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Removal of Reactive Blue Dye 19 from Textile Wastewater by Electrocoagulation Using Iron Electrodes.

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ABSTRACT

This work deals with the possibility of using electrocoagulation method for removal of reactive blue 19 dyes from textile industry wastewater. The effect of various operational parameters of the removal efficiency were investigated and optimized. The removal of dye using iron sacrificial anode was affected by the initial pH, the current density, the amount of sodium chloride and initial dye concentration. The removal efficiency reaching 99.6% at optimum operating conditions of pH 11.5, current density of 50mA/cm², electrolysis time of 10mins, 100mg/l initial dye concentration, 3g/l sodium chloride as supporting electrolyte, and 25^oC. Cyclic voltametry and linear polarization have been used to determine the electrochemical characteristics of the treated dye solutions and the process which occurred at the anode surfaces.

Keywords: iron electrode, electrocoagulation, textile wastewater, reactive dye, cyclic voltametry.

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INTRODUCTION

Direct dyes extensively used in dyeing process in Egypt, they have good water solubility and easily hydrolyzed into insoluble forms [6]. The large quantity of wastewater generated by textile industries becomes a dangerous environmental problem. Dye bath effluents, in particular characterized by intense color, high level of chemical oxygen demand (COD), dissolved solids highly fluctuating pH [2- 4]. Furthermore, dye effluent contains chemicals, which are toxic, carcinogenic, mutagenic, or teratogenic in various microbiologic, fish species [5]. Traditional methods of dyeing process wastewater treatment such as biodegradation [7,8] precipitation, adsorption [9,10], membrane filtration [11], photo degradation [12], chemical oxidation [13-15], ozonation [16], chemical coagulation or combination of two or more of the above mentioned methods are reported. Although these methods have been widely used, they have some certain limitation in their application. Moreover, these conventional methods are also usually having inadequate treatment efficiency because of large variability of the composition of textile wastewaters [19, 20]. One of promising methods for treating hard wastewater streams is the electrochemically based processes (electrolysis and electrocoagulation), which have been successfully demonstrated for removing pollutants in various industrial wastewaters [1-3]. Removal mechanisms reported in the electrolysis process generally included oxidation, reduction, decomposition, whereas the mechanisms of electrocoagulation process include coagulation, adsorption, precipitation and flotation [4-6]. Electrocoagulation utilizes iron anode to produce iron hydroxide flocks by reaction at the anode followed by electrolysis.

The electrocoagulation is simple and efficient method for the treatment of many wastewaters. In recent years, many investigations have been specially focused on the use of the electrocoagulation owing to the increase in environmental restrictions on effluent wastewater [7-9]. Electrocoagulation has been applied successfully to treat potable water, food, and protein wastewater [9-12], yeast wastewater [13], urban wastewater [14], restaurant wastewater [8, 15], and tar, sand, and oil shale wastewater [16]. The aim of this work was to investigate the decolorization of representative reactive blue 19 dyes by electrocoagulation process. The effects of several operating conditions such as pH, applied current density, electrolysis time, temperature, supporting electrolyte and its concentration were studied. The remaining dye concentration, decolorization efficiency, weight of dissolved iron, faraday anodic dissolution efficiency and adsorption capacity were investigated. The overall anodic and cathodic process studied by cyclic voltammetry in potentiostatic variant. Also rate of iron anode dissolution (corrosion) during electrocoagulation process was studied using Tafel test

MATERIAL AND EXPERIMENTAL METHODS

The solutions of the reactive blue 19 dyes were prepared via deionized water. All chemicals used were of analytical grade. The electrocoagulation cell consists of iron anodes and D.C. power supply (model GP4303D LG precision Co. Ltd, Korea). Iron electrodes of 2*2 cm were used, they were mechanically polished with different grade emery washed with distilled water and rinsed with acetone, and finally dried in a stream of air. The anode was weighed and

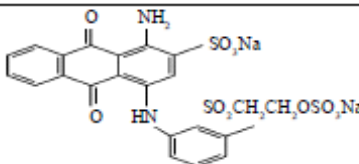
supported vertically in a parallel position midway between the cathodes. The gap distance between each cathode and anode was 2.5cm. The electrocoagulation cell was of 1.25liter capacity and filed with One liter wastewater in each experiment. All experiments were carried out under stirring and both of the voltage and current was measured using digital multimeter (kyoritus model 1008 Japan). The electrocoagulation experiments were carried out at the ambient temperature 25⁰C. at the beginning of the run, the dyestuff solution was feed into the reactor and the pH and conductivity were adjusted to the desired value. The conductivity of the solution was raised by adding the desired amount of the supporting electrolyte and dissolved completely then the pH adjusted to the desired value. The electrocoagulation cell then filed with one liter of the above prepared dyestuff solutions. Stirring is starting and direct current is applied for the required time then the system is switched off. The particulates of colloidal ferric oxyhydroxides gave yellow brown color into the solution after electrocoagulation and electrolytic flotation. The sludge was separated by filtration with Whatman filter paper (pore size 11µm). Then the liquid was subjected to analysis, and the dissolved iron weight was evaluated from the change in weights of the anode before and after the electrocoagulation process. Then calculate anodic dissolution percentage from equation

$$\text{Anodic diss. Eff.} = \frac{\text{wt. diss.}}{l} \times 100 / (\text{amp.}) \times t(\text{sec}) \times \text{ECE}$$

Where ECE electrochemical equivalent of iron

Table 1 shows the main characteristics of reactive blue 19 dyes.

