Electerocoagulation of Blue and Mixed Azo Dyes and Application in Treating Simulated Textile Effluent

Elham Keshmirizadeh* , R.Khosravi

Department of Applied Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran

Abstract

This study investigated the efficiency of electerocoagulation (EC) in removing color from synthetic and simulated textile wastewater. The study on decolorization of mixed dyes is a step toward an effective treatment of textile wastewater. Two representative reactive dye molecules were selected for the synthetic dye wastewater, a blue dye alone and mixed dye (black, blue, red, 1:1:1v/v). The EC technique showed satisfactory color (98 %) and chemical oxygen demand (85%) removal efficiency and reliable performance in treating both individual and mixed dye types. The removal efficiency and energy consumption data showed that, for a given pH and optimum current density:100A/m2, Fe or Al were used in treating the dyes with an initial concentration of 100-1200 mg/L, the energy cost in achieving above 98% color removal was on order of 0.73-1.27kWh/m³ wastewater in all systems, water recovery was 0.97. It was found that the operating parameters used for the synthetic dye wastewater were less effective for treatment of simulated textile wastewater.

Keywords: *Aluminum electrodes, Blue dye, Electerocoagulation, Iron electrodes, Mixed dye, Textile effluents.*

Introduction

Removal of dyes in textile wastewater has attracted a lot of interest because of the growing concern about residual color which is closely associated with toxicity and aesthetics of the discharged effluent [1]. Dyes exhibit a high resistance to microbial degradation; in particular azo dyes are readily converted to hazardous aromatic amines under anoxic conditions [2].Dye compounds are found in high concentrations in the residual waters of paint, paper and textile industries. The textile industry actually represents a range of industries with operations and processes as

*__*Corresponding author:__ Dr. Elham Keshmirizadeh, Assistant Prof., Karaj branch, Islamic Azad University, Karaj, Iran. Email: ekeshmirizadeh@yahoo.com. Cell: 09377807397, Fax: 0261-4418156.*

diverse as its products. It is almost impossible to describe a "typical" textile effluent because of such diversity [3].

There are many processes to remove dyes from colored effluents such as adsorption, precipitation, chemical degradation, photo-degradation, biodegradation, chemical coagulation and electrocoagulation [4,5]. Adsorption and precipitation processes are very time-consuming and costly with low efficiency. Chemical degradation by oxidative agents such as chlorine is the most important and effective methods, but it produces some very toxic products such as organo-chlorine compounds [6]. Photo-oxidation by UV/ H_2O_2 or UV/TiO_2 needs additional chemicals, and therefore causes a secondary pollution. Although biodegradation process is cheaper than other methods, it is less effective because of the toxicity of dyes that has an inhibiting effect on the bacterial development [7]. Conventional wastewater treatment system is inefficient because of the recalcitrant nature of dyes. Existing physical and chemical technologies are expensive, time consuming and produce a large amount of sludge or cause secondary pollution [4].

Treatments of wastewaters containing textile dyes have been studied by electrocoagulation method. The results of these studies show that COD, color, turbidity and dissolved solids at varying operating conditions are considerably removed [5]. In addition, it is clear that a technically efficient process must also be economically feasible with regard to its initial capital and operating costs, and practically applicable to the environmental problems. The economic aspect of the electrocoagulation (EC) process is not investigated well by the researches except a few of them [3]. Electrical energy consumption is a very important economical parameter in EC process like all other electrolytic processes. Treatment by electrocoagulation (EC) has been practiced to the treatment of the variety of dye effluents [8-9]. Compared with traditional flocculation and coagulation, electrocoagulation has, in theory, the advantage of removing small colloidal particles; they have a larger probability of being coagulated because of the electric field that sets them in motion. Addition of excessive amount of coagulants can be avoided, due to their in situ generation by electro-oxidation of a sacrificial anode. Electrocoagulation equipment is simple and easy to operate. Short reaction time and low sludge production are two other advantages of the technique [10-12].The EC technique is potentially considered to be an effective tool for the treatment of textile wastewater with high removal efficiency [5-7]. The main advantages of EC over other conventional techniques such as chemical coagulation and adsorption are in situ delivery of reactive agents, no generation of secondary pollution, and compact equipment [8]. The ability of EC

to carry out dye decolonization has recently achieved very much attention [9-15].

