Optimization of parameters of electrocoagulation/flotation process for removal of Acid Red 14 with mesh stainless steel electrodes

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ABSTRACT

Dyes are persistent compounds that are not easily biodegraded and are considered as carcinogenic. Electro-coagulation and electro-flotation method, due to its adaptability and compatibility with the environment, is regarded as one of the appropriate methods for the treatment of industrial wastewater containing dye. In this study in which stainless steel mesh electrodes with a horizontal arrangement are used, the most important parameters affecting the performance of the simultaneous system of electro-coagulation and electro-flotation, including electrodes area, of distance between electrodes, electrical conductivity of the solution, type of electrolyte, and initial pH were examined. The effect of every one of these parameters in color removal efficiency of Acid Red 14 from artificial wastewater, energy consumption and anode was determined and their values were optimized. The area of the electrode equals 20.5 cm^2, the distance between the electrodes is 0.5 cm, electrical conductivity 3,600 μS/cm, and initial pH 7 were selected as the optimum values, and dye removal efficiency of 99% with initial concentration of 150 mg/L and electric current density 40 mA/cm^2 (0.8 A) were obtained under optimum conditions and within 20 minutes. The advantages of this method are low energy and material consumption, and low sludge production.

Key words | Acid Red 14, anode dissolution, dye removal, energy consumption, sludge TSS

INTRODUCTION

Various amounts of different chemical dyes from different industrial applications including dyeing were utilized. Artificial dyes are regarded as pollutants of nature that enter into the environment with industrial waste and ultimately can cause contamination of natural ecosystems such as soil, surface waters, ground waters and living creatures. When colored wastewaters are discharged into the environment without treatment, they can affect aquatic ecosystems in different ways. The existence of a colored substance in water decreases the light penetration to the lower layers and so decreases the photosynthesis of plants which renders the water toxic resulting in the mortality of aquatic creatures and finally the rivers and streams that the wastewaters flow into, turning them to swamp in the longer term (Zodi *et al.* 2013).

Color removal is possible via different physical, chemical, and biological methods or a combination thereof. Physical methods include such as absorption, absorption, membrane filtration, and ultrasonic waves; chemical methods include ion exchange, electrolysis, coagulation, conventional, and advanced oxidation; and biological methods using algae, fungi, and bacteria can be mentioned (Alinsafi *et al.* 2005; Kobya *et al.* 2006; Hooshmandfar *et al.* 2016). In chemical coagulation, electrostatic gravity between the dye solution and polymeric molecules with opposite loads generate coagulation. The disadvantages of this method are high sludge production and high dissolved solids in treated wastewaters.
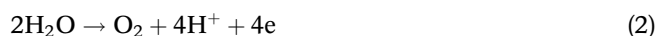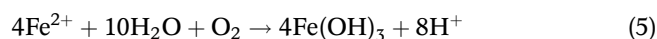
Chemical coagulation is efficient for sulfurous and disperse dyes. Acidic, direct, vat and reactive dyes coagulate with this method but do not settle, while cationic dyes do not even coagulate (Can *et al.* 2006).

The electrochemical method is a better treatment method with high efficiency for treating textile wastewaters which contain a high concentration of dye. This method has advantages over others for decolorization, such as the need for simple equipment, higher performance, and shorter retention time to remove contaminants, easier operation, and less need for chemicals (Yildiz 2008).

Electro-coagulation produces coagulating substances *in situ* using electrical decomposition of aluminum (Al) or iron (Fe) electrodes. Fe ions that are added electrically to water according to reaction (1), are much more active than Fe ions that are added chemically. Where there is wastewater between the positive anode and negative cathode, an electric field is established as a result of the solution's electrical conductivity. By electrolysis of water, fine bubbles of oxygen and hydrogen are produced according to reaction (2) and move upward and form a layer in the surface. Bubbles bring the suspended particles and oil to the surface and a sludge layer is produced that is mechanically collected. Therefore, free atomic oxygen is formed in the anode diffusion layer and enters the wastewater by convection and oxidizes organic and inorganic substances. In a similar trend, a change occurs in motivated electrical hydrogen that leads to the rehabilitation reaction of wastewater contents. According to reaction (3), alkalinity is produced in the form of OH^- at the cathode during the electrolysis. Gases producing oxygen and hydrogen (according to reaction 4) are very active, and when they attack the surface of the solids, change their buoyancy properties. These changes are called electrochemical effects which do not exist in other buoyancy (Matis & Peleka 2010). Chemical reactions occurring at the anode and cathode are shown below in reactions (1)–(4) (Khandegar & Saroha 2013):

$$4Fe \rightarrow 4Fe^{2+} + 8e \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \tag{2}$$

$$3H_2O + 3e \rightarrow 3H_2 + 3OH^- \tag{3}$$

$$8H^+ + 8e \rightarrow 4H_2 \tag{4}$$

and in general (reactions (5) and (6)):

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+ \tag{5}$$

$$4Fe + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2 \tag{6}$$

Electro-coagulation has been utilized successfully in wastewater treatment of different industries such as plating (Adhoum *et al.* 2004), chemical mechanical polishing (Drouiche *et al.* 2007), textiles (Pajootan *et al.* 2012; Wei *et al.* 2012; Yuksel *et al.* 2012; Khandegar & Saroha 2013), olive oil production (Tezcan Ün *et al.* 2006), laundry (Wang *et al.* 2014), tannery (Feng *et al.* 2007), dairy (Şengil 2006), paper-making (Khansorthong & Hunsom 2009) and oil refining (El-Naas *et al.* 2009). Also, the electro-coagulation process is applied in the removal of various substances (Akbal & Kuleyin 2011; Taheri *et al.* 2013; Zodi *et al.* 2013; Yavuz *et al.* 2014), phosphates (Vasudevan *et al.* 2009), kinds of heavy metals (Golder *et al.* 2007; Sayiner *et al.* 2008), and lignin and phenol (Uğurlu *et al.* 2008). For example, Zodi *et al.* (2013) conducted dye removal of Direct Red 81 by electro-coagulation and electrical buoyancy by aluminum electrodes. The experiments were performed using wastewater with pH 7.5, turbidity 380 NTU, chemical oxygen demand (COD) 120 mg/L, electrical conductivity 2,575 µS/cmat, at 20 °C, with an initital sludge concentration of 0.8 g/L and concentrated red color. Removal efficiencies for turbidity, COD and dye with electrical current density of 200 mA/cm² and current rate of 10 L/h were obtained at 99.9%, 76.1% and 90.2%, respectively. Dye removal efficiency was increased by enhancing the current density from 100 to 200 A/m². Specific energy consumption was from independent input current rate and between 52 and 58 kWh/kg Al. In all cases the resulting sludge was increased by enhancing current density.

Taheri *et al.* (2013) determined optimum conditions for dye removal Reactive Blue 19 by response surface methodology using an electro-coagulation/coagulation system. With an initial dye concentration of 162.15 mg/L, current density 215 A/m², time 12.65 minutes, initial pH 3.82, and

chloride poly-aluminum coagulating 297.5 mg, dye removal efficiency was reported at 99.67%.

Hooshmandfar et al. (2016) conducted dye removal of Acid Red 14 by simultaneous electro-coagulation and electro-flotation with aluminum electrodes. In optimum conditions with an initial dye concentration of 185 mg/L with mass of 5,000 mL, initial COD 291 mg/L and horizontal electrode arrangement, current density 60 mA/cm^2, initial pH 7, the distance between electrode 1 cm, electrode surface 24.86 cm^2, electrical conductivity 1,600 μS/cm and the duration of 180 minutes, a dye removal efficiency of 93% and COD removal efficiency of 81% were obtained.