Table 1: Main characteristics of RB19 dye

Chemical structure	
C.I generic name	C.I.Reactive Blue 19
Synonym	Remazol Brilliant Blue R
Molecular Formula	C ₂₂ H ₁₆ O ₁₁ N ₂ S ₃ Na ₂
Molecular Weight	626.5g/mol
λ_{max}	592nm
*from Dystar. CO, Germany	

Analytical methods the measure of the remaining:

The measure of the remaining dye R blue 19 concentrations (mg/l) was the analytical parameter used to evaluate the removal efficiency, the phenomenon of the variation of the color of the dyestuff solution, as result of electrocoagulation process, from the basis of colormetric analysis for determination of the remaining dye concentration [17]. The dye concentration was indicated by an absorbance value measured at maximum wavelength 592nm by a UV-visible spectrophotometer. The color removal efficiency was determined according to the following equation

$$D_{\text{eff. \%}} = (1 - (C/C_0)) \times 100$$

Where, ($D_{\text{eff. \%}}$) is the dye decolorization efficiency, solution dye concentration, and C_0 is the standard solution dye concentration.

The optimum operating conditions for the electrocatalytic degradation processes:

Several parameters were studied to investigate the optimum conditions for the degradation of synthetic textile wastewater (which prepared from R blue 19dye). The studied operating conditions were supporting electrolyte concentration which affecting solution conductivity, effect of pH, effect of applied current density, effect of electrolysis time, effect of initial dye dose and effect of temperature.

Cyclic voltammetry and electrochemical characterization:

Specimens used in the electrochemical measurements were machined from iron rod. The shape of the specimen was cylindrical, x cm long and y in diameter with a central cylindrical hole to fit on the stainless steel shaft, which rotate the specimen. Above the specimen the shaft was fixed in a long Teflon cylinder and below the specimen Teflon cap was screwed on to hold the specimen tightly. The diameter of the specimen was exactly the same as that of the upper Teflon coated shaft or lower Teflon cap. Thus the specimen became a part of the long cylinder exposing the peripheral surface of the specimen to the test solution. The specimens were polished on 600 grit silicon carbide paper, then rinsed with distilled water and finally dried in an air stream. The corrosive media were 3 g/l NaCl, the pH of the solution was adjusted to 11.5. Saturated calomel electrode and platinum electrode were used as references and counter electrodes, respectively. After 1 hour, when a constant potential was attained, ac and dc measurements were carried out. The readings were taken at rotation speed 100rpm.

RESULTS AND DISCUSSION

Effect of pH on dye removal:

Fig. 1a describes the effect of solution pH on the dye removal efficiency and faraday efficiency of iron dissolution during electrocoagulation process, while Fig. 1 b represents the relation between the remaining dye concentration, the amount of the dissolved iron and the adsorption capacity of the removed dye on the dissolved iron surfaces. The results were obtained at operating conditions as follows: 100 mg/l initial dye concentration, 3g/l NaCl as a supporting electrolyte, 50 mA/cm², 25°C and electrolysis time 10 min. The results show that the remaining dye concentration decreases as the pH value reaches to 11.5 and gives the minimum value equal to 0.33 mg/l (i.e. removal% = 99.67) . Also, as pH increases to 11.5 values the dissolved iron weight during the electrocoagulation process increases due to the formation of iron hydroxide species which absorb the dye molecules and causes the increase of the removal efficiency. Moreover, Fig. 1 (b) represents that using of the iron electrode as anode in the electrolytic cell, the optimum anodic dissolution of iron and adsorption capacity is acceptable at

pH 11.5. The effect of pH on the process performance is explained as follows: the dominant iron species are different according to the solution pH; at basic pH, dye removal efficiency is increased as concentration of OH⁻ ion increases which help in formation of different iron hydroxide complexes [18, 19, and 20].

