & Peleka 2010). Chemical reactions for an aluminum anode and continued production of oxygen include (Parsa et al. 2011):

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e \tag{1}
\]

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e \tag{2}
\]

Reactions at the cathode:

\[
2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \tag{3}
\]

\[
2\text{H}^+ + 2e \rightarrow \text{H}_2 \tag{4}
\]

The electrocoagulation process has been used successfully for the removal of various pollutants such as dyes (Akbal & Kuleyin 2011; Taheri et al. 2013; Zodi et al. 2013; Yavuz et al. 2014), phosphates (Vasudevan et al. 2009), heavy metals (Golder et al. 2007; Sayiner et al. 2008), lignin and phenol (Uğurlu et al. 2008). Pajootan et al. (2012) studied the removal of Acid Black 52 and Acid Yellow 220 from wastewater by electrocoagulation. With a dye concentration of 200 mg/L and aluminum electrodes, removal efficiency was 90% and 98%, respectively. Wei et al. (2012) improved dye removal by the electrocoagulation process and reduced costs by using a steel scourer as a cathode. Wei and colleagues conducted experiments with iron anode and wastewater containing 100 mg/L of dye. For the three dyes of Acid Black 1, Reactive Blue 4, and Eosin Yellow, removal efficiency was more than 98%. Khandegar & Saroha (2013) treated textile wastewater by electrochemical method under optimum conditions with dye concentration of 10 mg/L Acid Red 151 and using aluminum electrodes. They also obtained a dye removal efficiency of 98%.

The aim of this study was to assess the simultaneous performance of electrocoagulation and electroflotation techniques in an electrochemical system by using aluminum electrodes for the removal of Acid Red 14 from an aqueous solution. Using a simultaneous electrocoagulation/electroflotation unit, we expected a reduction in the need for a secondary gravity-settling unit. Research in the field of dye removal by electrochemical methods has focused on electrocoagulation, with the flotation property of produced bubbles rarely utilized. In this study, the design of the reactor intended to take advantage of electrocoagulation and electroflotation methods simultaneously. This study also examined the effect of four important parameters on the performance of electrochemical systems: electrical conductivity, current density, initial dye concentration and initial pH. The optimum values of these parameters were determined based on the amount of electrical energy and aluminum consumption and the best performance of coagulation and bubble generation. To investigate the formation of intermediate compounds and environmental compatibility of the employed method, liquid chromatography–ultraviolet (LC-UV) and liquid chromatography–mass spectroscopy (LC-Mass) tests were performed on the treated wastewater.

**MATERIALS AND METHODS**

**Materials and equipments**

As shown in Figure 1, the electrochemical process was developed in a rectangular cubic reactor (15 × 15 × 25 cm) made of Plexiglas with effective volume of 5 L. Two 99% pure aluminum electrodes (8 × 3.5 cm) with an effective area of 24.86 cm² and monopolar and horizontal arrangements were included as the anode and cathode. The distance between the electrodes was 1 cm. The cathode was placed above the anode because the generated hydrogen gas at the cathode plays the main role in floating the suspended particles. Before each experiment, the electrodes were sanded and then washed with a diluted acidic solution and distilled water. The experiments were performed in...
batch mode. The anode was 5 cm and the sampling outlet valve was 4 cm from the bottom of the container.

The synthetic wastewater was prepared using an anionic dye, Acid Red 14 (99% pure), as the main pollutant, containing an azo group (Daneshvar et al. 2004). The characteristics of Acid Red 14 are given in Table 1.