In this study, a wide range of initial blue dye concentrations (10-100) mg/L alone and initial mixed dye concentrations (100, 300, 500, 1000, 1200) mg/L were investigated, whereas most of other studies worked on initial dye concentrations up to 100 and 500 mg/L [16]. Some important operating parameters were optimized for the efficient degradation, analysis of dye removal and the exploitation of the EC for dye removal from dye mixtures. These parameters included electrode type, current density, time of EC, energy consumption, pH, on the process efficiency of the synthetic wastewater. The parameters that were found to be suitable for the EC treatment of the synthetic wastewater were then tested in an EC treatment of simulated textile wastewater. It should be noted that, in this investigation, the influences of various supporting electrolytes were studied to avoid electrode passivity. However, in this research "water recovery" was introduced and calculated in order to show the more economically feasible recycling of treated water.

Experimental

Materials

In our investigation all chemicals were of analytical grade. Two representative dye molecules were selected for the synthetic dye wastewater, a blue reactive dye alone and mixed dye (containing reactive black, reactive blue, reactive red, 1:1:1vol/vol) see Table1.All organic azo dyes, kindly provided by Ghazvin-Textile Processing industry, Ghazvin, Iran.

Methodology

The EC experiments were conducted at room temperature in an undivided electrochemical cell (net volume reactor was 0.7 L), using a batch mode with a sufficient magnetic stirring (200rpm). The cell contained two parallel planar electrodes with an inter-electrode distance of 1.5 cm, using iron or aluminum electrode as anode or cathode (6×6 cm^2) as reported in our previous work [17].The degradation started when the electricity was switched on and the current was set at the desired value. One DC power supply package having an input of 220V and variable output of 0–30 V, with variable current 0–4A, was used. The dye wastewater was synthesized with a certain amount of mixed dye (or blue dye) after pH adjustment (sulfuric acid solution and sodium hydroxide (0.1M)).

Sampling Preparation

The composition of simulated textile wastewater was represented in Table1.In order to standardize the textile wastewater in the runs, the industrial textile wastewater was synthetically prepared based on real process information of pretreatment and dyeing stages.

Measurements and Methods of Analysis

In all experiments[18], the pH was measured

with a Metrohm pH meter (Model No. 827), the conductivity was measured with an Hach/ Lange conductivity meter (APHA 2510-B standard method), chemical oxygen demand (COD) analyses was performed by using closed reflux, colorimetric method (APHA 5220-D), dye concentrations were determined from their absorbance characteristics in the UV–vis range (200–800 nm) with the calibration method from standard methods(method 2120-C), using an UV-vis spectrophotometer (Hach/ Lange (DR/2800)). Upon completion of the process, the test samples were filtered before dye analysis. Samples were taken at given time intervals for analysis.

The calculation of dye removal efficiency (decolorization) after EC process was performed using this formula:

$$\text{Decolorization (\%)} = 100\frac{[ABS_0^M - ABS^M]}{ABS_0^M} \quad (5)$$

Where ABS^M is the average of absorbance values as it is maximum absorbency visible wavelength. ABS_0^M:the value before EC, ABS^M: the value after EC(λ_{max} (black dye):600nm, λ_{max} (red dye):571nm, λ_{max}(blue dye):571nm, λ_{max}(mixed dye):597nm).

Electrical energy consumption (EEC) was determined as follows:

$$\text{EEC(kWh/m}^3 \text{ wastewater)} = VIt/v \quad (6)$$

V: operating voltage (volt), I : operating current(ampere), t (or t_{EC}): time of reaction (hr) and v :volume of wastewater (m³).

Table 1. The composition of simulated textile wastewater[19], and synthetic mixed dye (in this study).

