RECLAMATION AND REUSE OF TEXTILE DYEHOUSE WASTEWATER BY ELCTROCOAGULATION PROCESS

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ABSTRACT

The present study investigates the removal of the textile dyehouse wastewater [azo dye para red(reactive dye)and M-5R200%(disperse oranges dye)] by Electrocaogulation process. The effect of nature of the anode, current density, initial pH, rate of stirring and concentration of dyes on the removal efficiency were tested.

The experimental results showed that the color of dyes in the aqueous solution was effectively removed when aluminum was used as anodes and the current density 25mA/cm^2 , initial pH (3-9),stirring rate 200rpm, and the concentration of dyes was less than 100mg/l. When the concentration of reactive dye exceeded 300mg/l iron was a more suitable anode than aluminum.

For the electrocaogulation of disperse dye in aqueous solution aluminum as anode was more suitable than iron when the concentration exceeded 300mg/l. The removal efficiency of reactive dye was increased to 90% when using iron as anode and the removal efficiency of disperse dye 96% when aluminum was used as anode at different running time (10-30) minute.

الخلاصة

يقدم هذا العمل مساهمة في تطوير تقنيات متقدمة واقتصادية لمعالجة فضلات المياه . حيث تم دراسة معالجة فضلات مياه مصنع نسيج ، باستخدام الطريقة الكهروكيميائية لإزالة اللون وباستخدام أقطاب الألمنيوم وحديد حيث تم بحث عملية التخثير الكهربائي ودراسة تأثير نوع القطب، كثافة التيار، الدالة الحامضية، معدل الخلط، وتركيز الملوث على كفاءة الإزالة.

وقد وجد أن أفضل كفاءة لإزالة الملوث عند استخدام الألمنيوم كقطب انود تكون عند كثافة تيار 25 مليامبير/سم^2 وقيمة الدالة الحامضية 3-9 ومعدل خلط 200 دورة بالدقيقة وتركيز ملوث(اللون) اقل من 100 ملغرام/لتر وعند زيادة تركيز الملوث عن 300 ملغرام/لتر يكون الحديد مناسب أكثر كقطب من الألمنيوم للون متفاعل كفاءة إزالة 90% ويكون الألمنيوم مناسب أكثر كقطب من الحديد للون متشتت كفاءة إزالة 96% بزمن تشغيل يتراوح بين (10-30) دقيقة .

INTRODUCTION

Increasingly stringent effluent discharge permit limitations have been put into effect(4). The textile industry generally has difficulty in meeting wastewater discharge limits, particularly with regard to dissolved solids, ionic salts, pH, COD, colour and sometimes heavy metals. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals and require proper treatment before being released into the environment.

The problem of color in textile dyehouse effluent and the possible problems associated with the discharge of dyes and dye degradation products are of concern. The methods for dealing this kind of wastewater are as shown in table1

Table1, Possible treatments for cotton textile wastes and their associated advantages and disadvantages

Processes	Advantages	Disadvantages	References
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes	Pala and Tokat,2002; Ledakowicz et al.,2001
Coagulation-flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Gachr et al.1994.
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Arslan et al.,2000
Ozone treatment	Good decolorization	No reduction of the COD	Adams et al.,1995;Scott and Ollis,1995.
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge	Lin and Peng,1994;Lin and Chen,1997.
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Ghayeni et al.,1988;
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentration	------	Erswell etal.,1998;Xu et al.,1999
Ultrafiltration-microfiltration	Low pressure	Insufficient quality of the treated wastewater	Watters et al.,1991;Rott and Ranieri,2001

Electro-coagulation has been successfully used to treat textile industrial wastewater. The goal is to form flocs of metal hydroxide within the effluent to be cleaned by electro-dissolution of soluble anodes. Three main processes occur during electro-coagulation; electrolytic reactions at the electrodes; formation of coagulants in the aqueous phase and adsorption of soluble or colloidal pollutants on coagulants; and removal by sedimentation and floatation. The characteristic of electrocoagulation are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemicals and decreased amount of sludge. Therefore electrocoagulation has been widely used to treat waters containing food and protein wastes, oil wastes, synthetic detergent effluents, mine wastes, and heavy metal-containing solutions(13).

Electrocoagulation is complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into wastewater stream(13) . Principle of EC is catins generated by dissolution of sacrificial anodes induce flocculation of the dispersed pollutants contained by Zeta potential reduction system(13).

Electrocoagulation can also be used to remove phosphate, for defluoridation of water, and treat portables water, and textile waters. A direct anodic process or an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone,…etc . usually destroys the organic and toxic pollutants present in wastewater such as dyes and phenols.

Electrocoagulation is the distinct economical and environmental choice for meeting water treatment discharge standards and compliance requirement eliminating discharge fees and fines, harvesting resource, and significantly reducing water replacement costs, generally recover capital and operating costs(13).

In this paper the electrocoagulation of azo dye para red(reactive dye) and M-5R200%(disperse oranges dye) in aqueous solutions with aluminum and iron as anodes is described.