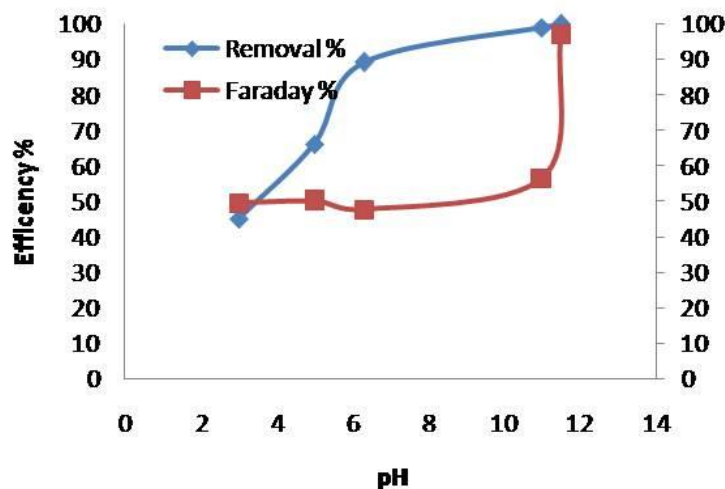


Fig. 1 a

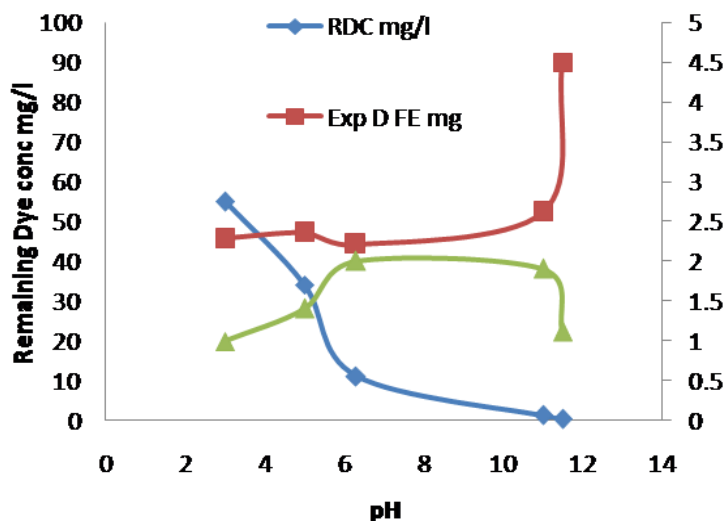


Fig.1b

Fig. 1(a, b) Effect of pH on R Blue 19 removal during Electrocoagulation process.

Effect of Current Density:

The current density is the most important parameter in all electrochemical processes. The current density determines the amount of Fe³⁺ ions released from the electrodes. Fig.2a and Fig.2b show the effect of current density at 25, 50, 100 and 150mA/cm² on remaining dye concentration, the weight of dissolved iron, faraday anodic dissolution % and the adsorption capacity of dye over dissolved iron. The operating conditions as mentioned before were fixed at

100 mg/l initial dye concentration, 3g/l NaCl, 25°C and pH 11.5. The results show that the optimum current density should be constant at 50 mA/cm² which gives minimum remaining dye concentration 0.33 mg/l with high removal efficiency value reached to 99.67%.