The aim of the present study is to examine the efficiency of electrochemical system in which two simultaneous electro-coagulation and electro-buoyancy methods were utilized for pollutant dye removal of Acid Red 14 using stainless steel mesh electrodes with a horizontal arrangement. It is expected that the simultaneous electro-flotation procedure removes the need for a gravity-settling unit for separating flocculation and leads to the separation of the pollutant and a reduction in treatment costs. The conducted researches on dye removal using the electrochemical method based on electro-coagulation and flotation properties of the produced bubbles have not been used except for Zodi et al. (2013) and Hooshmandfar et al. (2016). Among the innovations of this research are a special reactor design with a horizontal arrangement of electrodes in order to better utilize the electro-floating with the electro-coagulation properties, using stainless steel electrodes for lower solvent erosion with higher efficiency, and grid electrodes to increase surface area for producing bubbles and producing finer bubbles. The effect of important innovations in electrochemical performance, including the surface and distance of electrodes, electrical conductivity, type of electrolyte and initial pH, were studied and their optimum rate based on the energy and anode consumption rate, and supplying better performance in terms of producing coagulating material and bubbles were determined and relative intermediate products were also examined during the process.

MATERIALS AND METHODS

Materials and equipment

According to Figure 1, the electrochemical cell utilized for the electro-coagulation and electro-flotation process was made of Plexiglas in a rectangular cubic ($7 \times 7 \times 15$ cm) with effective volume of 735 ml. Two stainless steel mesh 316 electrodes (5×5 cm) with purity of 99% and monopolar and horizontal arrangements were included as the anode and cathode (with holes of different diameters for each effective area). Because the produced hydrogen gas in the cathode has a major role in floating suspended particles, the cathode was placed above the anode (see below). The experiments were performed discontinuously. The anode
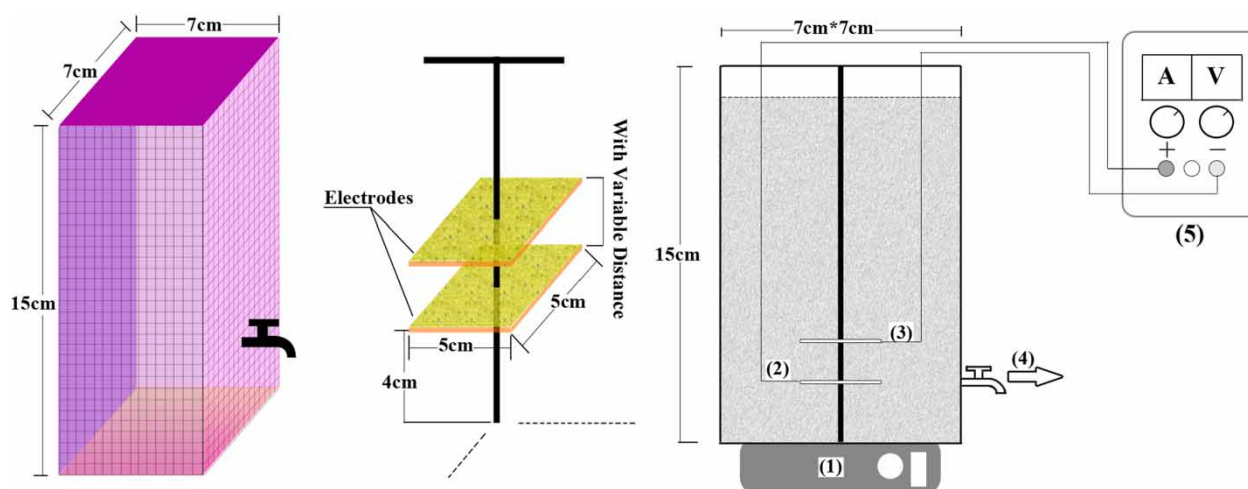

Figure 1 │ Schematic view of the electrochemical cell (1, magnetic stirrer; 2, wastewater container; 3, electrodes; 4, outlet valve; 5, power supply).

was 5 cm and the sampling outlet valve was 4 cm from the bottom of the container.

Dye Acid Red 14 was used as the main pollutant for preparing artificial wastewater in the present study using an anionic dye containing an azo group and natural pH 7, other particulars of which are shown in Table 1 (Hooshmandfar *et al.* 2016).

For measuring parameters the following instruments were used: spectrophotometer Hach DR-4000 model carry 50; a Martini MI805 EC meter; LC-MS model Xpert-MPD to determine the relative intermediate compounds; a digital scale model PLS 360-3 made in Kern Co. with accuracy of 0.001 g; a Metrohm 691 pH meter made in Switzerland; a Megatek PM-3005D power supply made in Taiwan; Shimi Fan centrifuge 8 branch model CE145; an IKA RH-Basic2 magnetic stirrer; Macherey-Nagel filter paper made in Germany for total suspended solids (TSS) experiment. NaCl (Merck) was used to obtain electrical conductivity in the solution, and Na_2SO_4 (Merck) and $MgSO_4$ (Merck) were used to compare types of electrolyte, H_2SO_4 (Merck) and NaOH (Merck) was used to adjust pH, and for preparing solutions, dilution and washing, double distilled water was utilized. All measurement experiments including dye (21010 C), (2510 A) EC, solids (2540) based on water and wastewater standards (APHA 2012) were conducted three times with repeatability and error percentage of 95% and 5%, respectively, and *in situ* (23 ± 2 °C).

Method

In order to determine the optimum effective area of parameters using single factor analysis (OFAT), synthetic wastewater was prepared with the desired characteristics

Table 1 │ Characteristics of Acid Red 14

Structure	
Formula	$C_{20}H_{12}N_2Na_2O_7S_2$
Molar mass (g/mol)	502.4
λ_{max} (nm)	515

and the magnetic stirrer was used to mix the solution in order to make the necessary mixing to the extent that does not create turbulence. By connecting the electrodes to the power supply, the electric current was kept constant at determined values and the required voltage was registered at the time of sampling and tests were conducted at laboratory temperature. According to the Beer Lambert law, with measuring the absorbance of samples at specified intervals at the maximum absorption wavelength of the dye (515 nm) in a spectrophotometer, dye concentration and removal rate were calculated based on Equation (7):

$$DR = \frac{C_0 - C}{C_0} \tag{7}$$

where DR is dye removal efficiency, C_0 dye initial concentration, C the sample concentration in terms of mg/L. It is worth mentioning that samples were centrifuged before measuring in a spectrophotometer in order to eliminate the error of existing flotation in solution.