Material And Methods

Materials

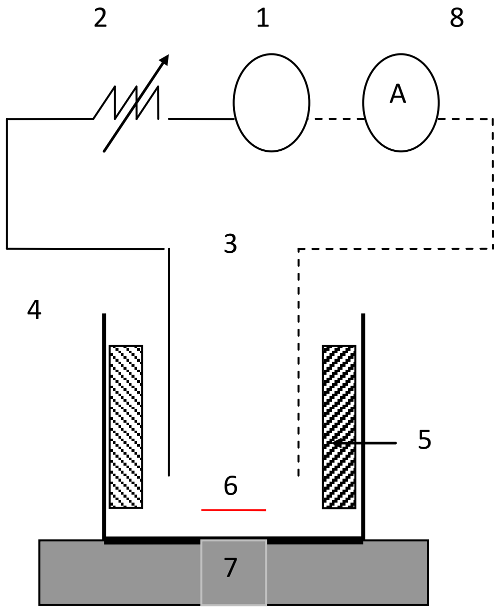
The wastewater sample used was collected after a bio-filter treatment from a textile dyehouse in Tripoli . It looked red and the composition of the sample after analysis presented ADMI color unit 850, COD=175mg/l, Turbidity=18NTU, TSS=269mg/l, pH=7.2.

A aluminum and iron(6*4)cm^2 plate was used as an anode while stainless steel of the same dimension served as a cathode in this system.

Sample color was analyzed by UV-Spectrophotometer(Hitachi, Japan), Solution pH values were detected by a pH meter(Thermo orion model 420A+). The turbidity was measure by using HACH DR14000(HACH Method 10047). To measure TSS, the wasrewater sample were filtered through a standard GF/F glass fiber filter. The residue retained on the filter was dried in an oven at 105±2 C until the weight of the filter remains unchanged. The increase in weight of the filter represents the total suspended solids(APHA Method 2540d).

Methods

The electrocoagulation set-up shown in fig.1 was composed mainly of aluminum or iron and stainless steel electrodes, a DC power source(Hampden, USA), a rheostat(Engield-Middlesex,U.K.) to keep the current invariant, and a 1.5 liter capacity test beaker used as a reactor. Two Pyrex glass strips (1*0.5*15) cm attached to the inside of the glass beaker the distance between them 20cm were used as baffles to create turbulence and facilitate proper mixing of the sample using a magnetic bar stirrer. Each electrode had an active surface area 48cm^2 and a spacing of 2cm between electrodes. The electrodes are inserted in the test beaker. An ammeter was used to measure the current and electrical switch was used to change the polarity of electrodes in order to reduce the passivation phenomenon that usually occur during the process and impedes the Redox reactions.



1:D.C. Power Supply

2: Variable Resistance

3: Stainless Steel, Aluminum and Iron Electrodes

4: Glass Beaker

5: Baffles

6: Magnetic Bar Stirrer

7: Magnetic Stirrer Controller

Fig. 1 (A): Schematic Diagram of Experimental Setup.

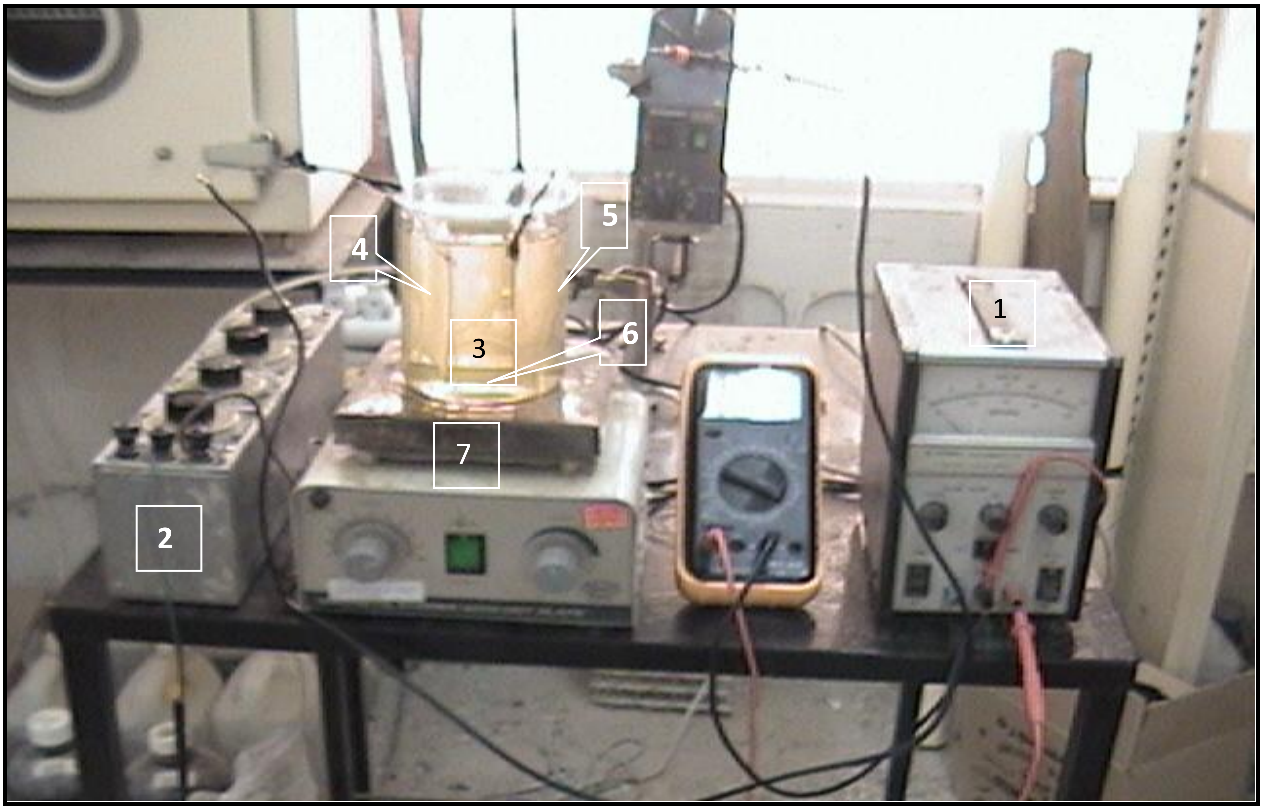


Fig. 1 (B): Photograph of Experimental Setup.