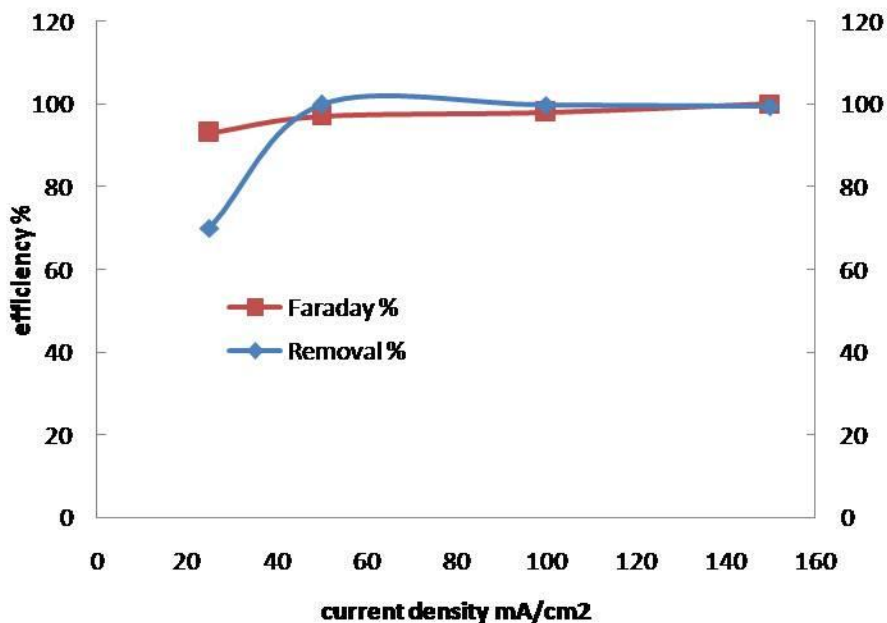


Fig.2a

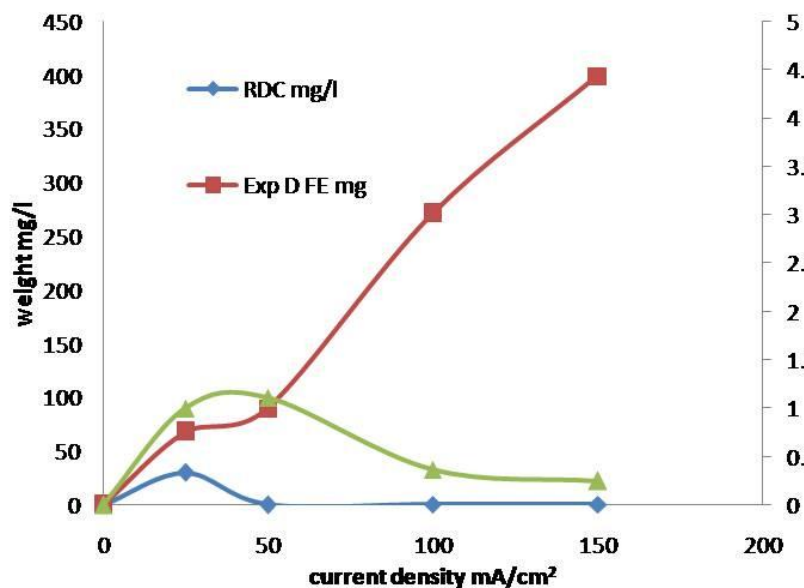


Fig.2b

Fig. 2 (a, b) Effect of current density on R Blue 19 removal during Electrocoagulation process.

Effect of electrolysis time:

Fig. 3(a) and Fig. 3(b) represent the effect of time of electrolysis on remaining dye concentration, the weight of dissolved iron, faraday anodic dissolution %, dye removal % and the adsorption capacity of dye over iron electrode. The operating conditions were constant as mentioned above and current density was 50 mA/cm². From these results; it is clear that as the electrolysis time increases the remaining dye concentration decreases and then removal efficiency of dye increased. This is attributed to during electrolysis, anodic dissolution leads to the release of coagulating species. The dye removal efficiency depends directly on the concentration of metal ions released from the anode surface. When the electrolysis time is increased, the concentration of metal ions and their hydroxide flocs increased [21]. At 20 min. maximum removal efficiency reached to 99.67% after that it slightly decreased.

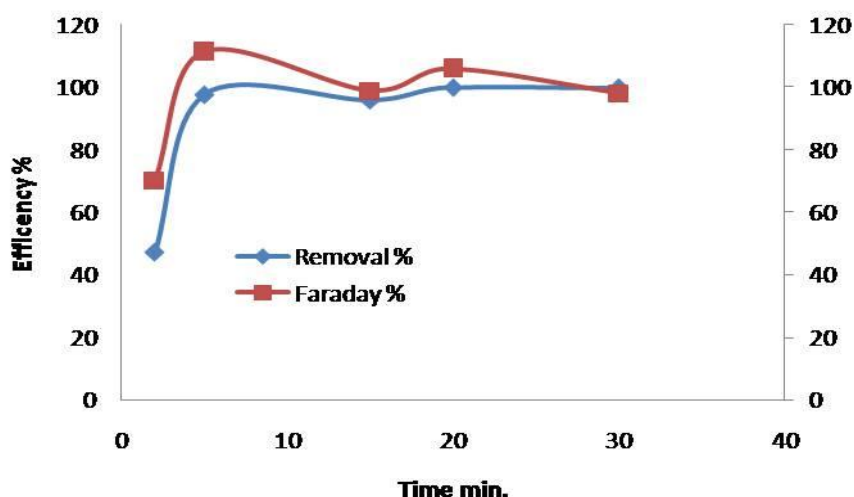


Fig.3a

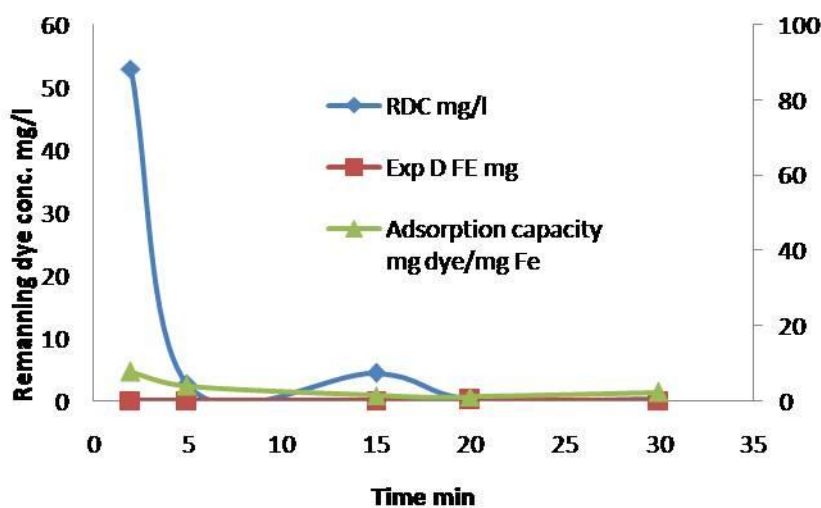


Fig.3b

Fig. 3(a , b) Effect of time of electrolysis on R Blue 19 removals during electrocoagulation process.