In the electrochemical process, energy consumption is highly important due to the presence of electricity as a source of energy. This energy that can have a high effect on justifiability of the application process was calculated via Equation (8) in which SEC is specific energy consumption (kWh/kg dye$_{removed}$), U is voltage (V), I is electric current (A), t is electrolysis time (hr), V is wastewater volume (L), C_0 and C are initial and instant dye concentration, respectively (g/L) (Khandegar & Saroha 2013).
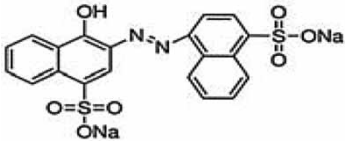
$$SEC = \frac{U.I.t}{V.(C_0 - C)} \tag{8}$$

Anode dissolution and consequently decomposing anode depends on the electric current passing through the water, and follows Faraday's Law where m is dissolved metal mass (g), I electric current (A), t electrolysis time (s), M molar mass, F Faraday constant (96,485 C/mol), and z metal valence (Khandegar & Saroha 2013):

$$m = \frac{I.t.M}{F.Z} \tag{9}$$

According to Equation (9), anode consumption (Kg), anode dissolution (Kg), dye removal using Equation (10)

was calculated (Parsa *et al.* 2011).

$$\text{Anode dissolution} = \frac{m}{V.(C_0 - C)} \qquad (10)$$

RESULTS AND DISCUSSION

Effective area of the electrodes

In order to determine the optimum effective area of the electrodes, experiments were conducted in three effective areas of electrodes 13.5, 20.5 and 24.5 cm^2 that were done according to the similar studies. On the basis of the initial experiments, other parameter rates were considered constant. The reason for considering the electrical current to be constant instead of electrical current density was the dependency of anode dissolution on the electrical current according to Faraday's Law. For any change in the electrical current, the changes in anode dissolution were proportionate to the changes in every one of the parameters and so

were not taken into consideration as an independent parameter. The results from these experiments are shown in Figure 2.

As can be seen in Figure 2(a), the highest dye removal efficiency within 20 minutes was obtained using electrode surface 13.5 cm^2 and equals 99.2%. According to the observations, by increasing electrode surface, the produced oxygen bubbles are trapped under the anode and big bubbles are constituted by continuing the production. These big bubbles, by releasing from the bottom of the anode, have an upward movement and encounter the produced tiny bubbles in the cathode thus forming bigger bubbles that are not able to separate the tiny flotation in wastewater (Phalakornkule *et al.* 2010). As a result, by increasing the anode surface area, coagulated dye removal efficiency is decreased with time. It is worth mentioning that the usual size of the produced bubbles in the electrochemical process is between 45 and 180 μm so that the bubbles' diameters in the cathode surface were 15–23 μm and this is increased by increasing bubbles in a short time (Sarkar *et al.* 2010).
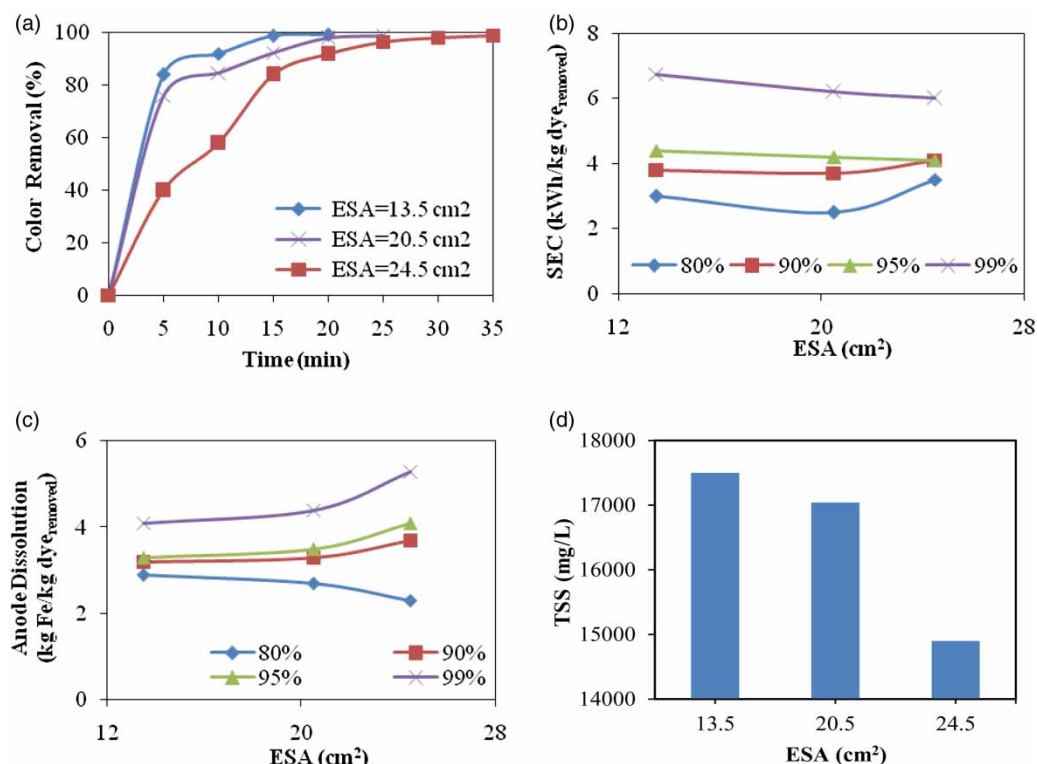

Figure 2 │ The effect of electrodes surface on: (a) dye removal efficiency in terms of time; (b) changes in specific energy consumption in different efficiencies of dye removal; (c) anode dissolution in different efficiencies of dye removal; (d) TSS of separated sludge (d = 0.5 cm, [dye] = 150 mg/L, conductivity = 2,000 μS/cm, I = 0.8 A and pH = 7).

In the present study, specific energy consumption (kWh/kg dye$_{removed}$) and anode consumption (Steel/Kg dye$_{removed}$) were examined as a criterion for better economic and environmental comparison. Figure 2(b) shows the changes in specific energy consumption in terms of dye removal efficiency for different electrode surfaces. By increasing electrode surfaces, due to the decrease in electrical resistance system, the necessary voltage for obtaining a constant electric current is decreased and consequently, total energy consumption is decreased (Hooshmandfar *et al.* 2016). Specific energy consumption in dye removal of 99% for electrode surfaces of 13.5, 20.5 and 24.5 cm^2 was obtained equal to 6.75, 6.2 and 6 kWh/kg dye$_{removed}$, respectively.

In Figure 2(c), the amount of steel anode consumption to the different electrode surface has been shown for different percentages of dye removal. According to this figure and with regard to the results obtained from Figure 2(a), the higher the speed of dye removal to the time, the less anode consumption for dye removed by unit weight. The less this amount, the less sludge is produced and thereby less management problems and disposal. Also, by reducing the cost of sludge disposal and steel consumption, the electro-coagulation and electro-floatation removal process would be more economical.

The amount of separated sludge TSS has been presented in Figure 2(d) as a criterion for the efficiency of the pollutant floatation process in different electrode surface. The amount of measured TSS was between 14,900 and 17,500 mg/L, which is considerably more than the conventional amount of separated sludge from the gravity settling tanks (Hooshmandfar *et al.* 2016).

In comparison, it can be said that the smaller electrode surface (13.5 cm^2) has the highest removal efficiency and the least amount of anode dissolution, and the larger electrode surface (24.5 cm^2) has the least amount of energy consumption. Consequently, as a final result the electrode surface of 20.5 cm^2 with dye removal of 99% within 25 minutes, special energy consumption 6.2 kWh/kg dye$_{removed}$ and anode consumption 4.4 KgFe/Kg dye$_{removed}$, regarding dye efficiency near to maximum efficiency, low anode consumption and also low energy consumption, has the optimum conditions.

In different studies the effect of electrode size on electro-coagulation and electro-floatation efficiency was not taken into consideration and constant sizes of electrodes in order to do the experiments were used. Hooshmandfar *et al.* (2016), Khandegar & Saroha (2013), Rahmani *et al.* (2013), Zodi *et al.* (2013), Pajootan *et al.* (2012), Parsa *et al.* (2011) and Chung *et al.* (2009) used electrodes with surfaces equal to 24.86, 16, 25, 10, 100, 69 and 15 cm^2, respectively.