The electrocoagulation current density from 15to40mA/cm2 of dye-containing aqueous solution was carried out in a beaker. At the beginning of a run, the desired concentration of dye in the sample was fed into the reactor, and the pH was adjusted to desired value. The reaction was timed starting when the DC power supply was switched on. Samples were periodically taken ($5cm^3$, 10min.)from the reactor used pipette.

The precipitate in the sample was centrifuged at 700rpm for 10min and the filtrate was obtained. Filtrate(1ml) was added into buffer solution(pH 7, 4ml) and the residual concentration of reactive dye and disperse oranges dye were determined according to optical adsorption at 400 and 500 nm, respectively.

Results and discussion

Aluminum as Anode

Effect of current density on the electrocoagulation of dyes

Figure (2) shown that the increase in current density from 15 to 40mA/cm^2 yields an increase in the removal efficiency of reactive dye and disperse dye from 21 to 83%, from 30-80% respectively, because when the current density increase, the efficiency of aluminum production on the anode and cathode increases. Therefore there is an increase in floc production in the solution and hence an improvement in the removal efficiency. For solution with a dye concentration of 100 mg/l, the optimum current density was 25mA/cm^2 where the maximum removal efficiency 88%, 86% for reactive and disperse dyes respectively. The decay in the anode 0.0437 gm/cm^2.min .

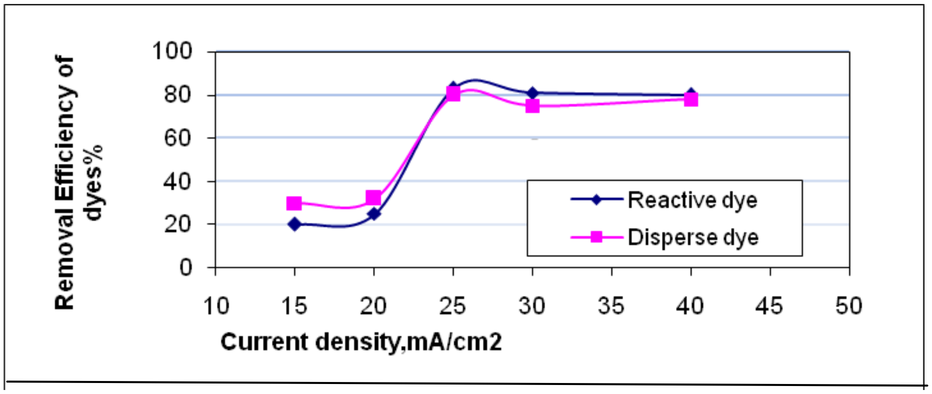


Fig.2.Effect of current density on the removal efficiency of dyes, conc.of dyes(100mg/l), using aluminum as anode

Effect of Stirring on the electrocoagulation of reactive dye

Figure(3) shown that the effect of stirring rate on the electrocoagulation of reactive dye, when the stirring rate increased from 100 to 200 rpm, the removal efficiency of reactive dye increased from 45 to 60% when the electrocoagulation period was 10min. Further increased of stirring rate to 500rpm, decreased the removal efficiency to 30%.The effect of stirring rate on electrocoagulation of reactive dye increased when the duration of electrolysis increased. In the initial state of coagulation, rapid mixing of dye and coagulant species was required. After that slowly mixing was needed for the chemical precipitate to grow large enough for removal.[10] Therefore increased stirring rate resulted in decreased coagulation/removal efficiency of reactive dye when reaction time exceeded 30min. The optimal rate of stirring of decolorization of reactive dye with aluminum as anode was 200rpm.

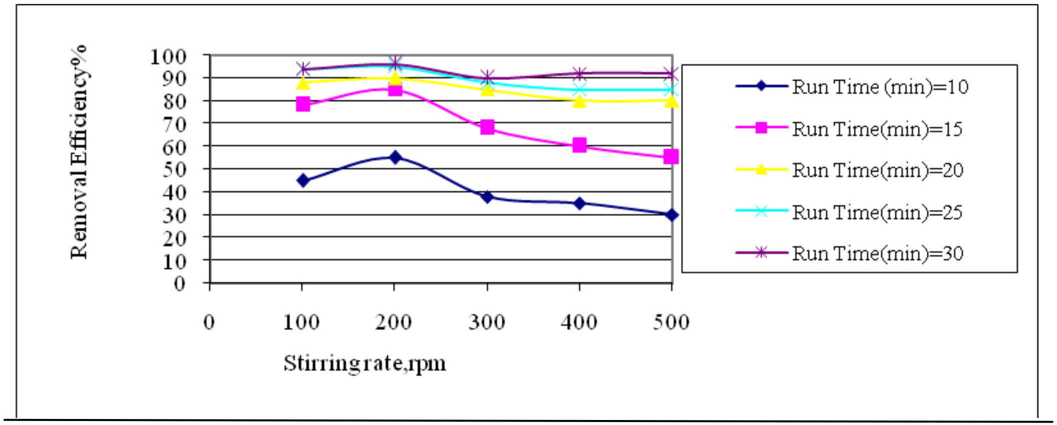
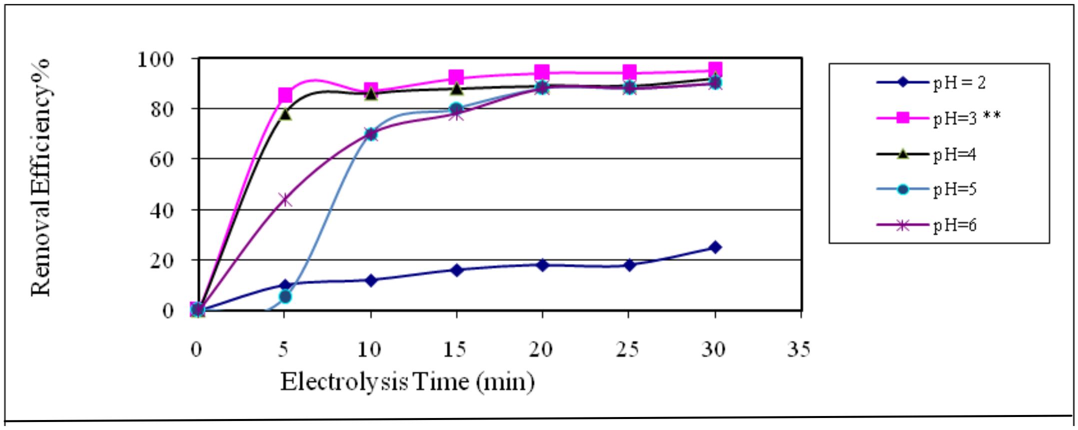