Effect of initial dye concentration:

To determine influence of initial dye concentration on remaining dye concentration, weight of dissolved iron, faraday anodic dissolution % and the adsorption capacity of dye over iron electrode during electrocoagulation, three dye solutions with different initial dye concentrations (50, 100 and 200 mg/L) were treated. Fig. 4a and 4b describe this effect at operating conditions (3g/l NaCl, C.D 50 mA/cm², pH 11.5, 25°C, electrolysis time 20 min.). The results indicate that at 100 mg/l dye concentration, the remaining dye concentration reached to the minimum value 0.33 mg/l with removal% equal to 99.67, also the dissolved iron electrode was 0.0826 mg at 100 mg/l while it decreased by increasing dye concentration to reach to 0.0427 mg. One of the most important pathways of dye removal by electrocoagulation is adsorption of dye molecules on metallic hydroxide flocs. According to Faraday’s law, a constant amount of Fe³⁺ released to the solution at same current, voltage, and time for all dye concentration. Thus same amount flocs would be produced in the solution. The adsorption capacity of flocs is limited and specific amount of flocs is able to absorb specific amount of dye molecules. So, with increasing of dye concentration, amount of produced flocs is insufficient to absorb all dye molecules, therefore the dye removal decreased (22).

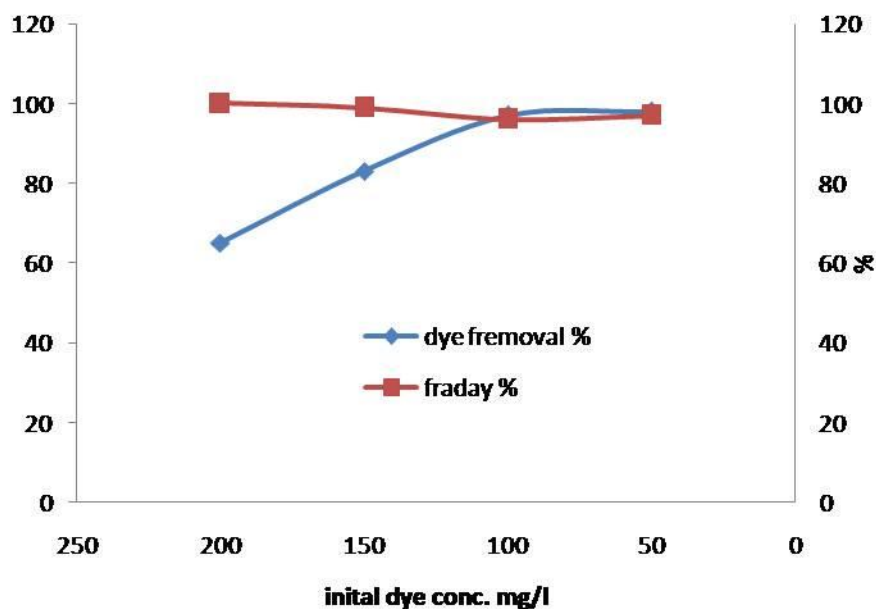


Fig. 4a

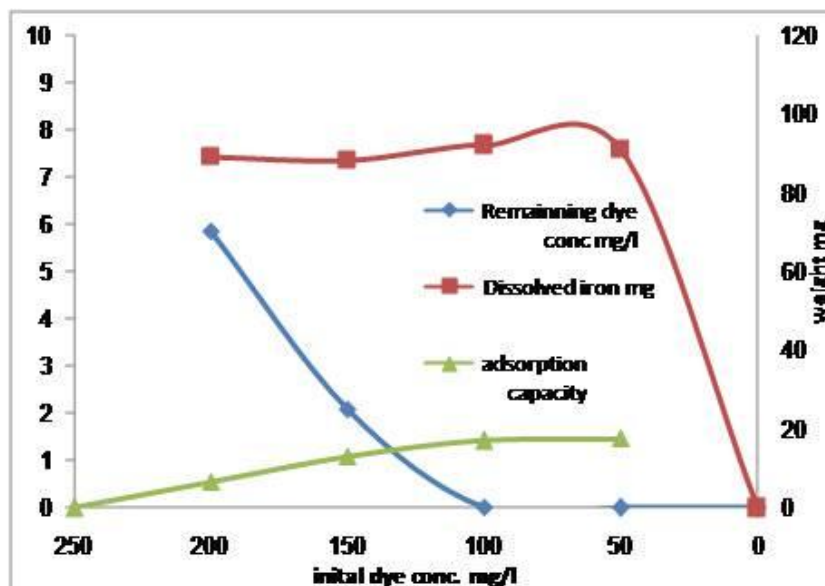


Fig. 4b

Fig. 4 (a,b) effect of initial dye concentration on R Blue 19 removals during electrocoagulation process.