Measuring equipment used in this study included a Hach DR-4000 spectrophotometer, a Mettler PJ300 digital scale with accuracy of 0.001 g, a Metrohm 691 pH meter, a Martini MI805 electrical conductivity meter, a Megatek PM-3005D power supply, and an IKA RH-Bassic2 magnetic stirrer. NaCl (Merck) was used to obtain electrical conductivity in the solution, and H₂SO₄ (Merck) and NaOH (Merck) were used to adjust pH. Synthetic wastewater was prepared with double distilled water. All measurements including dye concentration, electrical conductivity, and solids were made according to Standard Methods for the Examination of Water and Wastewater (APHA et al. 2012) and were replicated three times. Chromatography was used to investigate the probable formation of intermediates of dye-molecule oxidation by produced oxidants during the electrochemical process. A C18 reversed phase column (250 mm × 4.6 mm × 5 μm), mobile phase consisting of acetonitrile, and 0.05 M ammonium acetate (30/70v/v) at a flowrate of 0.9 mL/min was used. The injection volumes were 10 μL, and the UV detector was set at 254 nm. The mass spectrometer was operated under electrospray ionization mode in negative polarity and a mass range of 100–600 m/z (Wang et al. 2004; Lin et al. 2008).

### Methods

According to the literature and some preliminary experiments, in order to determine the optimum levels of the parameters, electrical conductivity (800, 1,600, 3,000, 4,000, 5,000 μS/cm) (Parsa et al. 2011; Wei et al. 2012; Khandegar & Saroha 2013), current density (10, 20, 30, 40, 50, 60 mA/cm²) (Khemis et al. 2006; Merzouk et al. 2010; Khandegar & Saroha 2013; Taheri et al. 2013; Zodi et al. 2013), initial dye concentration (65, 95, 120, 185, 260 mg/L) (Şengil & Özacar 2009; Parsa et al. 2011; Yuksel et al. 2012), and initial pH (3, 5, 7, 9, 11) (Koby et al. 2006; Martínez-Huitle & Brillas 2009; Akbal & Kuleyin 2011; Pajootan et al. 2012; Rahman et al. 2013; Tezcan & Aytac 2013), by one factor method, synthetic wastewater was prepared with the desired characteristics and a magnetic stirrer was used to mix the solution. Stirring should be done in such a way that no turbulence occurs. By connecting the electrodes to the power supply, the electric current was kept constant at a desired value and the required voltage was recorded at the times of sampling. Experiments were performed at room temperature. According to the Beer–Lambert law, by measuring the absorbance of samples at the maximum absorption wavelength of the dye (515 nm) in a spectrophotometer, dye concentration and removal rate (Equation (5)) were calculated, where CR is color removal efficiency (%), \( C_0 \) represents initial dye concentration, and C indicates
instant dye concentration. In order to eliminate floc errors, samples were filtered and centrifuged prior to placing them in the spectrophotometer. Changes in pH during the process and total suspended solids (TSS) of separated sludge were also measured.

\[ CR = \frac{(C_0 - C)}{C_0} \quad (5) \]

In the electrochemical process, energy consumption is highly important when one takes into account that electricity is the energy source. This can be a criterion for rationalizing the process application, and in this study was calculated by Equation (6), where SEC is specific energy consumption (kWh/kg dye\text{removed}), \( U \) voltage (V), \( I \) electric current (A), \( t \) electrolysis time (hr), \( V \) wastewater volume (L), \( C_0 \) and \( C \) initial and instant dye concentration (g/L).

\[ SEC = \frac{U \cdot I \cdot t}{(V \cdot (C_0 - C))} \quad (6) \]

Anode dissolution depends on the electric current passing through the solution, and theoretically, is according to Faraday’s equation (Equation (7)), which defines \( m \) as dissolved metal mass (g), \( I \) as electric current (A), \( t \) as electrolysis time (s), \( M \) as molar mass (Al = 27), \( F \) as Faraday constant (96,485 C/mol), and \( z \) as metal valence (Al = 3) (Khandegar & Saroha 2013).

\[ m_{\text{theo}} = \frac{(I \cdot t \cdot M)}{(F \cdot z)} \quad (7) \]