Fig.3, Effect of stirring rate on the removal efficiency of reactive dye using aluminum as anode

Effect of initial pH on the electrocoagulation of reactive dye

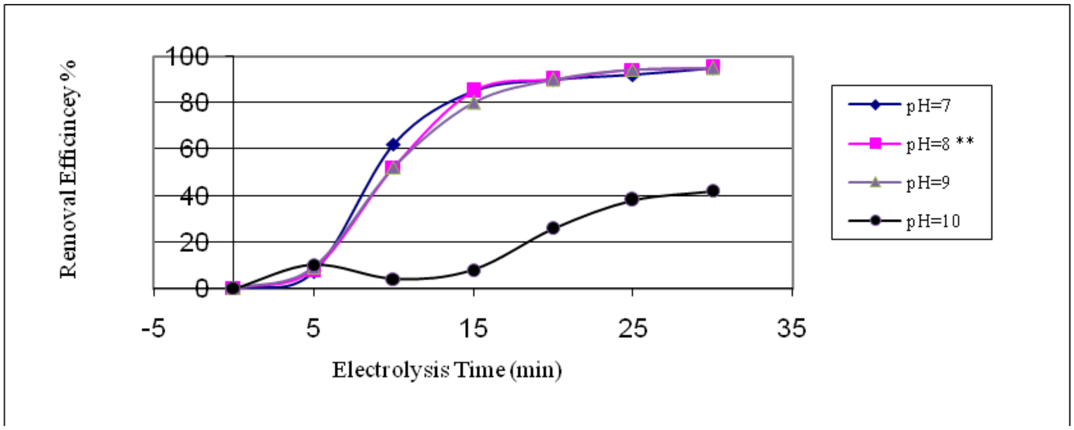
Figure(4) show that the decolourization of reactive dye was significantly affected by the initial pH under acidic conditions. The removal efficiency increased to 28% over thirty minutes with initial pH value 2. In contrast, the removal efficiency was increased to 90% when the initial pH exceeded 3. In this case (using aluminum as Anode), the dominant species are cationic monomers such as Al^{+3} and $Al(OH)^{-}{}_{2}$ when allow initial pH is applied. The main mechanism for the coagulation of dyes is double-layer compression. In this case, coagulant (Al^{+3}) at a high concentration is needed for effective removal of dyes in the aqueous solution. Hence the coagulation efficiency to removal reactive dye at initial pH 2 was small within 30 min. When the pH in the range 3-9, polymeric species (such as $Al_{13}O_4(OH)^{+7}{}_{24}$) and precipitate $Al(OH)_3$ (s) were formed. The dyes were effectively coagulated with the polymeric species and precipitated by the mechanisms of adsorption, charge neutralization and enmeshment. Therefore, the removal efficiency at the initial pH 2 was lower than that when the initial pH exceeded 3 in acidic solution.



**** THE BEST CASE**

Fig.4.Effect of electrolysis time on the removal efficiency of reactive dye in acidic solution using aluminum as anode

When the initial pH was less than 9 in the alkaline region and the electrolysis period was 15 min., the removal efficiency of reactive dye effectively increased to 90% fig.5. The removal efficiency was 42% when the initial pH was increased to 10. As described above, the coagulation efficiency was promoted by the enmeshment of reactive dye with $Al(OH)_3(s)$ in the neutral solution. When the initial pH increased to 10, the amount of $Al(OH)_3(s)$ decreased and concentration of monomeric anion $Al(OH)^{-}{}_{4}$ increased. The efficiency of electrocoagulation of reactive dye then decreased with initial pH large than 10.



**** THE BEST CASE**

Fig.5.Effect of electrolysis time on the removal efficiency of reactive dye in alkline solution using aluminum as anode

Effect of initial pH on the electrocoagulation of dispresve dye

Figure(6) shown that the decolourization of M-5R200%(disperse oranges dye) was significantly affected by the initial pH under acidic conditions. Increasing the initial pH from 2 to 3 and keeping the electrolysis period at 15min resulted in increasing removal efficiency in the aqueous solution from 15-95%. Upon further increase of the initial pH to 10 the removal efficiency remained constant. The final solution pH increased from 2.5 to 8.5 and remained constant when the initial pH was increased from 2 to 10. These results revealed that the pH of electrocoagulation of disperse dye with aluminum as anode was in the range 2 to 2.5 with initial pH 2. The absence of adsorption, charge neutralization and enmeshment in the electrocoagulation of disperse dye resulted in the small coagulation efficiency at the initial pH 2. With aluminum as anode, the disperse dye M-5R200% was more readily removed and has a greater operational initial pH than that of the reactive dye.

