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Treatment of colored textile wastewater containing acid dye using electrocoagulation process

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ABSTRACT

In this study, dye removal from synthetic colored wastewater using electrocoagulation process was studied. Acid Red 73 was used as model dye compound. The effects of operational parameters, such as current density, reaction time, initial dye concentration, electrolyte concentration, initial pH, and polyaluminum chloride (as a coagulant), on dye removal were investigated. The cost of wastewater treatment at optimal condition was investigated. The results showed that electrocoagulation process was able to remove 99% dye and 88% chemical oxygen demand. Using polyaluminum chloride as a coagulant had significant impact on improving process efficiency, time, and cost reduction. It can be concluded that electrocoagulation was a very effective and fast method to remove acid dye from colored wastewater.

Keywords: Electrocoagulation; Colored wastewater; Dye removal; Polyaluminum chloride

1. Introduction

Several industries, such as textile, paper, plastic, etc. produce high-volume colored wastewater due to consumption of dyes and water. Color is the first pollutant that can be detected in wastewater. Thus, a little amount of dye in water is highly visible [1–9]. In addition, discharge of colored wastewater to the environment due to being toxic and mutagenic and potential of bioaccumulation of many dyes and by-products of them is undesirable for living organisms [10,11].

Previous studies indicated some of dyes cause bladder cancer in humans (such as fuchsine and auramine) and chromosomal disorder in living organisms [12]. For example, Acid Red 73 is able to connect on proteins, such as serum albumin, and alert physiological protein function and create toxic and allergic effects [13].

Electrochemical methods of wastewater treatment have several advantages such as easy operation, high speed to remove contaminants, no need to add large quantities of chemicals and low sludge production [14,15]. Electrochemical process has been studied to remove pollutants, such as oil, grease, chemical oxygen demand (COD) [15], heavy metal of mercury [16], nitrate [17], phosphate [18], arsenic [19], natural organic matter [20], and dyes [8,14], from water and wastewater. During electrocoagulation process, electrodes are dissolved and metal ions, such as iron or aluminum, release in the solution. The released ions neutralize charge of soluble pollutants and produced metal hydroxide coagulants at the site of reaction, attract and remove contaminants by sedimentation [14,15].

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A literature review showed that Acid Red 73 was not removed from colored wastewater using electrocoagulation process. In this research, electrocoagulation process was used to remove Acid Red 73 from colored wastewater. The effect of operational parameters on electrocoagulation performance was evaluated.

2. Experimental

2.1. Material

Acid Red 73 was obtained from CIBA. The chemical structure of Acid Red 73 was shown in Fig. 1. Hydrochloric acid, sulfuric acid, sodium hydroxide, sodium chloride, and the reagents needed to test the COD were products of Merck Company of Germany. Polyaluminum chloride been used had following characteristic: bright yellow powder with a purity of 30 ± 1% based on Al_2O_3 and chemical formula $[Al_2\ (OH)_n\ Cl_{6-n}.YH_2O]_z$, and it was purchased from Shamim Kosar company (Iran). Concentration of dye was measured by spectrophotometer (CECIL-Aquarius Double beam, UK) at 510 nm and COD in accordance with the method no. 5220 B in the book of Standards Methods for Examination of Water and Wastewaters [21].

For adjusting the pH, NaOH and H_2SO_4 were used. Voltage and current were measured by digital Multimeter (DEC-RE330Fc, Taiwan). For conducting experiments, a cube shape tank with dimensions of 14 × 12 × 14 cm was made of Plexiglas. Reactor was equipped with two aluminum electrodes as anode and 2 stainless steel electrode as cathode. Dimension of each electrode was 11.2 cm (length) × 10.8 cm (width) × 0.2 cm (thick).

2.2. Procedure

Before each run, distance between each electrode was 1 cm when they placed in reactor. For proper mixing, 2 cm distance between bottom of electrodes and reactor bottom was considered. Electrodes, by wire, in a monopolar connection mode were connected to DC power supply (MICRO, Iran). Then, 2 L of synthetic wastewater containing certain amount of color was poured in the reactor. In this experiment, current density in fixed amounts of 2, 8, 12, 16, or 20 mA/cm^2, was regulated, and voltage changes, during the experiment continuously, were measured. Samples were withdrawn at 0, 5, 15, 30, 45, and 60. Then, the samples were centrifuged (4,000 rpm, 5 min) and analyzed. To determine mass of consumed electrode, the electrodes before and after the process were weighted by the digital scale. After each run, the electrodes for 30 min. were dipped in 1.3 M hydrochloric acid and then washed with a plastic brush and rinsed with tap water and dried. All tests were performed at 25°C.