Current efficiency (\( \varphi \)) of the electrochemical process was determined using Equation (8) and is based on the difference between the actual decrease in anode mass (\( \Delta m_{\text{exp}} \)) during the electrochemical process and theoretical anode dissolution (\( \Delta m_{\text{theo}} \)) according to Faraday’s law. This parameter depends on the type of species present such as anions. This ratio was 1.25.

\[ \varphi = \frac{\Delta m_{\text{exp}}}{\Delta m_{\text{theo}}} \quad (8) \]

Thus, according to Equations (7) and (8), anode consumption (kg Al/kg dye\text{removed}) was obtained by Equation (9) (Parsa et al. 2011).

\[ \text{Anode consumption} = m_{\text{theo}} \cdot \varphi / (V \cdot (C_0 - C)) \quad (9) \]

Mass-transfer coefficient was determined according to Equation (10) (Yahiaoui et al. 2012):

\[ K_m = \frac{K_{app} \cdot V}{S} \quad (10) \]

where \( K_{app} \) is the apparent rate constant, \( V \) is the volume of the solution (mL), and \( S \) is the anode surface area (cm\(^2\)).

**RESULTS AND DISCUSSION**

**Electrical conductivity**

Electrical conductivity has a direct impact on energy consumption. Enhancing the electrical conductivity and consequently decreasing the electrical resistance of the solution decreases the necessary voltage when obtaining a fixed electric current. The existence of salts and ions provides electrical conductivity in the solution; on the other hand, these ions may cause precipitation and corrosion on the electrodes and thus disrupt the process, enhance the electrical resistance, and impose additional costs on the treatment process. To investigate the effect of this parameter, our experiments were carried out at different ECs (different electrolyte concentrations). The results concerning removal rate, energy, and aluminum consumption are shown in Figure 2(a)–2(c).

There is a slight difference between the removal rates at 800 and 1,600 \( \mu \)S/cm, while with further increase in conductivities the removal rates decrease due to the disruption to the process caused by corrosion and presence of excessive ions. Corrosion of the electrodes’ surface disrupts uniform-sized bubble generation. At an electrical conductivity of 1,600 \( \mu \)S/cm in comparison to 800 \( \mu \)S/cm, specific energy consumption was much less and equaled 130 kWh/kg dye\text{removed} with a removal rate of 90%, while it was 231 kWh/kg dye\text{removed} at electrical conductivity of 800 \( \mu \)S/cm. Aluminum consumption at an electrical conductivity of 1,600 \( \mu \)S/cm equaled 2.615 kg Al/kg dye\text{removed}, which was lower compared to other conditions. The lower anode consumption produces less sludge and will reduce the problems of sludge management and disposal. Reducing the costs of sludge disposal and aluminum consumption will make the process of electrocoagulation/electroflotation more affordable.

Figure 2(d) shows the TSS of separated sludge as a criterion for the efficiency of the flotation of the pollutant. Our observations indicated that by enhancing the electrical conductivity and offering more time to completely separate the pollutant, the amount of aluminum in the separated sludge increased, observed by the sludge’s color turning into a deeper shade of gray. Increasing the aluminum flocs containing water in the sludge causes the TSS to decrease. Nevertheless, the amount of measured TSS was between
14,100 and 15,050 mg/L, which is considerably more than the amount of separated sludge from the conventional gravity settling tanks. This indicated a high ability of the system in flotation, eliminating the need for another unit for separating the formed flocs. We continued the experiment with an electrical conductivity of 1,600 μS/cm, with a removal rate of 90% in less than 90 minutes by consuming energy and aluminum of 130 kWh/kg dyeremoved and 2.615 kg Al/kg dyeremoved respectively, and with the sludge TSS of 15,050 mg/L.

Parsa et al. (2014) changed the NaCl concentration from 0.25 to 5 g/L (500–10,000 μS/cm) and obtained the optimum electrolyte concentration of 0.5 g/L (1,000 μS/cm) with the least specific energy consumption.