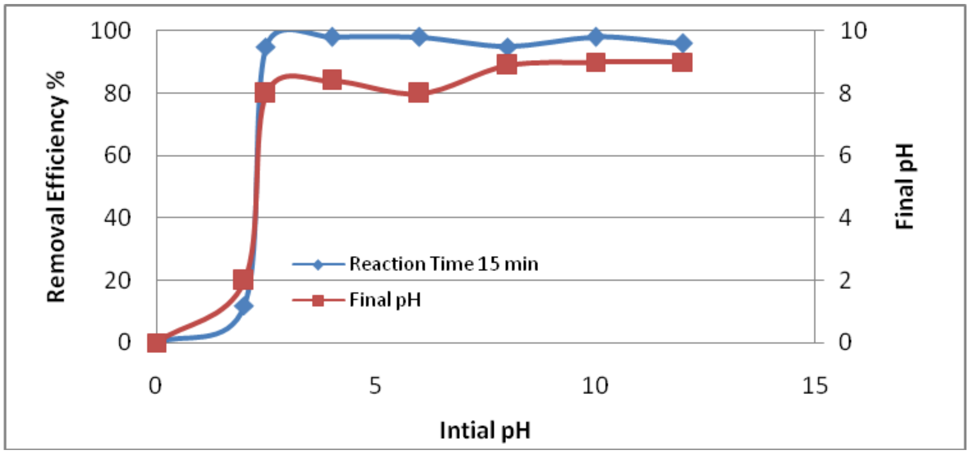


Fig.6. Effect of initial pH value on the removal efficiency of disperse dye and the final pH value using aluminum as anode

Effect of concentration of dye in aqueous solution

Fig.7.shown that, using aluminum as anode and maintaining the initial pH at 7, with the concentration of reactive dye in the range 100-600 mg/l ., the removal efficiency decreased from 95 to 40% with an electrolysis time of 15min . Under the same conditions, the removal efficiency of disperse dye decreased from 100 to35% when the initial concentration of disperse dye was increased from 100 to 600mg/l . as shown in fig.8. The amount of coagulant species for the coagulation dyes needs to be increased when the dye concentration increases. Hence the increase in dye concentration subsequently caused decrease in the removal efficiency when the electrolysis time was fixed. With the concentration of disperse dye increased from 300 to 600mg/l, the removal efficiency was increased to 96% when the electrocoagulation time 30min.Fig.8. At the same electrolysis time, the removal efficiency of reactive dye decreased from 75 to 60% when the concentration increased from 300 to 600mg/l . The results revealed that the removal of disperse dye was easier than that of the reactive dye with aluminum as anode.

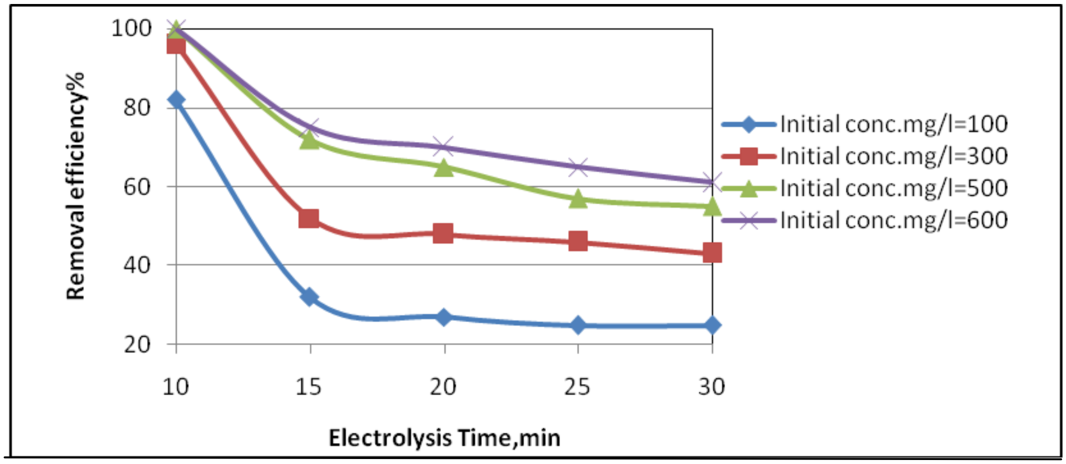


Fig.7. Effect of initial concentration on the removal efficiency of reactive dye in aqueous solution.