Effect of supporting electrolyte concentration:

Fig. 5a and 5b show the effect of supporting electrolyte concentration NaCl on remaining dye concentration, weight of dissolved iron, faraday anodic dissolution % and the adsorption capacity with 20 min. time of electrolysis keeping the pH 11.5, current density at 50 mA/cm² and 100 mg/l initial dye concentration. It can be seen that in the presence of NaCl, the removal efficiency was increased (remaining dye conc. = 0.289 mg/l) with a subsequent decrease in the applied voltage. The results show that, as the supporting electrolyte concentration increased, the remaining dye concentration and the dissolved iron weight increased due to the increment of the electrical conductivity reaching the maximum value at 5g/l NaCl. However, with the increase in NaCl concentration > 5 g/l the removal efficiency decreased (remaining dye concentration reached to 1.34 mg/l). This behavior may be explained as at constant voltage with increasing of electrolyte concentration, conductivity of dye solution increases and resistance decreases, so the current passed increases and the produced amount of metallic hydroxide also increases (22). So, increase in pH value may be occurred and iron may precipitate in the oxide form.

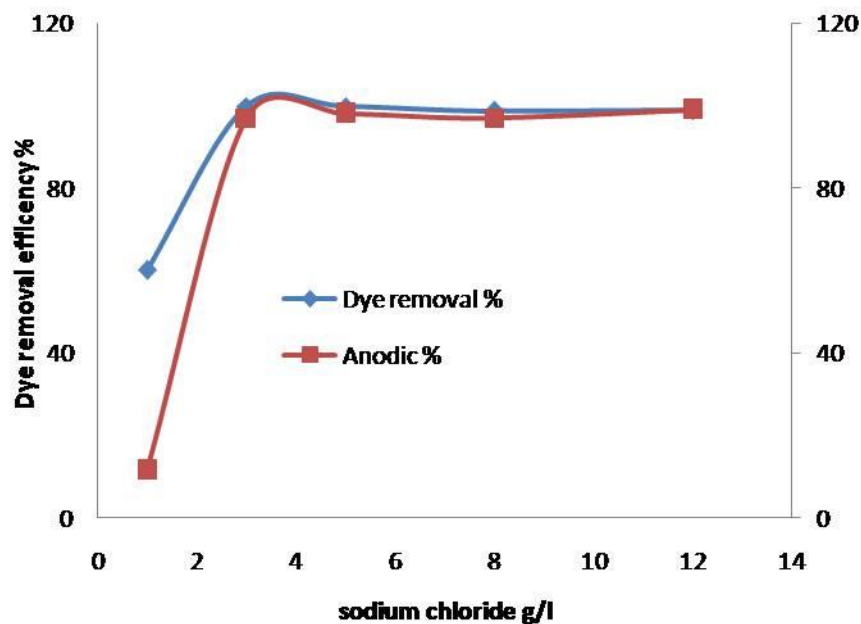


Fig. 5 a

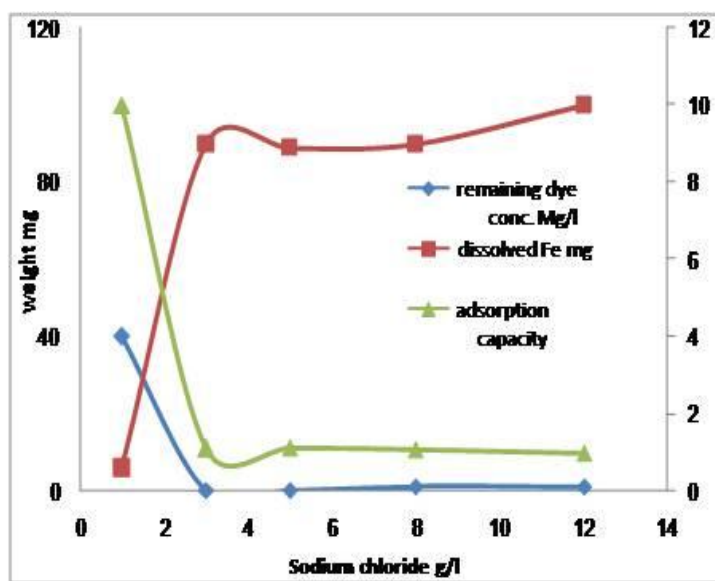


Fig. 5 b

Fig. 5 (a, b) effect of supporting electrolyte on R Blue 19 removals during electrocoagulation process.

Effect of Temperature:

Fig. 6 represents the effect of temperature. The working conditions are fixed at (100 mg/l initial dye concentration, 3g/l NaCl, 50 mA/cm² and pH 11.5). These results indicate that increasing temperature has a negative effect on removal efficiency % of dye, where at 25 °C remaining dye concentration reached to 0.33 mg/l (i.e. Dye removal% = 99.67) while at higher temperature value (50°C) the remaining dye concentration was 38.8 mg/l and removal%

dropped to 61.2. However, it should be noted that the operation of electrocoagulation process at higher temperature significantly reduced electrical energy consumption and fluid conductivity increases (23). So, the production of hydroxide species increases rapidly then enhances pH value. The increase in pH may be affecting on iron species to be in the oxide form and did not exist in the hydroxide form which is the coagulant species that should remove the dye.