### Current density

The effect of current density on removal rate, specific energy, and aluminum consumption are shown in Figure 3(a)–3(c). According to Figure 3(a), the rate of color removal increased with an increase of the electric current. This is due to an increased speed in the production of coagulants and gases because of enhanced electric current density leading to quicker coagulation, flocculation, and separation of the pollutant (Zodi et al. 2013).

At a higher current density, the amount of produced gas is increased, and the quick release of gases from the electrodes’ surface leads to quicker removal of pollutants due to the mixture of the produced coagulants in the solution along with simultaneous floating (Khemis et al. 2006; Merzouk et al. 2010). The dye removal followed a pseudo first order kinetics. By enhancing the current density from 10 to 60 mA/cm² the apparent rate constant ($K_{app}$) increased from 0.007 to 0.041 min⁻¹. Also, the mass-transfer coefficient ($K_m$) increased from 1.408 to 8.246 cm.min⁻¹.

A higher electric current requires more voltage; hence, electric energy consumption increases by the kilowatt-hour and increases the dissolution rate of an electrode by the gram. According to Figure 3(b) and 3(c), there is an upward–downward trend in both specific energy and aluminum consumption. The reason for the decline in these amounts is that the removal rates significantly increased by turning up the current densities.

Figure 3(d) shows the measured amount of TSS in different electric current densities. Based on these results, the TSS increased by enhancing the current density. According to the observations at low current density, the sludge did not float well, and after flotation, it returned into the wastewater, making the process of pollutant removal more dependent on continuous separation of sludge due to the low volume of produced gases. Thus at low current density, the efficiency

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**Figure 2** | Effect of electrical conductivity on (a) color removal rate, (b) specific energy consumption (SEC) at different removal rates, (c) anode consumption at different removal rates, and (d) TSS of separated sludge ([dye] = 65 mg/L, current density = 60 mA/cm², initial pH = 7).
of the process will be low in high pollutant concentration and load shock (Kobya et al. 2006).

Therefore, the best result was obtained at an electric current density of 60 mA/cm² with a dye removal rate of 90% in less than 90 minutes, a specific energy consumption of 130 kWh/kg dye_{removed}, an anode consumption of 2.615 kg Al/kg dye_{removed}, and a sludge TSS of 15,050 mg/L. Khandegar & Saroha (2013) investigated the effect of current density in the range of 6.8 to 125 mA/cm² (0.1 to 2 A) and observed that the dye removal rate increased with the current density of 6.8 to 62.5 mA/cm², yet at higher levels, there was no change in the removal rate. They then selected 62.5 mA/cm² as the optimum value. Zodi et al. (2013) obtained a higher dye removal rate by enhancing the current density from 100 to 200 A/m².

**Initial concentration**

The experiments were performed with different initial dye concentrations. The results are indicated in Figure 4. As can be seen in Figure 4(a), the rate of color removal decreased with an increase of initial concentration, and more time was needed for a fixed removal rate. At a fixed current density, the production rate of metal hydroxide coagulating compounds is constant and is not sufficient for coagulation and flocculation of a larger amount of pollutant (Yuksel et al. 2012). The removal efficiency trend in relation to time for the concentrations of 120 and 185 mg/L was similar, and the removal rates of 94 and 93%, respectively, were obtained in 180 minutes. Along with the coagulation and flocculation, the adsorption of dye molecules on the formed flocs aids the dye removal process (Sengil & Özcar 2009).

Energy and aluminum consumption are shown in Figure 4(b) and 4(c), respectively, for determining the optimum initial dye concentration based on the economic criterion. The general trends of changes in the energy and aluminum consumption were similar. Specific energy consumption at the removal rate of 90% for concentrations of 65, 95, 120, 185, and 260 mg/L was 130, 132, 160, 102, and 148 kWh/kg dye_{removed}, respectively. Aluminum consumption equaled 2.61, 2.68, 2.98, 2.09, and 3.15 kg Al/kg dye_{removed}, respectively.