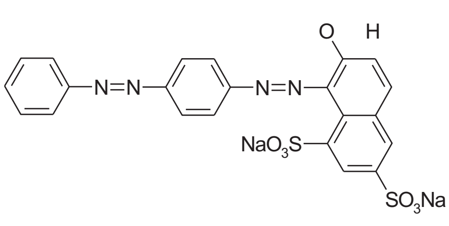

Fig. 1. The chemical structure of Acid Red 73.

3. Results and discussion

The main reactions that occur during the electrocoagulation process when using aluminum electrodes are anodic and cathodic reactions.

$$\text{Anodic reaction}: \ Al \rightarrow Al^{3+} + 3e^-$$

$$\text{Cathodic reaction}: 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

As the result of electrolytic anode dissolution, the produced trivalent aluminum ions immediately settle under spontaneous hydrolysis reactions and produce various monomeric species in following steps:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$$

In addition to above reactions products, dimeric, trimeric, and multinuclear hydrolysis products of aluminum (such as $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$) also can take form. Finally, the cationic hydrolysis products of aluminum react with hydroxyl ions, and they are converted to amorphous and insoluble $Al(OH)_3$ that the pollutants can be trapped and removed from the solution through precipitation.

Pollutants were removed by different species of aluminum produced during electrocoagulation process with two mechanisms [22]:

(1) Neutralizing charge of soluble pollutants or colloids containing negative charge by cationic hydrolysis products
(2) Trapping of colloids in sediments hydroxide (sweeping flocculation) and their elimination by sedimentation.

3.1. Effect of current density on dye removal efficiency

Current density affects the efficiency of electrocoagulation process because it determines the dose of coagulant. The results (Fig. 2) showed that with increasing current density from 2 to 20 mA/cm^2 at 60 min, removal efficiency of dye increases from 73.24 to 99.5%. By increasing current density and time of reaction, anodic dissolution and coagulant production increase, and consequently, the production of metal hydroxides increase. Energy consumption in current density of 2, 8, 12, 16, and 20 mA/cm^2 at 60 min was 0.35, 3.5, 7.27, 12.05, and 18.02 kW/h m^3 of treated wastewater, respectively. On the other hand, increasing the current intensity increased production of hydrogen bubbles and bubbles size reduced which increased the removal efficiency of pollutants by flotation using hydrogen bubbles [23,24]. The previously published article have shown within 90 min of electrocoagulation, with increasing current density from 25 to 35 mA/cm^2 COD removal efficiency has been increased from 70 to 94.5% [23].

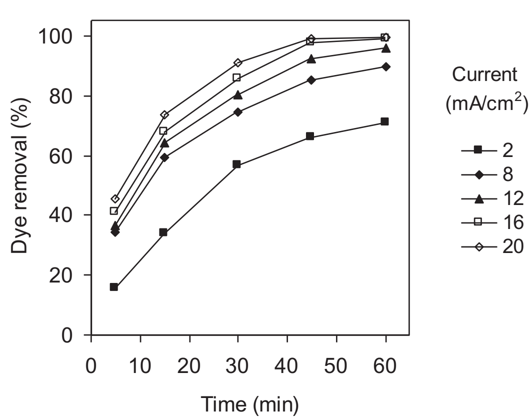

Fig. 2. Effect of current density (mA/cm^2) on dye removal efficiency (dye concentration: 50 mg, pH: 7, electrolyte concentration: 1,000 mg/L).

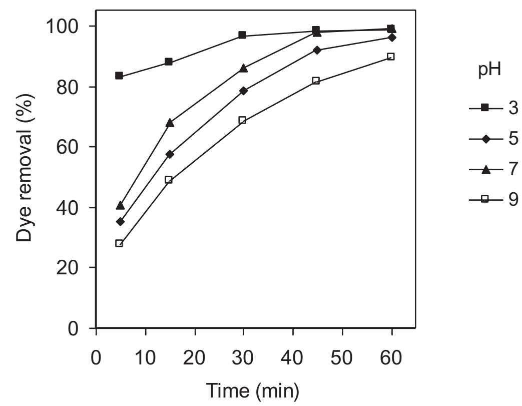

Fig. 3. Effect of Initial pH on dye removal efficiency (Current density: 16 mA/cm^2, dye concentration: 50 mg/L, electrolyte concentration: 1,000 mg/L).