Distance between the electrodes

In order to determine the optimum distance between electrodes, the experiments were conducted in four electrodes of distances 0.25, 0.5, 1 and 2 cm based on the initial experiments, other parameters are considered constant. The obtained results are given in Figure 3.

As can be seen in Figure 3, the increase in the distance between electrodes causes the reduction of removal efficiency and delays the time of reaching a specified efficiency so that 99% efficiency for distances of 0.25, 0.5, 1 and 2 cm within 20, 24, 30 and 36 minutes were observed. The reason for these observations, i.e. reduction of dye removal efficiency to time by increasing the distance between electrodes is the delay in forming coagulation substances with regard to the dependency of this act on mobility and transfer of substances and produced ions in the electrodes (Khandegar & Saroha 2013).

Figure 3(b) shows the changes in specific energy consumption in terms of dye removal efficiency for different electrode distances. By reducing the distances between electrodes, due to the decrease in resistance of electrical system, the necessary voltage for obtaining a constant electric current is decreased and consequently, total energy consumption is reduced. To obtain the 99% dye removal efficiency, the specific energy consumption for distances between electrodes of 0.25, 0.5, 1 and 2 cm was equal to 6.6, 6.25, 7 and 7.6 kWh/Kg dye$_{removed}$, respectively. The reason for the increase in energy consumption in very low distances of electrodes (2.5–5 mm), is the absence of proper transferring of materials and fluids that leads to accumulation of solid particulars and bubbles between anode and cathode, and as a result an increase in electrical resistance (Phalakornkule *et al.* 2010).

Figure 3(c) shows the amount of steel anode dissolution to the distances between electrodes for different percentages of dye removal. Anode consumption for distances between
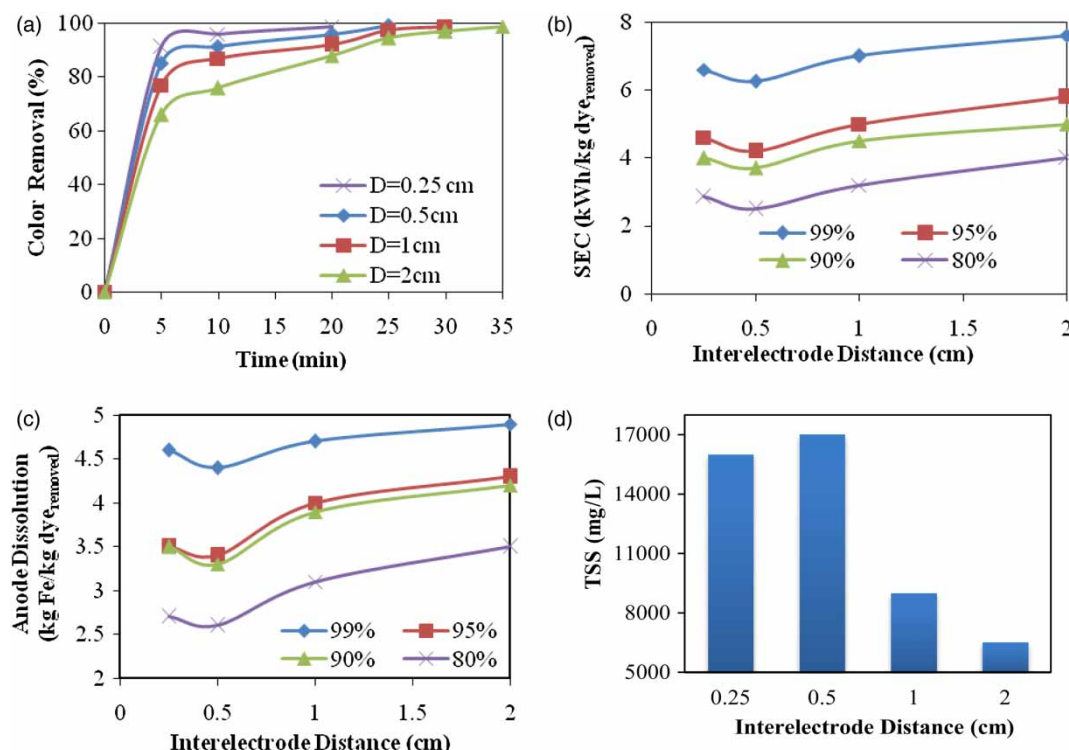
Figure 3 | The effect of distances between electrodes on: (a) dye removal efficiency in terms of time; (b) changes in specific energy consumption in different efficiencies of dye removal; (c) anode dissolution in different efficiencies of dye removal; (d) TSS of separated sludge (ESA = 20.5 cm², [dye] = 150 mg/L, conductivity = 2,000 µS/cm, I = 0.8 A and pH = 7).

electrodes was obtained for 0.25, 0.5, 1 and 2 cm and a dye removal efficiency of 99% equals 4.6, 4.4, 4.7 and 4.9 steel Kg/Kg dye$_{removed}$, respectively. This little difference is also visible in other efficiencies according to the figure. The reason is the direct dependency of electrode consumption on the time of electrolyzation as per Equation (9) and because, based on Figure 3(a), the trend of dye removal to time is almost similar for different distances of electrodes, and consequently anode consumption would be also similar for different distances.

In Figure 3(d), the TSS of separated sludge resulting from the process for different distances between electrodes has been shown. This amount was obtained for distances of 0.25, 0.5, 1 and 2 cm, respectively equals to 16,000, 17,000, 9,000, 6,500 mg/L which indicates the high ability of the system in floatation and no need for another unit in order to separate the formed coagulations, specifically in low distances between electrodes. Therefore, the optimum distance between electrodes was selected to be 0.5 cm with dye removal of 99% during 24 minutes, specific energy and anode consumption of 6.4 kWh/kg dye$_{removed}$

and 4.24 kg Fe/kg dye removed, respectively, and TSS sludge 17,000 mg/L.

Khandegar & Saroha (2013) observed an increase in dye removal efficiency with an increase in the distance between electrodes from 1 to 3 cm, but with greater increase in the distance between electrodes up to 4 cm, dye removal efficiency was decreased. Phalakornkule *et al.* (2010) did not observe any change in dye removal efficiency in the time for three distances of 5, 8 and 12 mm between electrodes, but the least amount of energy consumption for distances between electrodes was 5, 12 and 8 mm, respectively.