In Figure 4(d), the TSS of separated sludge is presented for different initial concentrations. With the initial concentration of 185 mg/L, the TSS of separated sludge had the greatest amount of 15,050 mg/L. This initial concentration was chosen as this parameter’s optimum amount. Since effluent concentrations of various textile industries depend on the type of their process, variations of 185 mg/L should be taken into consideration in order to apply the results of this study to a particular case.
Parsa et al. (2014) obtained a decrease in removal rate by enhancing the dye concentration from 30 to 100 mg/L. This decrease was more obvious at the beginning of the electrocoagulation process compared to the end of the process. Yuksel et al. (2015) observed a decrease in the dye removal rate by its concentration enhancement from 100 to 500 mg/L while the amount of energy and electrode consumption decreased by the kWh/kg dye removed and kg dissolved anode/kg dye removed.

Initial pH

Figure 5(a) presents the results of the effect of pH on color removal. With initial pH = 3 in the first 30 minutes, removal rate was high. This trend slowed as the process continued. Considering that the samples were filtered and centrifuged for the color concentration determination, the increase in concentration was because of desorption. After this efficiency decline, color removal again increased. After 60 minutes, the sludge lost its flotation property and settled down. At the initial pH of 5, 7 and 9, color removal was efficiently completed and the sludge floated well. Observations on the initial pH of 11 found that the sludge did not rise well and was grey in color, indicating a low amount of dye and high amount of aluminum compounds in the sludge, as well as a poor system performance. Based on the measurements, the final pH for experiments with an initial pH of less than 11 was approximately 9 and with an initial pH of 11 was fixed at 9.6.

Monomeric and polymeric aluminum species vary at different pH, and the coagulation mechanism is dependent on pH. To justify the process, various studies have suggested the existence of different species. Flocs of Al(OH)₃, as adsorbents in the environment, and their performance at different pH are considered. The amount and size of generated bubbles also depend on pH. Due to the changes in pH during the process, and by applying the mentioned principles, the effect of pH on dye removal in electrocoagulation and electroflootation can be explained.

At pH 2–5, the produced Al³⁺ converts to soluble monomeric species such as Al(OH)₂⁺ and Al(OH)²⁺ (Martínez-Huitle & Brillas 2009). When pH = 4–9, soluble monomeric and polymeric species such as Al₂(OH)₄⁺, Al₆(OH)₁₅³⁻, and Al₃O₄(OH)₂₄⁷⁺ are formed, they convert to insoluble amorphous Al(OH)₃ flocs by a set of complex reactions, and coagulation is performed through adsorption, charge neutralization and trapping (Martínez-Huitle & Brillas 2009; Akbal & Kuleyin 2011). According to the (pH-activity) diagram of the equilibrium between Al³⁺ species and solid phase Al(OH)₃, the lowest solubility of aluminum hydroxide is at about pH = 6.2, at which more coagulants become available (Peterson 2005).
In acidic conditions at the cathode, H\(^+\) is reduced to H\(_2\) gas, and OH\(^-\) accumulation enhances the pH (Chen 2004). According to the measurements, with initial pH of less than 9, due to buffering capacity of the Al\(^{3+}/\)Al(OH)\(_3\) system the pH is gradually increased and becomes fixed at approximately 9. When the initial pH is more than 9, soluble monomeric anion (Al(OH)\(_4^+\)) is produced according to Equation (11), which leads to a gradual finite decrease in pH. Al(OH)\(_4^+\) has no decolorization capability, which causes a removal efficiency reduction at a pH above 9 (Kobya et al. 2016).

\[
\text{Al(OH)}_3 + \text{OH}^- \leftrightarrow \text{Al(OH)}_4^+ \quad (11)
\]

Flocs of Al(OH)\(_3\) have great specific area that can quickly adsorb dissolved organic compounds and trap colloidal particles (Bayramoglu et al. 2004). Considering that the used dye is anionic and the point of zero charge (pH\(_{\text{pzC}}\)) of Al (OH)\(_3\) is 5 (Brezonik & Arnold 2011), if the pH is below the pH\(_{\text{pzC}}\) of adsorbent, positive charges increase on the adsorbent surface, and the anionic dye molecules will be well bound. Adsorbing ability is reduced by increments in pH to above the pH\(_{\text{pzC}}\) of the adsorbent, which leads to desorption.