3.2. The effect of initial pH on process performance

The effect of initial pH on dye removal efficiency was shown in Fig. 3. In electrocoagulation process, different species of aluminum hydroxide compounds are formed in the reaction environment at different pH values. Cationic monomeric species of aluminum, such as $Al(H_2O)_6^{3+}$, are the dominant species at pH < 4. In the pH of between 5.2 to 8.8, polymeric species and insoluble $Al(OH)_3$ are dominant species. In the pH > 9, $Al(OH)_4^-$ is the dominant species and in pH > 10, $Al(OH)_4^-$ is only species in solution [23]. Sedimentation and adsorption were studied as main mechanisms of pollutant removal at different pH values [25]. Sedimentation is dominant mechanism of pollutant removal at low pH values. While adsorption is the dominant mechanism of pollutants removal at pH > 6.5 [19,20].

Sedimentation: At pH in the range of 4–5, neutralization of opposite charges and elimination are due to reaction of dye with monomeric aluminum species such as $Al(OH)_2^+$ and $Al(H_2O)_6^{3+}$:

$$\text{Dye} + \text{monomeric Al} \rightarrow [\text{Dye-monomeric Al}]_{(s)}$$

At pH in the range of 5 to 6, neutralization of opposite charges and elimination are due to reaction of dye with polymeric aluminum species, such as $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}^{3+}$, and $Al_7(OH)_{17}^{4+}$

$$\text{Dye} + \text{polymeric Al} \rightarrow [\text{Dye-polymeric Al}]_{(s)}$$

Adsorption: At pH more than 6.5, dye molecules adsorbed on $Al(OH)_3$ flocs and produced suspended particles:

$$\text{Dye} + Al(OH)_{3(s)} \rightarrow [\text{particle}]$$

$$[\text{Dye} + \text{polymeric Al}]_{(s)} + Al(OH)_{3(s)} \rightarrow [\text{particle}]$$

Surface of $Al(OH)_3$ flocs could attract dissolved organic compounds or trapped colloid particles and caused their separation and removal of them from solution through precipitation or flotation by hydrogen bubbles [25]. Results of other studies have shown that the optimum pH for the formation of $Al(OH)_3$ is pH between 4 and 9 and the highest dye removal efficiency also has been achieved in this range [8,20]. Results of this study also showed that highest dye removal efficiency rate of 99% during 60 min at pH 7.

3.3. Effect of electrolyte concentration on dye removal efficiency

Electrical conductivity of solution depends on the type and concentration of electrolyte. Sodium chloride is used as the electrolyte in the electrochemical processes due to the relatively high electrical conductivity, high solubility, low cost, oxidizing properties of chlorine, low toxicity, and no significant effect on the pH of environment [14,26]. Chloride ions in the structure of sodium chloride can be oxidized in the anode to produce active forms of chlorine such as hypochlorite ion. The active chlorine species can oxide dye molecules and increase dye removal efficiency. Therefore, to determine the effect of electrolyte concentration on the efficiency of electrocoagulation process, sodium chloride was used as the electrolyte. As shown in Fig. 4, with increasing electrolyte concentration from 500 to 1,500 mg/L, dye removal efficiency has decreased. It can be attributed that in a constant current density with increasing electrolyte concentration, solution electrical conductivity increases and the ohmic resistance decreases. In addition, electrochemical cell voltage decreases [26]. Thus, energy consumption and producing of flocs reduce and consequently dye removal efficiency reduces. Results showed that energy consumption in concentrations 500, 1,000, and 1,500 mg/L during 60 min was 19.7, 12.05, and 9 kW/h m^3 of treated wastewater, respectively. High concentration of electrolyte leads to excessive electrode consumption and excessive surface electrodes can be destroyed [26]. Therefore, in selecting an appropriate concentration of electrolyte, energy consumption, proper efficiency of dye removal and prevent excessive destruction of the electrodes should be considered and the optimal concentration of electrolyte should be selected.