Pollutant	Concentration (simulated textile wastewater)	Concentration (synthetic mixed dye, in this study)
Cottoclarin F(mg/L)	500	
Dextrin(mg/L)	1600	-
Sucrose(mg/L)	640	-
Hydrogen peroxide (35-40%, d=1.133(mL/L)	4	-
Sodium hydroxide(mg/L)	1200	-
Acetic acid(mg/L)	165	-
Reactive dye(mg/L)	1200	1200
Sodium carbonate(mg/L)	700	-
Sodium chloride(mg/L)	5000	-
Ethylene dinitro tetra acetic acid(EDTA)(mg/L)	300	-
Detergent(mg/L)	300	-
Silicon oil(mg/L)	20	-

The current density (CD) was measured according to equation (7):

$$CD = \frac{I(A)}{2S_{electrode}(m^2)} \quad (7)$$

I: current (*A*), S: surface area of the electrode (m^2).

$$\text{Water recovery} = \frac{\textit{volume of product water}(\textit{afterEC})}{\textit{initial volume of wastewater}(\textit{beforEC})} \quad (8)$$

Indeed the clear supernatant is product water or treated water. The optimum operating conditions are described below.

Results and discussion

The EC process was controlled by several operational parameters, such as CD, time of electrolysis, initial pH, initial dye concentration, type of electrolyte, type of electrode and energy consumption. In order to enhance the process performances, the influences of these parameters were studied as follows:

Effect of Current Density on the Blue Dye Removal Efficiency

According to Faraday's law [5] CD determines the coagulant production rate and regulates the rate and size of the bubbles and growth of flocks. A series of EC tests were carried out by solutions containing constant initial dye concentrations with current densities varied from 60 to 120 A/m^2. It is obvious that the dye removal efficiency increases at higher CD. The blue dye removal efficiency versus different CD (for example blue dye alone: 100 mg/L, treatment time: 3min) was evaluated. The optimum CD of 100Am^{-2} was used. The results show some improvement over previous attempts [12]. It should be noted that an increase in current density from 100 to 120 A/m^2 yielded an increase in the efficiency of color removal from 98 to 99%, which was not a significant change. As a result of increasing the CD, the applied potential increased. Thus, it is advisable to limit the CD in order to avoid excessive oxygen evolution like heat generation [5]. Therefore, 100A/m^2 was a reasonable CD in our experiments. In this study, the CD that was found to be suitable for the EC treatment of blue dye was then tested in EC treatment of mixed dye and also simulated textile effluent (see Figure 1).
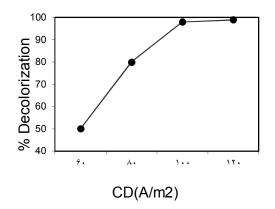

Figure 1.Effect of current density on the blue dye removal efficiency.

Conditions: Black dye concentration: 100 mg/L, pH Initial: 9, Initial conductivity: 2.75 mS/cm, Initial volume of wastewater: 700mL, Electrode:Fe/Al, Electrolyte:NaCl.

Effect of Initial pH on the Blue Dye Removal Efficiency

The kinetic of Fe^{2+} conversion to Fe^{3+} is strongly affected by the pH, the surface charge of the coagulating particle also varies with pH. In general, at lower and higher pH, Fe is increasingly soluble [20].The dependence of EC time on initial pH values in blue dye and mixed dye were investigated over pH range of 3-9. The maximum removal efficiency (depending on concentrations) was 98% in pH 3 and 9 for blue dye, similar effects were reported by Phalakornkule in pH 9.5 [16] and 98% in pH 7 for mixed dye (also 95% in pH:3, 5.5, 9). Even though the typical pH of real textile effluent was high, ranging between 8.5 and 9.6 (see Figure 2).
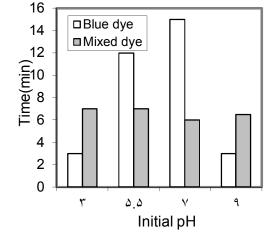

Figure 2. The influence of initial pH on the time of EC for blue and mixed dye.