In pH 3–8, strong oxidizing chlorine species help remove dye (Martínez-Huitle & Brillas 2009). The pH affects the amount and size of bubbles. Since hydrogen bubbles play a main role in electroflotation, production of more hydrogen gas with smaller bubble size is desirable. In acidic conditions, hydrogen production increases, while the size of the gas bubbles increases, and therefore the ability for floating tiny particles decreases. In basic conditions, the bubbles are smaller, but their amount decreases (Brandon & Kelsall 1985; Rahmani et al. 2013). Therefore, an optimum pH should be chosen to provide appropriate coagulation and flotation.

To determine the optimum initial pH based on economic aspects, specific energy and aluminum consumption are indicated in Figure 5(b) and 5(c), respectively. At pH = 7, dye removal was efficient and there was no need for chemicals to adjust pH. For obtaining a dye removal of more than 90%, specific energy consumption increased with an initial pH = 3, decreased for an initial pH of 5 and 7, and increased again for an initial pH of 9 and 11. This amount was 152, 104, 102, 172, and 299 kWh/kg dye removed for 90% dye removal with the mentioned initial pH, respectively. A similar trend was observed for aluminum consumption: 3.07, 2.11, 2.09, 3.46, and 6.01 kg Al/kg dye removed for 90% removal efficiency with initial pH of 3, 5, 7, 9, and 11, respectively.

In Figure 5(d), separated sludge TSS is shown for different initial pH. Sludge at pH = 3 was collected only in the first 60 minutes. The results of the diagram are consistent with the expected trends.
with the observations, and as expected, the lowest TSS was at pH = 3 and 11. In pH 5–9 electrocoagulation and flocculation were efficient and electroflotation had good performance. As a result, initial pH = 7, with a dye removal efficiency of 90% within less than 180 minutes, a specific energy consumption of 102 kWh/kg dye removed, an anode consumption of 2.09 kg Al/kg dyeremoved, and a sludge TSS of 15,050 mg/L, was selected as the optimum value. Also, the amount of sludge was 20 mL/L of treated wastewater in overall optimum condition.

Akbal & Kuleyin (2011) chose the natural pH of Levafix Brilliant Blue E-B solution (5.5) as an optimal value; although maximum removal of the dye was obtained with initial pH of 8, there was no need to add chemicals by applying the natural pH. Pajootan et al. (2012) studied the effect of pH in the range of 2.5–10 and chose pH = 5 as the optimum value according to removal efficiencies. Tezcan & Aytac (2013) did not observe much difference in the dye removal efficiency at different pH values. Only in the first 10 minutes of electrocoagulation with an initial pH of 3 was dye removal higher than with an initial pH of 5 and 9; so by continuing the process to 90 minutes, equal removal efficiencies were achieved.

Intermediate compounds

The chlorine ions in wastewater form oxidant compounds according to reactions (12) to (14) (Matis & Peleka 2010), which are able to break down the dye molecules. Therefore, a further investigation into the production and accumulation of intermediate compounds during and at the end of the process was needed. For this purpose, LC-UV and LC-Mass chromatographic analyses were conducted on the samples of 0, 60, and 300 minutes.

\[ 2Cl^- \rightarrow Cl_2 + 2e \]  
\[ Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \]  
\[ HOCl \rightarrow OC^- + H^+ \]