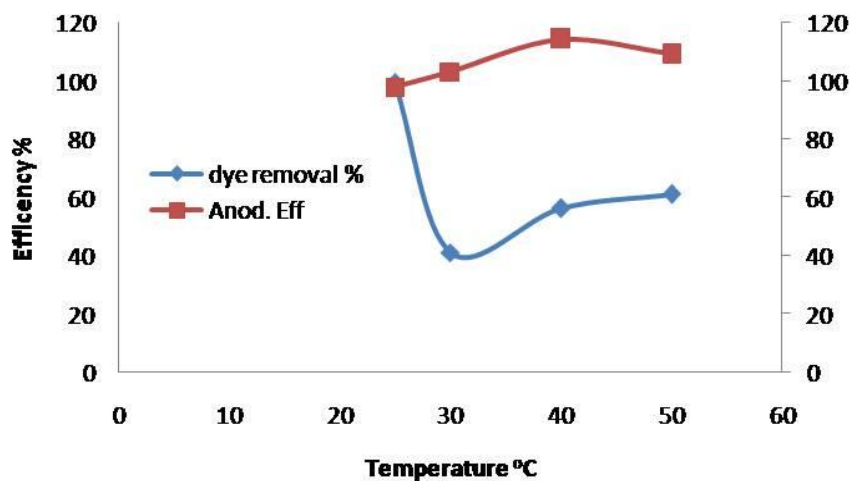


Fig.6a

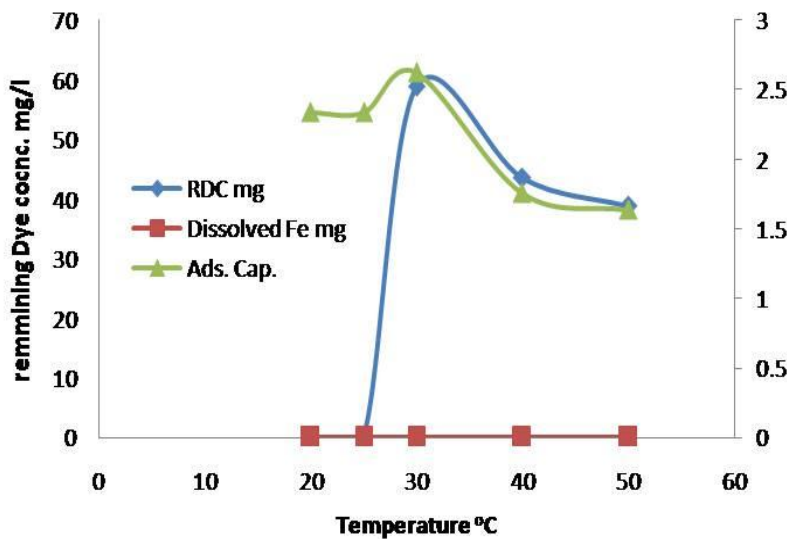


Fig.6b

Fig. 6 (a ,b) effect of temperature on removal of dye R blue 19 during electrocoagulation process.

Potentiostatic polarization data

Cyclic voltammetry

To determine the electrochemical characteristics of the treated dye solutions and the processes, which occurred at the electrodes, a series of experiments were carried out using cyclic voltammetry. The potential scan used for the study was -0.2 to -1.7 V. The dye solution showed two anodic peaks at -1 V, -0.4 V correspond to the electrochemical oxidation of the dye while the cathodic peaks were recorded at -0.5 V, -0.8 V.

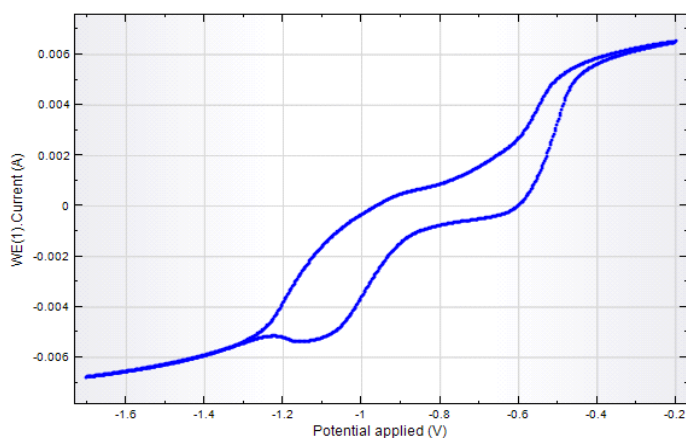


Fig. 7 Cyclic voltammograms of R blue 19 dye at scan rate $10 \text{ mV}\cdot\text{sec}^{-1}$ versus dye concentration of 100 mg/L and supporting electrolyte concentration of 3 g/l

Cyclic voltammograms generated by cyclic voltammetry test of the electrocoagulation of R Blue 19 dye wastewater using iron electrode at the optimum treatment conditions obtained is presented in Fig.7. It was found that during electro-coagulation treatment, ferrous/ferric redox couple was generated. However, its concentration (or peak area) borne no linear correlation with the applied current. This indirectly explained the removal rate variations of electrical conductivity with the applied current. Due to the existence of activated ferrous/ferric redox couple, in addition to the redox reactions at the electrodes, the flocculation effect was thus enhanced and led to greater removal of dye concentration.