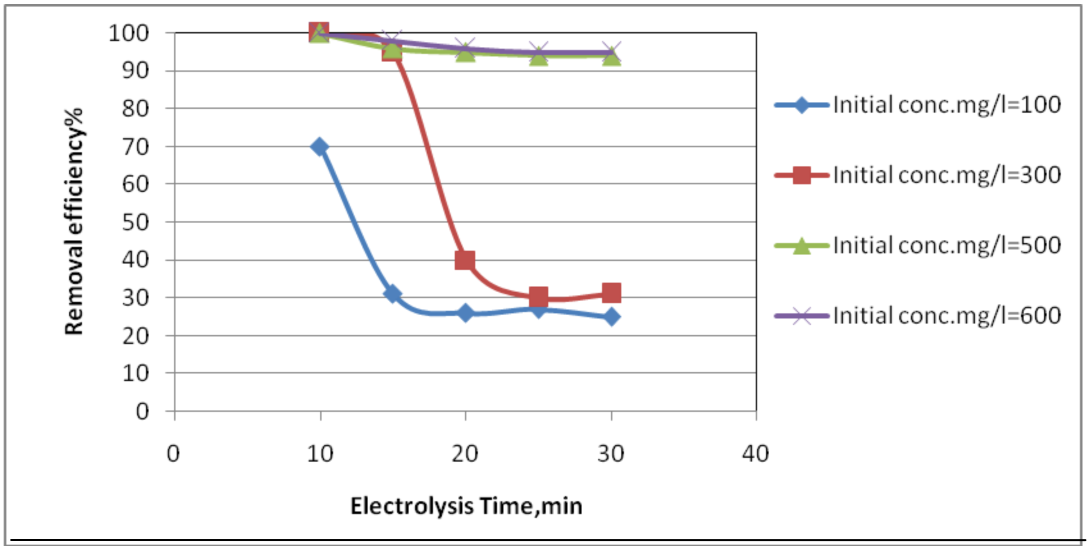


Fig.8. Effect of initial concentration on the removal efficiency of disperse dye in aqueous solution.

IRON AS ANODE

Effect of Stirring on the electrocoagulation disperse dye

Figure(9) Shown that, when stirring rate increased from 100 to 500rpm, the removal efficiency of disperse dye decrease from 80to45% at 15min. under the same conditions, the removal efficiency decrease from 90 to 70% at 30min.. As described above, the rapid mixing inhibited, thus resulting in an decrease in the removal efficiency and increased stirring rate the removal efficiency of disperse dye altered slightly Fig.(9). The results indicated that the time for electrocoagulation increased with stirring rate The optimal rate of stirring of decolorization of disperse dye with Iron as anode was 200rpm.

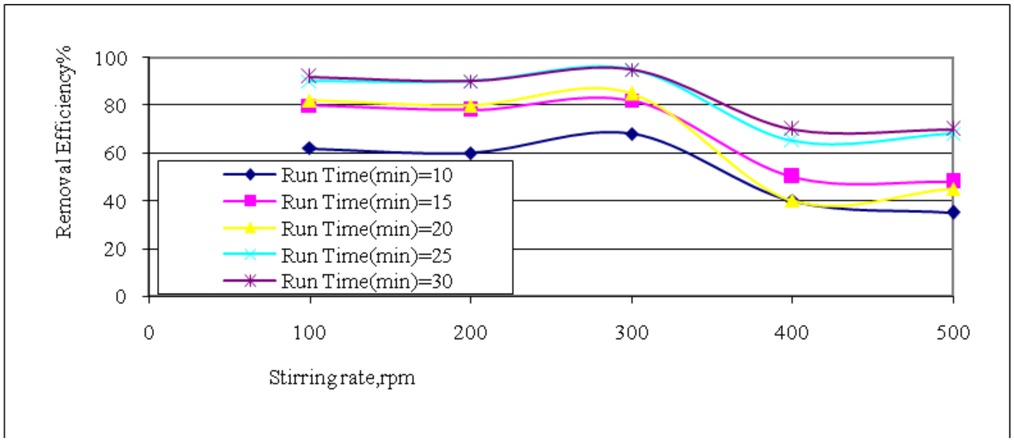


Fig.(9)Effect of stirring on the removal efficiency of disperse dye,Iron as anode

Effect of initial pH on the electrocoagulation of dyes

The removal efficiency of reactive dye increased significantly with time in the acidic range except for pH 2 as shown in fig.10. At lower pH, the dominant species of coagulant generated from iron anode were cationic monomers such as Fe^{+3} and Fe^{+2} (10). As described above, the efficiency of coagulation of dyes with cationic monomer was small. Furthermore, the increase of the concentration of Fe^{+3} and Fe^{+2} might result in the increase of light absorption in the analytical process. The importance of coagulation of reactive dye due to adsorption, neutralization and enmeshment increased when the initial pH increased in the acidic solution. Hence the electrocoagulation efficiency increased and the removal efficiency of reactive dye increase when the initial pH increased in the acidic range.

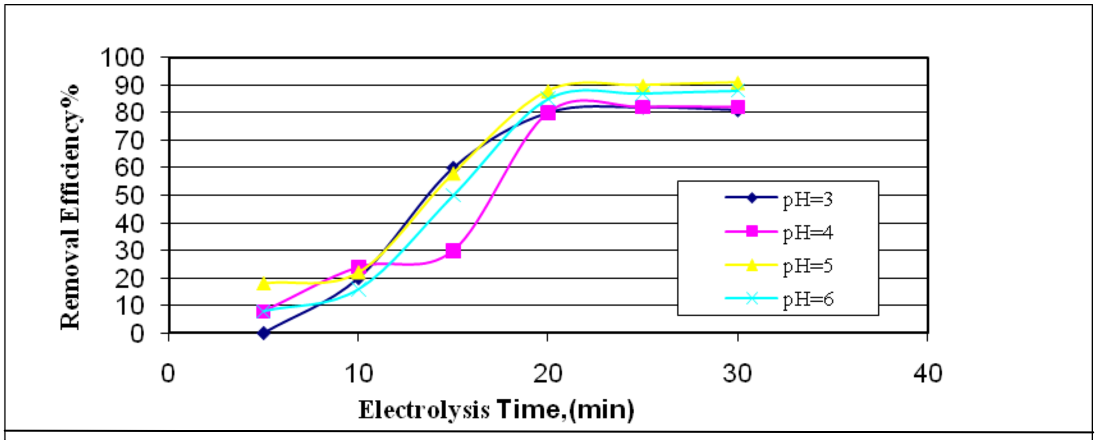


Fig.10.Effect of electrolysis time on the removal efficiency of reactive dye in acidic solution using iron as anode

The removal efficiency of disperse dye increased to 90% with initial pH greater than 2 when the electrolysis time exceeded 15min. as shown in fig.12. The removal efficiency of disperse dye increased to 10% at initial pH 2 over 15min. (fig.11) . The small electrocoagulation efficiency of disperse dye with iron as anode was due to the poor coagulation ability of cationic monomer as described above.