Figure 6 presents the diagram of absorption at \( \lambda = 254 \) nm in relation to exit time from the chromatographic column for the injected samples. As can be seen in Figure 6(a), the initial sample was not treated, and there was a peak on the diagram with the absorption level of 90 within 3.5 minutes, which was related to the existing dye in the wastewater. For the samples at 60 and 300 minutes, this amount decreased gradually because of the decrease in the dye concentration. The absorption at 3.5 minutes for the sample that had been treated for 300 minutes was 7. According to Figure 6(c) related to the sample of 300 minutes, a new peak was apparently formed at 2.8 minutes by more treatment along with a reduction in the dye concentration. The initial chemical oxygen demand (COD) corresponding to the initial dye concentration of 185 mg/L was 297 mg/L. While color removal reached high efficiency of 99% after 300 minutes, COD removal had a slower trend and residue COD was 17 mg/L. This is in agreement with the LC-UV-Mass results that indicate the presence of intermediates. COD removal of 99% was obtained after 420 minutes.

The new peak indicated the formation and accumulation of intermediate compounds because of oxidation and the breaking down of the big dye molecules into smaller ones when in contact with chlorine oxidants. The mass spectrums of the dye compound and the formed intermediate are presented in Figure 7(a) and 7(b), respectively. Figure 7(a) shows the peaks of 140.8, 216.8, 386.6, and 468.6 m/z related to \( C_{10}H_7N_2 \), \( C_{15}H_{14}N_6^2 - \), \( C_{13}H_{18}N_3^2 \times 2 \), and \( C_{10}H_7N_2 \times 3 \), respectively, that were formed by ionization of the dye molecule. The mass spectrum of the major intermediate formed during the process in Figure 7(b) was related to a...
compound with formula of $\text{C}_{16}\text{H}_{12}\text{N}_{2}$ (232.7 m/z) $[\text{M} - 2\text{Na}^+ - \text{OH} - 2\text{SO}_4^2^- - \text{C}_4\text{H}_4\text{N}_2]^+$. The compound name was (E)-1-(naphthalen-1-yl)-2-phenyldiazene. It had an azo bond ($-\text{N}=\text{N}-$) and could absorb light in the ultraviolet-visible region.

None of the similar research studies investigated the formation and existence of intermediate compounds. This subject is important with respect to intermediate compounds, which are probably hazardous, owing to the reuse or discharge of treated wastewater into the environment. According to our results, the electrocoagulation/electroflotation method in treating textile wastewater that contains chloride should be utilized more cautiously, especially for obtaining higher removal rates. When the wastewater is in contact with chlorine oxidants for a longer time, the formation of intermediate compounds is more likely.

**CONCLUSION**

Electrocoagulation and electroflotation have many advantages, such as less sludge than similar methods and the possibility of fully automated, continuous operation. The process can easily be controlled and equipment used can be considered safe. This process also produces tiny bubbles of the same size, and there is less need to add chemicals. Efficiency in hydraulic, organic and toxic shocks, reduction in the number of process units and a decrease in the required area for a treatment plant, as well as lower operation costs are the other advantages of this technique. Previous studies have focused on electrocoagulation, and the flotation property of produced bubbles is rarely utilized for electrochemical dye removal methods.

Anode dissolution, and the need for replacing the anode, and cathode corrosion are the greatest disadvantages. According to the results of LC-UV and LC-Mass analyses and due to the possibility of toxic intermediates formation in the presence of organic compounds and chloride, the electrochemical method should be used with caution. Nevertheless, 90% dye removal was achieved with a 185 mg/L initial concentration in less than 180 minutes, with a 102 kWh/kg dye$_{\text{removed}}$ specific energy consumption, 2.09 kg Al/kg dye$_{\text{removed}}$ anode consumption, and 15,050 mg/L sludge TSS. Simultaneous electrocoagulation and electroflotation is an appropriate method for treating wastewater containing dye with low energy and material consumption. Less sludge also leads to lower treatment and disposal costs, and the problems associated with sludge will be reduced. Therefore, this method can be considered a convenient alternative to conventional treatment methods such as chemical coagulation. In case of need for high quality water, a complementary treatment is suggested.

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