R. blue 19 linear polarization

Tafel S.Rate 1 mV.sec-1, range 250 to -250 mV around the OC P (700 mV)

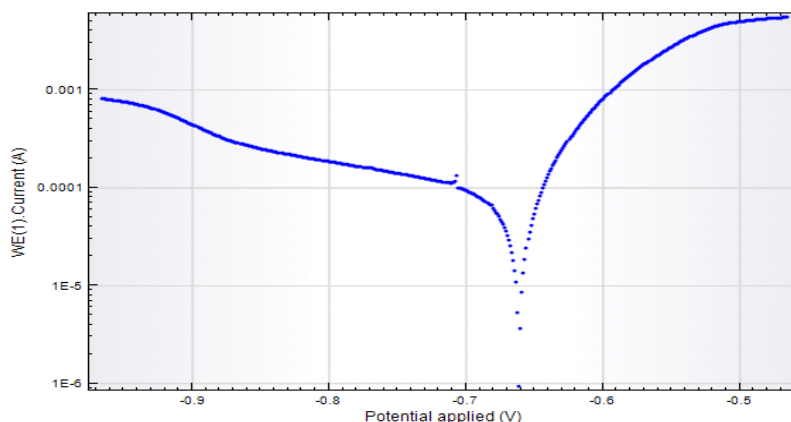


Fig. 8 linear polarization of R.blue 19 linear polarization

Corrosion rate was 1.1942mm/year at corrosion current of 0.0001277A and corrosion potential (calculated -0.6657V and observed -0.6611V). It was found that at the working treatment current (50mA/cm²) the anode corrosion rate will be 581mm/year (i.e. 0.001105mm/min). For the Tafel curve it was found that both the anodic polarization curve and cathodic polarization curve obeys Tafel equation. At high pH the concentration of hydroxyl ions will be high, which support the formation of active surface ferric hydroxide instead of ferric oxide, where at higher current densities the formation of inactive ferric oxide will be present. It is well known that ferric hydroxide is more active than ferric oxide in dye adsorption. So from the above mentioned cyclic voltametry curve and Tafel curve the removal of R blue 19 using electrocoagulation via iron anodes at the selected optimum conditions could be described as follows:

At high over potential, positively and negatively charged electrodes in the electrolytic cells produced the necessary electrical field for the induction of dipole coupling. This establishment of electric field was followed by iron salvation process which could be described at the following steps.

Coupling of pollutant particles

Under suitable field strengths, pollutant particles in wastewater are influenced by the external field induced internal realignment of electrical charges and formation of dipoles that shall help subsequent flocs formation.

Aggregation of pollutant particles

In the electrical field, the polarized particles will see the positive charged end of particle A approached by the negative charged end of particle B. The attractive effect of the different

polarity might cause them to collide and stick together forming a new particle of larger size. The new particle may undergo the same process again and again and gradually aggregate to a much larger size. Such effect is termed self-aggregation. Parts of dissolved and colloidal particles may thus precipitate out as SS (suspended solids).

Formation of micro-flocs

Polarized pollutant particles in the aeration tank will collide with the activated ferrous/ferric redox couples causing flocculation to occur. Micro-flocs thus formed may grow persistently. During the growth process the flocs will interact with the entrained air in the wastewater or the gases generated by electrolysis (oxygen and hydrogen) and form sponge-like flocs.

Formation of macro-flocs with flocculent addition

The micro-flocs entraining minute air-bubbles will mutually aggregate and form macro-flocs upon the addition of polymer flocculent. Macro-flocs will precipitate in short period of time.

CONCLUSION

Electrocoagulation has been applied successfully to investigate the removal of reactive blue 19 dyes from its solutions using iron electrode as anode and cathode. The optimum operating conditions for the effective removal were: pH 11.5, applied current density of 50 mA/cm², At electrolysis time of 20 min., 100 mg/l dye concentration, supporting electrolyte concentration of 5g/l NaCl and room temperature. The removal efficiency at these optimum operating conditions was 99.6%. With respect to cyclic voltamgrams and Tafel linear polarization carried out during Electrocoagulation of R blue 19 dye it was found that, ferrous/ferric redox couple was generated in addition to the redox reactions at the electrodes, the flocculation effect was thus enhanced and led to greater removal of dye concentration.

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