The removal efficiency of disperse dye significantly increased in the initial range pH 7-10 when the duration of electrocoagulation increased from 10-30min. as shown in fig.12. The apparent decrease of removal efficiency of disperse dye in the initial stage of electrocoagulation was due to light absorption by ferrous and ferric ions generated from the anode. The time for removal of disperse dye increased with initial pH increase in the alkaline range.

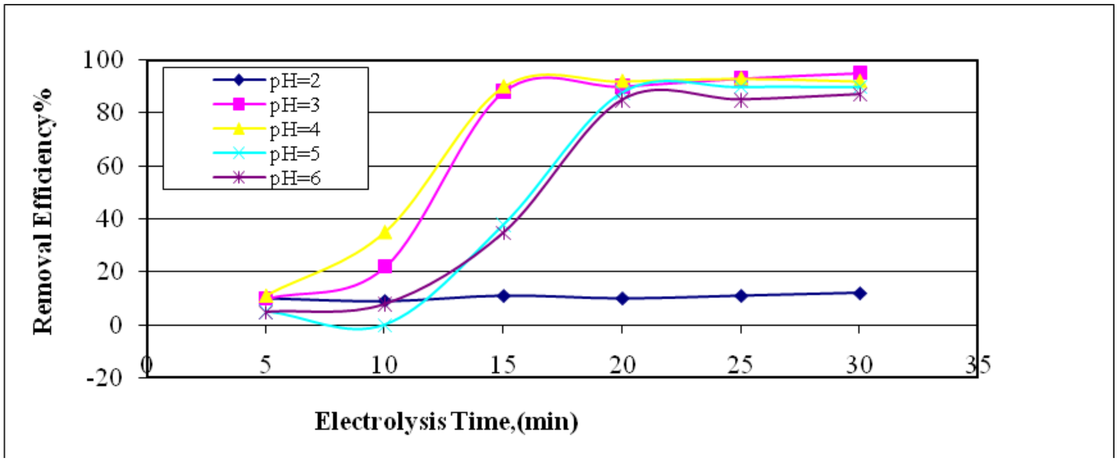


Fig.11.Effect of electrolysis time on the removal efficiency of disperse dye in acidic solution using iron as anode

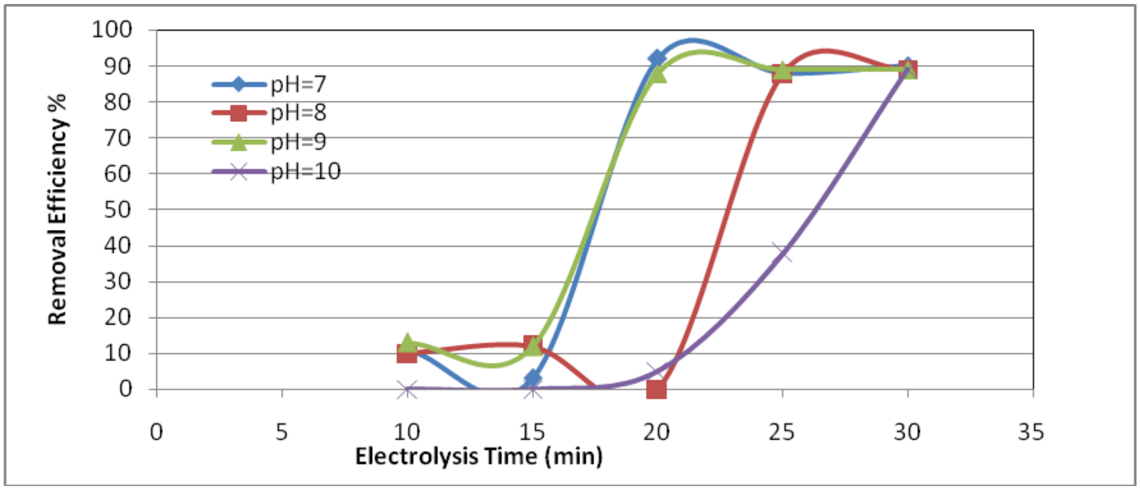


Fig. 12.Effect of electrolysis time on the removal efficiency of disperse dye in the alkaline solution using iron as anode

Effect of concentration of dyes in the aqueous solution

Using iron as anode. The removal efficiency of reactive dye was effectively increased to 90% when the initial concentration was in the range 100-600 mg/l. and the electrolysis period exceed 20 min as shown in fig.13. When the initial concentration was 100mg/l., the removal concentration was increased to90mg/l in 20min. Increasing the initial concentration of reactive dye required increased electrolysis time for electrocoagulation of reactive dye. Under the same electrocoagulation conditions, the removal efficiency of disperse dye reduced to 30% when the initial concentration of disperse dye was larger than 300mg/l and the time of electrocoagulation was 20min. as shown in fig.13. These results might be due to the high concentration of disperse dye causing an altered range of pH for removal of disperse dye with coagulant (10). The removal efficiency was increased to 95% when the initial concentration was 100mg/l. These results showed that the removal of reactive dye with iron as anode was easier than that of disperse dye, especially when the concentration of dye exceeded 300mg/l. In comparison with result in fig.7. Aluminum used as anode for the electrocoagulation of disperse dye was more suitable than iron. Comparing the results in fig.8and fig.5. ,it is seen that the electrocoagulation of reactive dye with iron as anode was superior to that with aluminum.