Electrical conductivity

The experiments in electrical conductivity of 400, 1,000, 2,000, 3,600 and 5,200 µS/cm were done in order to determine the optimum amount of these parameters in conditions of optimum surface and distance and by keeping other parameters constant. The obtained results are given in Figure 4.
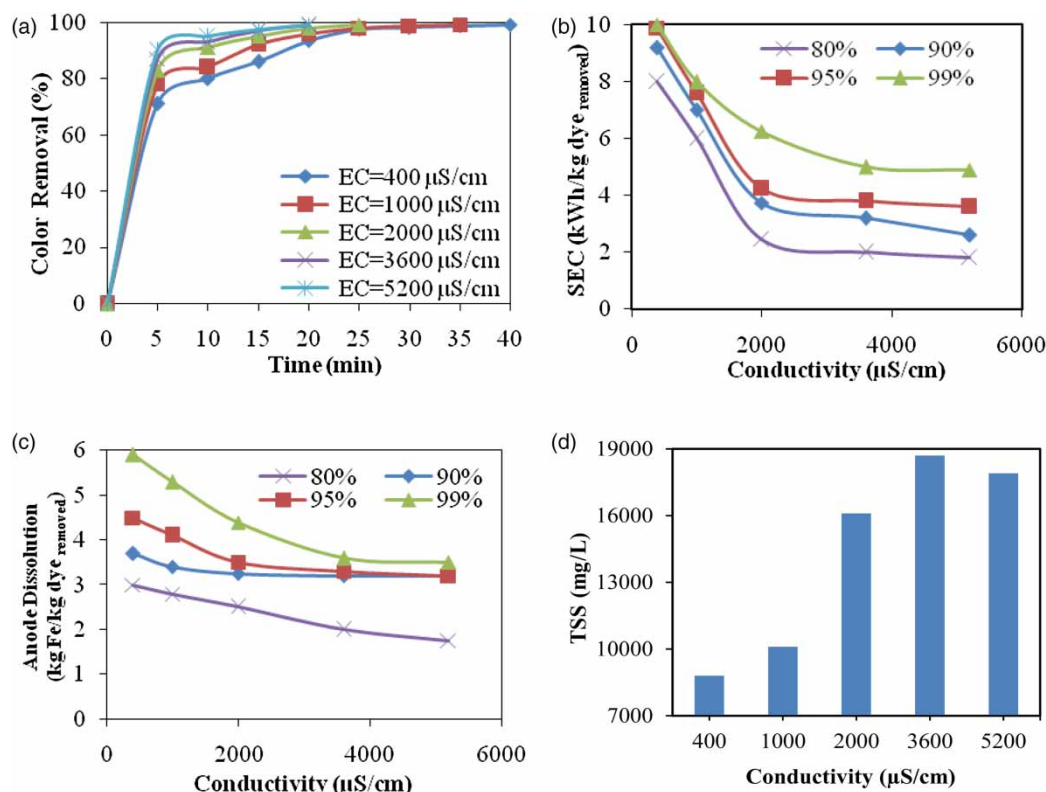
Figure 4 │ The effect of electrical conductivity on: (a) dye removal efficiency in terms of time; (b) changes in specific energy consumption in different efficiencies of dye removal; (c) anode dissolution in different efficiencies of dye removal; (d) TSS of separated sludge (ESA = 20.5 cm^2, d = 0.5 cm, [dye] = 150 mg/L, I = 0.8 A and pH = 7).

As can be seen in Figure 4(a), dye removal efficiency is increased by the increase in solution's electrical conductivity, so that for electrical conductivities of 400, 1,000, 2,000, 3,600 and 5,200 µS/cm, 99% of removal efficiency within 39, 34, 25, 21 and 19 minutes were observed, respectively.

Electrical conductivity has a direct impact on energy consumption. By incrementing electrical conductivity and consequently, the decline in electrical residence of the solution, the necessary voltage for obtaining a fixed electric current is decreased and as a result, as can be seen in Figure 4(b), energy consumption is greatly reduced by increasing electrical conductivity. As an example, for a removal efficiency of 99%, the specific energy consumption for electrical conductivities of 400, 1,000, 2,000, 3,600 and 5,200 µS/cm was 4.9, 5, 6.25, 8 and 10 kWh/kg dye$_{removed}$, respectively. The reason for this decline is that is, according to the figure, the decrease in the required voltage as the result of reducing resistance which itself results from the increase in the solution's electrical conductivity.

Also, as per Figure 4(c), energy consumption rates for electrical conductivities of 400, 1,000, 2,000, 3,600 and 5,200 µS/cm at 99% efficiency were 3.5, 3.6, 4.4, 5.3, 5.9 kg Fe/kg dye$_{removed}$, respectively.

In Figure 4(d), separated sludge at different electrical conductivities is shown. According to our observations, reducing the electrical conductivity means more time is needed to completely separate the pollutant, thus the amount of Fe in the separated sludge increased turning the sludge's color to black. Increasing the aluminum flocs containing water in the sludge causes the TSS of separated sludge and consequently floatation efficiency to decrease.

Studying the different parameters, we observed that electrical conductivity of 3,600 and 5,200 µS/cm has a better condition than other electrical conductivity and could be selected as the optimum electrical conductivity, such that the electrical conductivity of 3,600 µS/cm with 99% of dye removal efficiency within 21 minutes, energy consumption of 5 k Wh/kg dye$_{removed}$, anode consumption

of 3.6 kg Fe/kg dye$_{removed}$ and TSS sludge of 18,700 mg/L were selected as the optimum rate for continuing the research.

The reason for this choice was the higher rate of TSS sludge for electrical conductivity of 3,600 μS/cm indicating better floatation and as a result better performance of the system in treating higher dye concentrations. Furthermore, it should be noted that the presence of salts and ions causes electrical conductivity within the solution, and precipitation and corrosion by these ions on the electrodes causes the enhancement in electrical resistance and imposes an additional cost for treatment. Consequently selecting electrical conductivity of 5,200 μS/cm as the optimum electrical conductivity with regard to a high rate of salt consumption was not optimal both economically or environmentally. Pajootan *et al.* (2012) observed a slight change (4%) in dye removal efficiency by the increase in electrical conductivity of from 4 to 14 mS/cm. By increasing electrical conductivity, the required voltage and consumption energy

was decreased (Parsa *et al.* 2011). The optimum concentration of electrolyte with the least specific energy consumption (0.5 g/L) was obtained by changing NaCl concentration from 0.25 to 5 g/L.

Type of electrolyte

Different electrolytes can be used to generate electrical conductivity in wastewater solutions. The effect of an electrolyte on removal efficiency and energy consumption due to changes in the rate of a solution's electrical conductivity, and forming precipitation and corrosion in electrodes, is important. For this purpose, the impact of the three commonly used electrolytes, NaCl, Na_2SO_4 and $MgSO_4$, was examined. It is worth noting that in all the previous studies, NaCl was used for supplying the required electrical conductivity. In Figure 5(a), the impact of the type of electrolyte on dye removal efficiency to time is shown. Dye removal from solution using NaCl had a faster trend than the two other
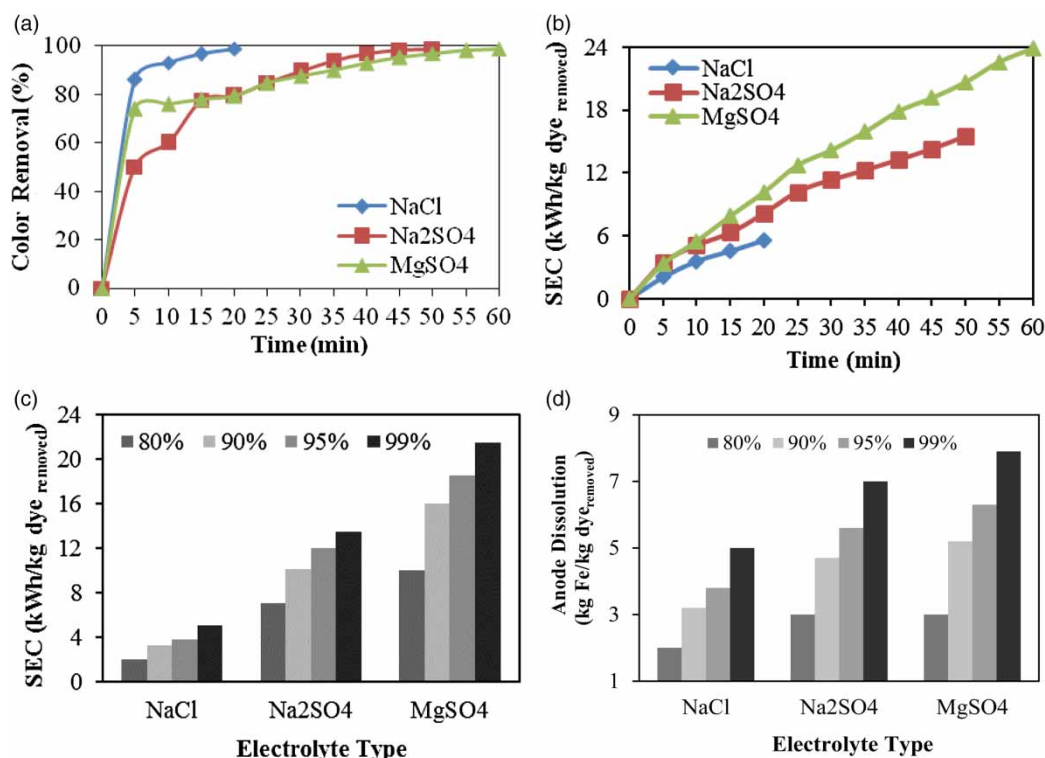