Conditions: Initial blue dye concentration: 100 mg/L, Dye removal efficiency: 98%. Initial conductivity: 2.75 mS/cm, CD: 100A/m2, Initial volume of wastewater: 700mL, Electrolyte: NaCl.

Effect of Electrode Type on the Blue Dye and Mixed Dye Removal Efficiency

To examine the effect of electrode type in more detail, the anodes were changed between iron, aluminum and combined iron and aluminum.

The detailed conditions of the 3 electrode types as a function of EC time are represented in Table 2. Even though sharp increases of removal efficiencies could be observed with 3 min EC time for Fe/Fe and Fe/Al in blue dye and for mixed dye in 6 min. Table 2 also compares the energy consumption and water recovery for each electrode type. The iron anode required the lowest energy ranging between 0.73-0.78kWh/m³ of wastewater for blue dye and between1.234-1.278kWh/

m^3 of wastewater for mixed dye. A possible explanation is based on the difference in physical characterization of the particles in the treated wastewater. The Fe/Al was ranked over the Fe/ Fe in treating blue dye and mixed dye, because the Fe/Al resulted in better dye removal efficiency and lower consumption of electrical energy.

Table 2. Optimized operational parameters for various electrodes.

Electrode [Anode/Cathod]	Operating time (min)		Energy consumption (kWh/m^3 of wastewater) Eq.(6)		Water recovery (m^3/m^3 of wastewater) Eq. (8)	
	Blue dye	Mixed dye	Blue dye	Mixed dye	Blue dye	Mixed dye
Fe/Al	3	6	0.738	1.234	0.97	0.97
Fe/Fe	3	6.3	0.780	1.278	0.97	0.97
Al/Al	5	10	0.851	1.731	0.97	0.94

Conditions: Initial dye concentration: 100 mg/L, %Decolorization: 98%. Initial conductivity: 2.75 mS/cm, CD: 100A/m^2,Initial volume of wastewater: 700mL, Electrolyte:NaCl.

Effect of Initial Concentration on Mixed Dye Removal Efficiency

Dye solutions with different initial concentrations in the range of 100–1200 mg/L were treated by EC process; however, other studies worked on initial dye concentrations up to 500[9-10].Consequently, optimized operational parameters such as CD, time of reaction and electrical energy consumption (EEC) values are represented based on various initial mixed dye concentrations in Table3. According to the results, at high initial mixed dye concentrations, the dye removal efficiency was near 98% while operating time, voltage and the energy consumption increased, however, some authors [10,15] obtained different results.

Table 3. Optimized operational parameters for various mixed dye and simulated textile wastewater initial concentrations.

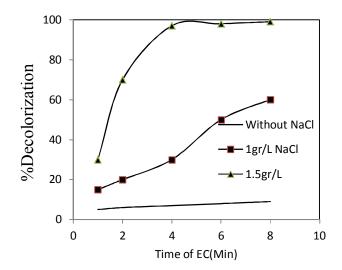| Type of dye in the wastewater	Initial dye concentration (mg/L)	Operating time (min)	Energy consumption (kWh/m^3 of wastewater)	Water recovery (m^3/m^3 of wastewater)
Mixed dye	100	6	1.234	0.97
Mixed dye	300	6	1.728	0.97
Mixed dye	500	6	1.810	0.97
Mixed dye	1000	6	1.892	0.97
Mixed dye	1200	10	3.291	0.95
Simulated textile wastewater	1200	40	13.210	0.64

Conditions**:** Electrode: Fe/Al, Electrolyte: NaCl, ,% Decolorization: 98%. Initial conductivity: 2.75 mS/cm, CD: 100A/m^2,Initial volume of wastewater: 700mL.