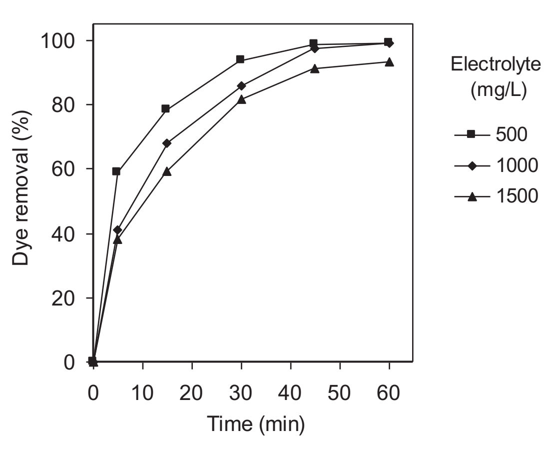

Fig. 4. Effect of electrolyte concentration (mg/L) on dye removal efficiency (current density: 16 mA/cm^2, dye concentration: 50 mg/L, pH: 7).

3.4. Effect of initial dye concentration on efficiency of process

Fig. 5 shows that with increasing dye concentration from 25 to 200 mg/L, dye removal efficiency decreases from 99.54 to 88%. In a constant current density, a certain amount of metal hydroxide is produced which adsorption capacity of this hydroxide flocs is limited. Therefore, the amount of floc to attract all dye molecule is not sufficient, and removal efficiency is reduced with increasing the dye concentration [14,24]. On the other hand, in fixed operating conditions, releases of hydroxyl ions are nearly constant so in case of the number of metal ions increases, still the amount of hydroxyl ions for flocs production in inadequate amount is not enough and dye removal efficiency decreases. At high dye concentration, dye molecules in

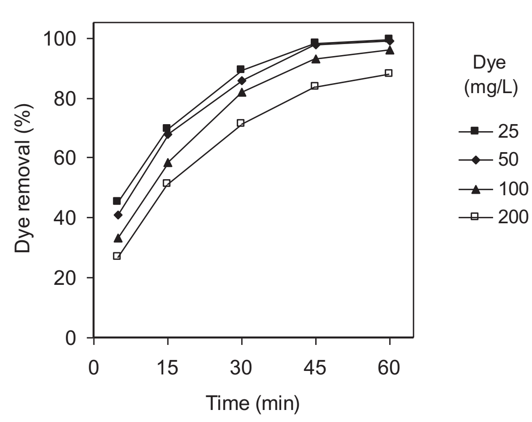

Fig. 5. Effect of initial dye concentration (mg/L) on dye removal efficiency (current density: 16 mA/cm^2, pH: 7).

victim electrode electrically coagulated. Diffusional resistance increases with passing process time and with transferring large number of dye molecules to surface of anode, resistance occur and electrocoagulation and dye removal efficiency decreases [24].

3.5. Effect of adding polyaluminum chloride on the performance of electrocoagulation process

Polyaluminum chloride is a prepolymerized species of trivalent aluminum and contains range of hydrolysis and polymeric species that have a large surface and carry highly positively charged (cationic). Enhanced surface activity and high ability make polyaluminum chloride as an effective material for pollutant removal. Polyaluminum chloride has advantages such as rapid accumulation rate, creating larger and heavier flocs and requires fewer doses than other coagulants to remove a certain amount of pollutants. Therefore, polyaluminum chloride was used as aid coagulant to improve the efficiency of electrocoagulation process for the removal of dye. As can be seen in Fig. 6, adding PACl at doses of 50 and 100 mg/L has significant impact on improving efficiency of electrocoagulation process and reduces the required time for dye removal. Polyaluminum chloride removes organic matters and improves efficiency of electrocoagulation process by destabilizing of particles and increasing particle size [23]. With adding polyaluminum chloride at a concentration of 100 mg/L, the needed time to remove 99% dye from 60 to 15 min has been reduced. Reducing required time for dye removal can reduce amount of energy and electrode consumption and reduces cost of wastewater treatment. In addition, by adding polyaluminum chloride in the optimum operation conditions, COD removal efficiency increases from 71% to 88%.