Figure 5 │ The effect of the type of electrolyte on (a) dye removal efficiency in terms of time; (b) changes in specific energy consumption in terms of time; (c) specific energy consumption in different efficiencies of dye removal; (d) anode dissolution in different efficiencies of dye removal (ESA = 20.5 cm², d = 0.5 cm, [dye] = 150 mg/L, conductivity = 3,600 μS/cm, I = 0.8 A and pH = 7).

electrodes. For example, 99% dye removal for NaCl, Na_2SO_4, and $MgSO_4$ was observed after a duration of 20, 50 and 60 minutes, respectively.

The specific energy consumption using three different electrolytes in Figure 5(b) in terms of the time and Figure 5(c) independent of time is shown. As can be observed in the figure, energy consumption using NaCl is less than Na_2SO_4 and $MgSO_4$ and is equal to 5, 13.5 and 21.5, respectively, for a dye removal efficiency of 99%. The required voltage for supplying fixed electrical current using NaCl is less and thus, total energy consumption is lower. Electrical conductivity of the water sample can be obtained using Equation (11) as a good approximation:

$$EC = \sum (C_i . f_i) \tag{11}$$

where EC is electrical conductivity ($\mu S/cm$), C_i the ion concentration (mg/L) and f_i factor of electrical conductivity for ions (Schröer & Weingärtner 2004). In the conducted experiments, the calculation of electrical conductivity created by different electrolytes is as according to Table 2. As can be seen, the higher voltage needed for supplying a fixed electric current using NaCl as electrolyte based on the conducted calculation is justifiable.

The electrical conductivity created by NaCl in solution is higher than the two other electrolytes at equal concentrations. Greater electrical conductivity means higher electrical conductivity of the solution, and for creating a fixed current conductivity, a higher voltage is needed. Therefore, for creating a fixed current conductivity, less NaCl is needed than other electrolytes and because NaCl is cheaper, the cost of treatment will be lower. In justifying higher electrical conductivity created by $MgSO_4$ to NaCl, it can be said that electric current is transferred both by cations and anions but the degree of conductivity is different. The created electrical conductivity by multivalent cations is higher than univalent cations. But this is not the case for anions (Gray 2005).

The amount of anode consumption using different electrolytes is shown in Figure 5(d). Anode dissolution rate using NaCl is lower due to the quicker trend of dye removal than other electrolytes, i.e., NaCl, Na_2SO_4, and $MgSO_4$ was 5, 7 and 7.9 kg Fe/kg dye$_{removed}$, respectively, obtained at dye removal efficiency of 99%.

Passing current in an aquatic environment like wastewater occurs due to the movement of ions towards the electrode with negative load. NaCl has a higher ionization speed and mobility due to the lower radiuses of Na and Cl than other ions like potassium, carbonate or nitrate and as a result, more current passes through wastewater and by increasing passing current, the speed of anode dissolution increases. On the other hand, producing acidic species such as HCl and ClO^- enhances the desirability of revival conditions (Golder et al. 2007). Therefore, using NaCl as electrolyte has the advantage of lower price. Also, textile and dyeing industries use plenty of NaCl and wastewaters of these industries include ions of this salt. Cl^- ions decrease the negative effect of other ions such as HCO_3^- and SO_4^{2-}. The existence of carbonate causes the formation of intruder precipitation of Ca^{2+} and Mg^{2+} on electrodes. These precipitations increase the electrical resistance of system and energy consumption and disturb the treatment trend (Parsa et al. 2011). Chen (2004) has suggested the existence of Cl^- at the rate of 20% from all ions to ensure the natural electrical coagulation process.

Initial pH

Experiments at different initial pHs have been conducted in order to determine the optimum amount of this parameter in optimized conditions at the electrode surface, distances between electrodes, electrical conductivity and the type of electrolyte and the results obtained are presented in Figure 6.

At an initial pH of 3, dye process was completed within 5 minutes with high efficiency. Following this process becomes slow and because in order to measure the dye concentration, the samples first have to be treated then

Table 2 │ Calculated electrical conductivity for different electrolytes

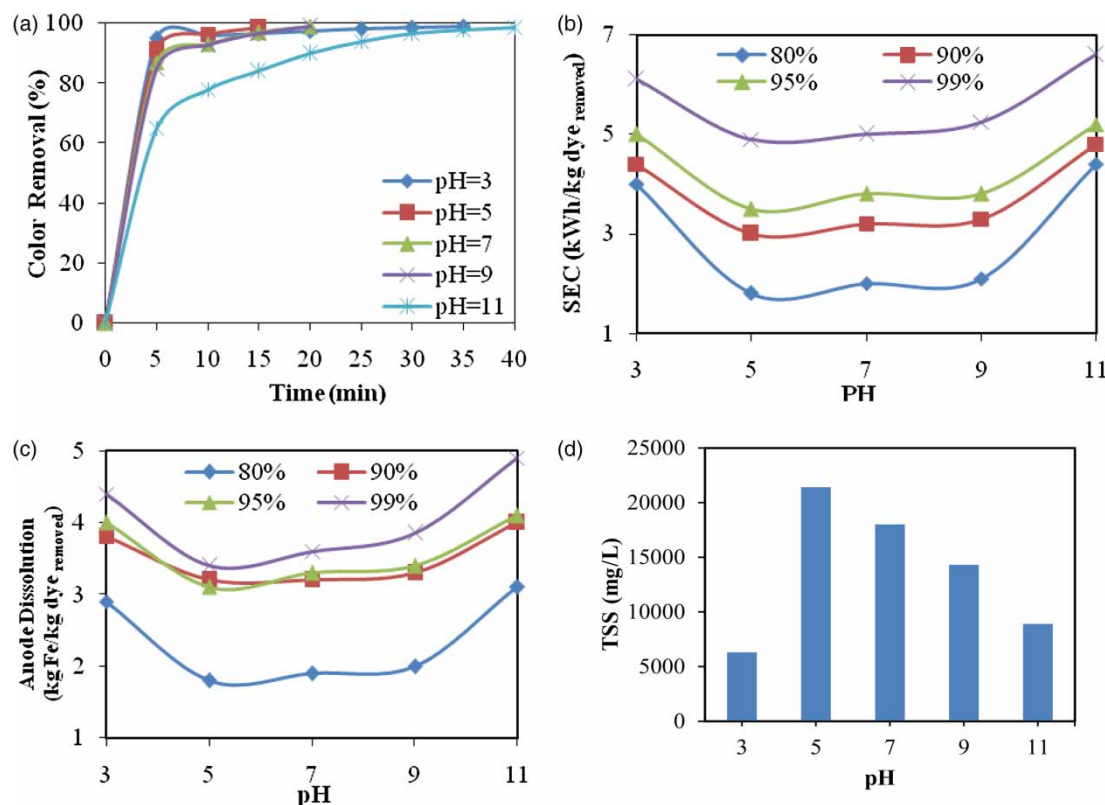| Electrolyte (1,000 mg/L)	Ion	Concentration (mg/L)	CF (μScm^{-1}/ mgL^{-1})	EC	Total EC ($\mu S/cm$)
NaCl	Na^+	393	2.13	837	2,136
	Cl^-	607	2.14	1,299	
Na_2SO_4	Na^+	324	2.13	690	1,731
	SO_4^{2-}	676	1.54	1,041	
$MgSO_4$	Mg^{2+}	203	3.82	775.5	2,003
	SO_4^{2-}	797	1.54	1,227.5	