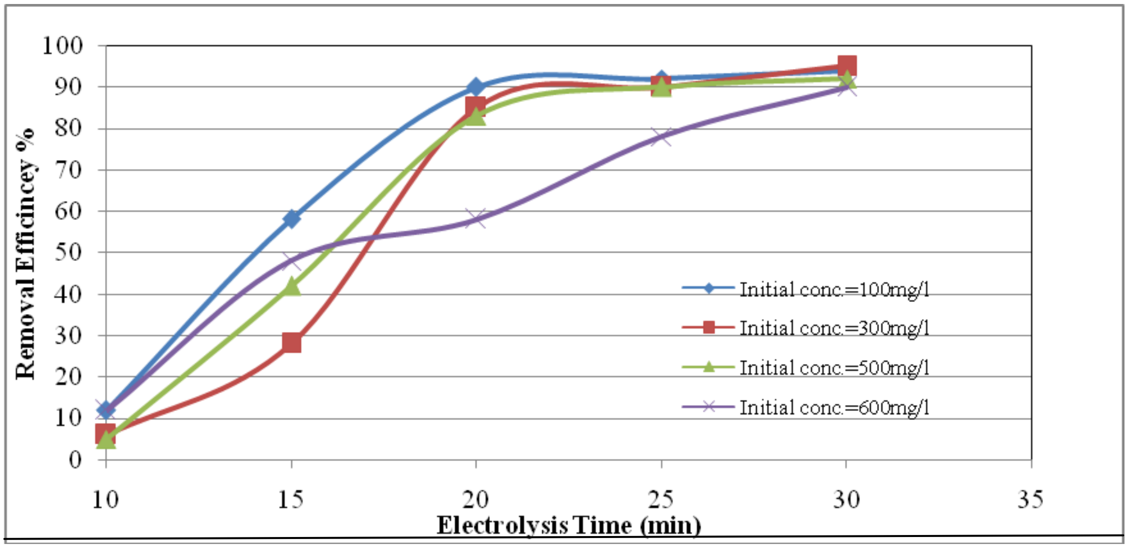


Fig.13 Effect of electrolysis time on the removal efficiency of reactive dye for various initial concentration using Iron as anode

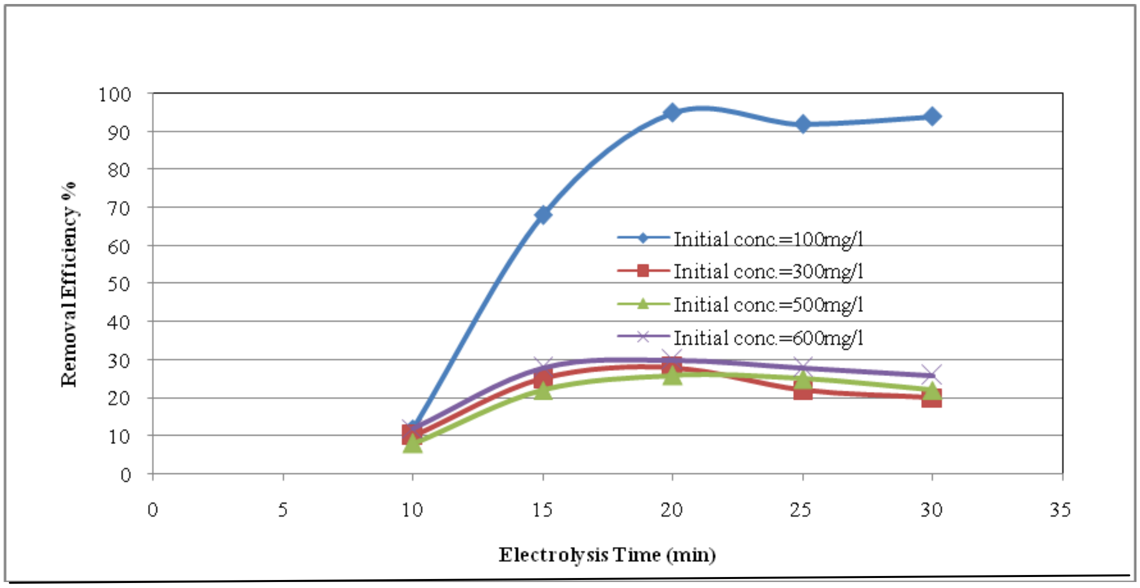


Fig.14 Effect of electrolysis time on the removal efficiency of disperse dye for various initial concentration using Iron as anode

CONCLUSIONS

The results shown that the removal of the azo dye para red(reactive dye)and M-5R200%(disperse oranges dye) by electrocoagulation was effected by the nature of the anode, current density, stirring rate, initial pH, and dye concentration. The dyes were effectively removed at initial pH 3-9 when the initial concentration of dye was 100mg/l, current density 25mA/cm2, stirring rate 200rpm. The results also indicated that the removal fraction of reactive dye was increased to 90% when iron was used as anode and the initial concentration of reactive dye exceeded 300mg/l. The removal efficiency of reactive dye exceeded 75% when aluminum was used as anode for decolonization of reactive dye was superior to aluminum. With aluminum as anode, the removal efficiency of disperse dye was increased to 95% when the initial concentration of disperse dye exceeded 300mg/l. The removal efficiency of disperse dye was less than 30% when iron was used as anode. This showed that aluminum was a suitable anode for electrocoagulation of disperse dye.

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