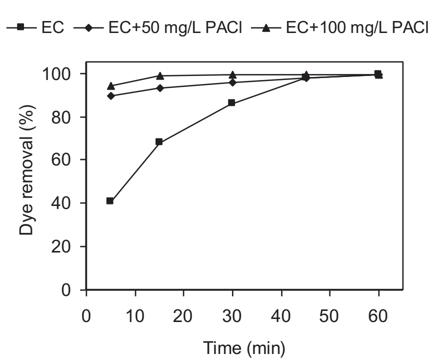

Fig. 6. Effect of adding polyaluminum chloride (PACl) on the efficiency of electrocoagulation for dye removal (current density: 16 mA/cm^2, dye concentration: 50 mg/L, electrolyte concentration: 1,000 mg/L, pH: 7).

3.6. Economic analysis

Operating cost is one of the most important factors that can affect selecting of a method for wastewater treatment. In electrocoagulation process, the most important operational parameter is cost of electricity and metal mass consumption. Therefore, these two parameters for calculating the operating costs when using the electrocoagulation process alone and the cost of polyaluminum chloride when aid coagulant was used with electrocoagulation process (to achieve 99% dye removal efficiency), in this research, were considered and calculated. It should be noted that the calculated costs were based on the Iranian market prices (price of polyaluminum chloride 0.65 US$/kg, the price of aluminum sheet 3 US$/kg, and price of electricity 0.0773US$/KWh). While using electrocoagulation, energy and metal mass consumption to achieve 99% efficiency of dye removal were 12.5 kW/h and 0.709 kg/m^3, respectively, of treated wastewater. The amount of energy and electrode consumption was 3.03 kW/h and 0.18 kg/m^3, respectively, when the aid coagulant with dose of 0.1 kg/m^3 of wastewater with electrocoagulation process was used. Thus, cost of treatment per cubic meter of wastewater decreases using aid coagulant with electrocoagulation.

3.7. Current efficiency

Current efficiency is an important parameter that can affect the lifetime of the electrodes during the electrocoagulation process. Experimental dose of aluminum dissolved during electrocoagulation process to its theoretical value, as the current efficiency is defined. This parameter is calculated according to the following equation [16]:

$$\varphi = \frac{\Delta M_{\text{exp}}}{\Delta M_{\text{theo}}} \times 100$$

The amount of theoretical aluminum dissolution in accordance with Faraday's law is calculated according to the following equation:

$$\text{Al}^{3+} \text{ theoretical} = \frac{M \times I \times t}{ZF}$$

where M, I, t, Z, F, ΔM_{exp}, and ΔM_{theo} are molecular mass of aluminum (26.98 g/mol), the electrical current (A), time of reaction (s), number of electron moles (equal to 3 for aluminum), Faraday's constant (96,487 coulomb/mol), current efficiency (%), experimental Al dosage, and theoretical Al dosage, respectively.

The experimental Al dosage was determined by weighting of electrodes before and after each run, and weight loss of aluminum was calculated. The result of this study showed that the actual consumption of aluminum after 15 min of process (in optimum operation conditions) was 0.36 g in 2 L of wastewater, while the theoretical value was calculated 0.335 g. Therefore, current efficiency was 107%. The excessive consumption of aluminum can be due to chemical hydrolysis of the anode. It can be attributed that during electrocoagulation process using aluminum electrodes, anode and cathode are chemically attacked by hydroxide ions produced at the cathode, according to the following equation [16].

$$2Al + 6H_2O + OH^- \rightarrow 2Al(OH)_4^- + 3H_2$$

4. Conclusion

Electrocoagulation is a very effective and fast way to remove acidic dye from colored wastewater. Treatment of colored wastewater using electrocoagulation process was influenced by current density, initial pH, electrolyte concentration, initial dye concentration, and using aid coagulant. Using the aid coagulant with electrocoagulation has significant impact on improving process efficiency and reducing energy consumption and metal mass and consequently reduces the cost of wastewater treatment. At optimum operating condition (current density of 16 mA/cm^2, electrolyte concentration: 1,000 mg/L, initial pH: 7, polyaluminum chloride: 100 mg/L, time of 15 min), dye removal and COD removal efficiency were 99 and 88%, respectively. The results showed that electrocoagulation can be used as a proper option for the treatment of wastewater containing acidic dye.

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