Figure 6 │ The effect of pH on: (a) dye removal efficiency in terms of time; (b) changes in specific energy consumption in different efficiencies of dye removal; (c) anode dissolution in different efficiencies of dye removal; (d) TSS of separated sludge (ESA = 20.5 cm², d = 0.5 cm, [dye] = 150 mg/L, conductivity = 3,600 µS/cm, I = 0.8 A).

centrifuged, the increase in dye concentration (no increase in efficiency) is related to desorption (Hooshmandfar *et al.* 2016). After this lull, the efficiency increases. It is worth noting that the produced sludge lost its flotation property and settled. According to Figure 6(a) at an initial pHs of 5, 7 and 9, the dye separated well from solution and the sludge floated. As per our observations, in experiments with an initial pH = 11, the sludge did not separate well and was black which indicated a low amount of dye and high amount of Fe compounds in the sludge as well as a poor system performance in dye separation.

Monomeric and polymeric Fe species vary at different pH, and the coagulation mechanism is dependent on pH. Different researchers have stated various Fe species in solution to justify the process of pollutant removal. Producing $Fe(OH)_3$ coagulation as an adsorbent in the environment, and their performance at different pH are important. Due to changes in pH, the time in process and considering the aforementioned mechanisms, the effect of pH in dye

removal with electro-coagulation and electro-floatation can be explained. At pH = 3–9, there are strong oxidizing chlorine species that help remove dye (Martínez-Huitle & Brillas 2009).

pH affects the amount and size of bubbles. As in electro-floatation, hydrogen bubbles play the main role, producing more hydrogen gas with smaller bubble size is desirable for the floatation of the produced coagulations. At acidic pH, the number of bubbles increases but their sizes also increases and therefore the ability to float tiny particles decreases. At basic pH, the number of bubbles decreases and their size reduces (Brandon & Kelsall 1985; Rahmani *et al.* 2013). Therefore, no difference in significant efficiency in pH 5–9 according to Figure 6 can be explained by the above-mentioned reasons.

In order to determine the optimum conditions of initial pH and an economic comparison between them, the amount of specific energy and anode consumption are shown in Figure 6(a) and 6(b). As can be seen, for obtaining

a dye removal of more than 90%, specific energy consumption increased from an initial pH of 3, decreased for an initial pH of 5, 7 and 9, and increased again for an initial pH of 11. Specific energy consumption was 6.1, 4.9, 5, 5.25, and 6.6 kWh/kg dye$_{removed}$ for 99% dye removal with these mentioned initial pH, respectively. A similar method was observed for anode consumption, with results of 4.4, 3.4, 3.6, 3.85 and 4.9 kFe/kg dye$_{removed}$ for 99% removal efficiency, respectively.

In Figure 6(d), separated sludge TSS is shown for different initial pH. As can be seen, the amounts related to TSS for initial pH of 3, 5, 7, 9 and 11 were 6,300, 21,400, 18,000, 143,000 and 8,900, respectively. The results in the diagram are consistent with observations, and as expected the least amount was related to pH 3. For pH 5–9 electro-coagulation and forming coagulation is well done, electro-floatation has shown good performance. In acidic pH, Fe^{2+} is easily converted to Fe^{3+} such that $Fe(OH)_{3(s)}$ formed in solution turns into suspended gelatin that can separate waste materials from wastewater through the formation of a surface complex or electrostatic adsorption and finally coagulation; this issue can be the reason for higher TSS and consequently better floatation of coagulations in acidic pH. It should be noted that $Fe(OH)_3$ has more optimal coagulating properties than $Fe(OH)_2$ (Zaroual *et al.* 2006).

According to the results of Figure 6, the general performance of dye treatment system with initial pH = 5 was better than at other pH. However, due to the proximity of values of the four parameters of removal efficiency, energy and anode consumption and sludge TSS between pH 5 and 7, and because there is no need to add chemicals for adjusting the solution pH containing Acid Red 14 which equals to 7, an initial pH = 7 was selected as optimum for this study.

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

adjust pH solution containing dye (5.5), they considered this as an optimum value.

Intermediate compounds

In order to study the effect of the electro-coagulation and electro-floatation system on the structure of constituents of Acid Red 14 and determine the intermediate production compounds in this response, LC-MS analyses was conducted on the samples of 0, 20 and 120 minutes, the results of which are shown in Figure 7.

Figure 7 shows the three mass spectra of the samples after being injected into an LC column. According to Figure 7(a), the first sample before the start of the reaction, the first peak with molecular weight of 502.4 m/z shows M as the molecular weight of Acid Red 14 and the remaining symbols are the other compounds in dye. Signals for 478.6, 268.5, 220.8 and 169.9 in the first figure can be allocated to [M-Na], [M-$C_{10}H_6$-2Na-SO_3-2N-H] and [M-$C_{10}H_6$-2Na]. These compounds are lighter than the initial dye, each were created by separation of 1-2-sulfur trioxides, sodium, nitrogen, and or a naphthalene ring in the structure of the dye or separating of a mixture of these.

The second sample was taken within 20 minutes after the onset of the reaction for dye removal, efficiency of 99% had been recorded and LC-mass experiment was conducted. In Figure 7(b), two new peaks with low intensity were formed which are the intermediates of the colour-making agent with molecular weights of 377.7 and 172.7 m/z resulting from azo bond failure. Molar mass of 377.7 and 172.7 m/z can be also allocated to [M-2Na-SO_3^+] and [M-$C_{10}H_6$-2Na-$2SO_3^+$H], respectively. As can be seen in figure, after 20 min from the start of the reaction, there is no mother peak of Acid Red 14 and this is a confirmation of dye removal efficiency within 20 min in optimal conditions. Also, two peaks at 268.5 and 221.7 m/z are seen in this figure that exist in the previous figure with the difference that the former is increased and the latter is decreased.