Treatment of Synthetic Mixed Dyes and Simulated Textile Wastewater

When reactive blue and reactive red and reactive black were mixed, the synthetic mixed dye turned black. The same set of design parameters effective for treating blue dye individually may also treat the mixed dyes effectively. The set of parameters that were effective for both dyes was further employed to treat the simulated textile wastewater. Table 3 shows that removal of dye from simulated textile wastewater is expected to be more difficult than from synthetic mixed dye wastewater for several reasons. The simulated textile wastewater might contain some components which interfere with the curtailed mechanism. Another possible explanation was that the simulated textile wastewater might contain other dye molecules that could not be removed by the EC process.

The Effect of Electrolyte Dosage and Type of Supporting Electrolyte

In this research, 2 tasks were investigated: (1) access to maximum dye removal efficiency (2) a study on water recovery or treated water reuse. If the conductivity of water recovery is near 2.75mS/cm or less, recycling is more economically feasible. In this study, electrolyte consumption for enhancement of EC was optimized in the range of 2.75mS/cm for low to high concentrations of dye, (Table 3). However, other authors [10, 20] reported a conductivity level of up to 15mS/cm. A series of EC tests were carried out by solutions containing constant initial dye concentrations with electrolyte concentration varied from 0, 1 and 1.5 g/L NaCl. Thus electrolyte consumption in the highest dye concentration (1200 mg/L) was optimized at 1.5 g/L in this study; whereas in previous research values up to 10 g/L were reported (see Figure3).

Figure 3. Variation of dye removal efficiency with time for different NaCl concentration. Condition**s:** Initial dye concentration: 100mg/L, CD: 100A/m^2, Initial volume of wastewater: 700mL.

In order to reduce the solution resistance potential [21], conductivity of the solution should be sufficient. To study the effect of electrolyte type on the removal efficiency of blue dye and mixed dye, theirs removal by EC in the presence of different supporting electrolytes including NaCl, KCl, Na2SO4, K2SO4, MgSO4 and NaNO3was studied. CD of 100 A/m2 and initial conductivity of 2.75 mS/cm were uniformly applied to the experiments. It can be seen from Figure4 that in the presence of NaCl the removal efficiency of blue dye and mixed dye were 98%at the

electrolysis time of 3, 6 min respectively. This is compared with the EC time of7 to 20 min for the same experiments performed in the presence of other electrolytes. The difference could be attributed to the passivity of electrodes. However in the presence of chloride ion, the passivation is curtailed since the adsorbed chloride ion promotes the dissolution of iron [22]. Comparison of EC time revealed that sulfate and nitrate ions have less influence on corrosion of iron than chloride (Figure 4).
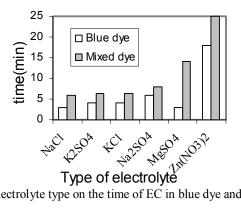

Figure 4. Effectof electrolyte type on the time of EC in blue dye and mixed dye systems.

Conditions: Initial dye concentration: 100mg/L, %Decolorization: 98%, Initial conductivity: 2.75 mS/cm, CD: 100A/m2, Initial volume of wastewater: 700mL.

Conclusions

The setup described in this study is simple in design and operation. Previous studies have shown that suitable parameters for treating single dye by EC can be different. The study on decolorization of mixed dyes is a step toward

an effective treatment of textile wastewater. In this study, the removal efficiency and energy consumption and water recovery data showed that Fe/Al was superior in treating reactive blue dye. For synthetic mixed dye, Fe/Al also gave an effective means of treatment. In addition, the study showed that the influence of initial pH was different for each dye. A set of operating parameters that could be used to treat blue dye only and a mixture of these dyes was: iron anodes, CD:100 A/m² for 3 min EC

time, 0.97 water recovery and EEC: 0.738kWh/ m3 of wastewater. However, removal of dye from simulated textile wastewater was found to be more complicated than from synthetic mixed dye wastewater. Further study will be needed to comprehend the problem in order to increase the reliability performance of the technique. It is clear that a technically efficient process must also be economically feasible (based on energy consumption) with regard to its initial capital and operating costs, and practically applicable to the environmental problems.

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