The third sample for mass analysis was taken 120 min after the onset of reaction as observed in Figure 7(c). As can be seen in the figure, the predominant peak in this figure, just as in the two previous figures, is related to a compound with molecular weight of 221.7 m/z, and as mentioned before its molecule formula can be guessed as [M-$C_{10}H_6$-2Na-SO_3-2N-H]. This
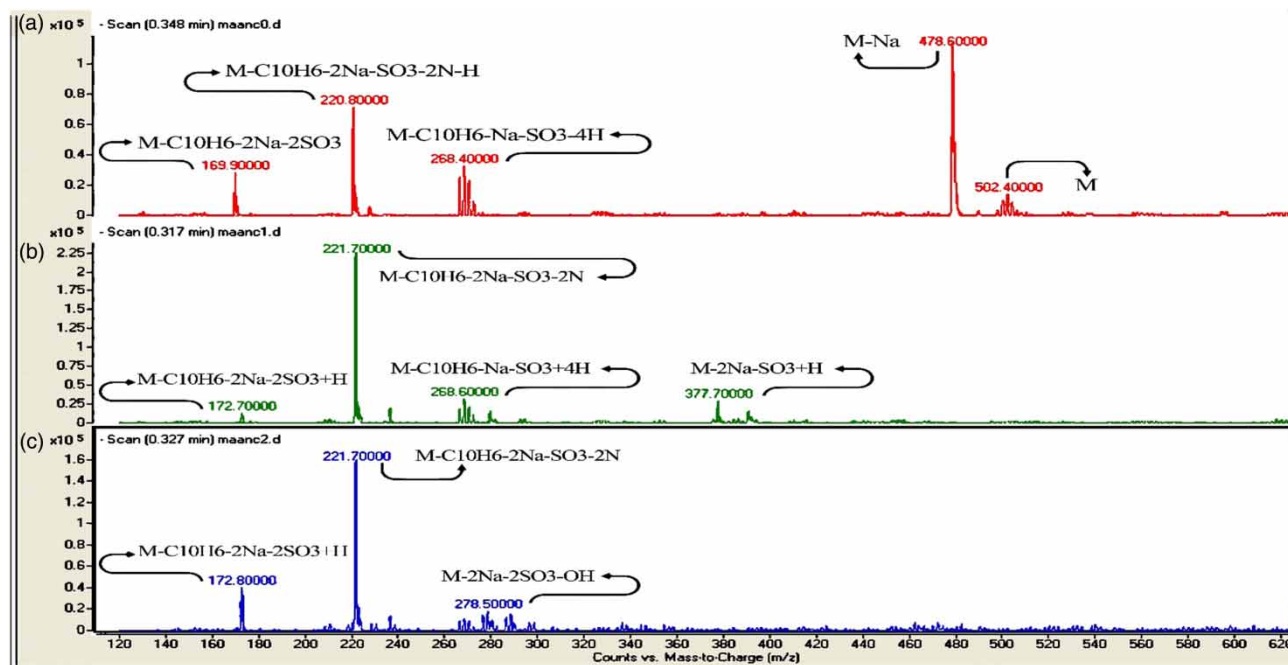
Figure 7 | LC-Mass spectrum related to Acid Red 14 at times: (a) 0 min; (b) 20 min; and (c) 120 min.

compound, which is considered to be the structure of Acid Red 14, is the derivative of α-naphtole or 1-naphtole that existed in the analysis of the first sample in Figure 7(a). This compound is recognized as an environmentally hazardous compound and harmful for the aquatic environment but the degree of its toxicity is less than Acid Red 14. In this figure, in addition to a peak related to α-naphtole, there are also two other peaks. One with a molecular mass of 172.8 m/z that was shown in Figure 7(b) and is not a new peak, and the other one at 278.5 m/z is of much lower intensity and can be ascribed to [M-2Na-2SO$_3$-OH]. It can be said about this compound that due to the separation of the hydroxyl bond (OH) there is no phenol in it at all and for this reason its danger in comparison to derivatives of α-naphtole is insignificant.

Regarding the failure of the azo bond and complete dye removal in the first 20 min and complete disposal of other heavy intermediate compounds such as compounds with molecular weight of 377.7 and 268.6 m/z within 120 min, the only predominant compound in the system at the end of the reaction is a compound with molecular mass of 221 m/z. Considering that azo dye Acid Red 14 with its very high toxicity and molecule weight of 502.4 m/z decomposed during the 120 min process to a compound with lighter molecular weight (221 m/z) and simpler structure,

so it can be concluded that electro-coagulation and electro-floatation are effective methods in azo dye removal of Acid Red 14 and probably other similar compounds.

CONCLUSION

Produced oxygen is trapped under the anode and continuing production produces more bubbles and big bubbles. By increasing electrode surface, due to the decrease in electrical resistance of system, the required voltage for obtaining a fixed electric current declined and consequently, total energy consumption decreased. Therefore, from the three electrode surfaces, the intermediate surface (neither maximum nor minimum) was selected as optimum.

On increasing the distance between electrodes (from 0.5 to 2 cm), due to the delay in constituting coagulating materials with regard to the dependency of this action on mobilization and transfer of materials and produced ions in the electrodes, dye removal efficiency showed a decrease to time. Also, on decreasing the distance between electrodes, due to the decrease in electrical resistance of system, the required voltage for obtaining a fixed electric current declined and consequently, total energy consumption

decreased. But, with a further decrease in the distance between the electrodes (less than 0.5), an increase in energy consumption was observed the reason for which was non-transferring of materials and fluids that causes a concentration of solid particles and bubbles between the anode and the cathode and thus an increase in electrical resistance.

The increase in electrical conductivity of the solution using NaCl causes a decrease in the required voltage in a fixed electric current due to the decline in electrical resistance of the wastewater, and electrical energy consumption which is proportionate to voltage multiplication in electric current is decreased (significant decrease in energy consumption with the increase in electrical conductivity from 400 to 3,600 μS/cm). Given that the existence of salts and ions causes the creation of electrical conductivity in solution, sediment and corrosion by these ions on electrodes causes an increase in electrical resistance and incurs an additional price for treatment. As a result, very high electrical conductivity cannot be selected as optimum conductivity for the excuse of increase in removal efficiency or the decrease in energy consumption (resulting in non-selection of electrical conductivity of 5,200 μS/cm as the optimum conductivity in comparison to electrical conductivity of 3,600 μS/cm).

The performance of the system did not show much dependency on initial pH and environment. In acidic pH, the number of bubbles is increased but their size gets bigger which decreases their ability for flotation of tiny coagulations. In basic pH, the amount of bubbles is decreased but their size gets smaller. In pH 5–9 electro-coagulation and forming coagulations is done well, electro-flotation had good performance and high dye removal efficiency was obtained for the three pHs. Therefore, selection of pH = 7 as an optimal pH was adopted due to economic and environmental parameters.

In conclusion, the results of this research with 99% of dye removal within 20 min, specific energy and anode consumption was 5 kWh/kg dye$_{removed}$ and 3.6 kg Fe/kg dye$_{removed}$ and sludge TSS 18,700 mg/L provide an electro-coagulation and electro-floatation method for dye-containing wastewater treatment with low material and energy consumption.

Using stainless steel mesh electrodes with a horizontal arrangement that emphasizes electro-coagulation properties by creating more surface for producing more bubbles of

smaller sizes could be one reason for the higher removal efficiency with lower energy consumption and lower anode dissolution in comparison with the similar studies (particularly Hooshmandfar *et al.* 2016), as it simultaneously uses both properties of electro-coagulation and electro-floatation. Also, the produced sludge causes a decrease in treatment costs and sludge disposal and its related problems. Consequently, using this method is considered to be a good option for constituting with usual methods of treatment like chemical coagulation and flocculation and/or pre-treatment before complementary treatment.

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