Comparison of Electrocoagulation and Chemical Coagulation Processes in Removing Reactive red 196 from Aqueous Solution

Ali Assadi[a,*], Armita Soudavari[a], Mehran Mohammadian Fazli[a]

[a] *Department of Environmental Health Engineering, School of Public Health, Zanjan University of Medical Sciences, Zanjan, Iran.*

*Corresponding Author. E- mail address: assadi@zums.ac.ir

A R T I C L E I N F O

A B S T R A C T

Background: Conventional chemical coagulation is considered as an old method to dye and COD removal in textile effluent. Electrocoagulation (EC) process is a robust method to achieve maximum removal.

Methods: This study was designed to compare the result of operational parameters including optimum pH and coagulant concentration for chemical coagulation with ferric chloride and alum also, voltage, electrolysis time, initial pH, and conductivity for EC with iron electrodes to remove reactive red 196 (RR 196).

Results: The outcomes show that ferric chloride and alum at optimum concentration were capable of removing dye and COD by 79.63 % and 84.83% and 53% and 55%, respectively. In contrast, EC process removed the dye and COD by 99.98% and 90.4%, respectively.

Conclusion: The highest treatment efficiency was obtained by increasing the voltage, electrolysis time, pH and conductivity. Increase initial dye concentration reduces removal efficiency. Ultimately, it could be concluded that EC technology is an efficient procedure for handling of colored industrial wastewaters.

1. Introduction

Textile industries are one of the most important environmental pollutants with much volume water consumption resulting in effluent. This is extremely variable in contaminant content such as color, BOD5, COD, pH, and suspended particles (1). Dyeing processes are responsible for colored effluent with potential toxicity and carcinogenicity. The direct discharge poses a major problem for the surroundings. Adsorption, precipitation, chemical coagulation, EC, photo degradation and biodegradation are processes for the treatment of textile wastewater (2-3).

Adsorption and Biological degradation is not a feasible solution for all sorts of dyes because of high molecular weight and structure. Photo oxidation needs additional chemicals and has a secondary pollutant (4).

Coagulation or flocculation process is the most significant and efficacious method to achieve maximum removal. Besides, EC process is another simple and reliable treatment method (5).

Aluminum sulfate (alum), ferrous sulfate, and ferric chloride were commonly used as coagulants. In this situation coagulant concentration and pH

are found by the Jar-Test technique. It is proved that depending on textile characteristics of effluent, COD and BOD5 can be reduced between 50% and 70% respectively after operating chemical coagulation (1). It should be noted that chemical coagulation may be a possibility to produce toxic product such as organochlorine compounds and aluminum coagulant associated with Alzheimer's disease (4,6). Hence, EC process is considered an effective tool without the demand for extra chemical and low quantity of sludge. Decolorization can be accomplished by applying a direct current source between metal electrodes. Electro –Oxidation creating metallic hydroxides flows with non–soluble anodes (7,8). The most commonly used electrode materials are aluminum and iron. Hence, the application of these methods does not generate secondary pollution with no need for compact equipment (9).

The reactive dyes are normally employed in dyeing with high molecular weight, hydrophilic structure and often have an aromatic ring which is utilized as a bridge between reactive group and dye. The problem related to the function of these dyes is due to the hydrolysis of the reactive groups that happens during the dyeing operation. The RR196 is a commercial dye widely employed in the textile industry in Iran. Therefore, removal of this kind of dye from textile wastewater seems a requirement.

The aim of this study is to look into the performance of an EC process against chemical coagulation of synthetic textile wastewater containing RR 196. This comparison discusses dye and COD abatement. Moreover, the outcome of operational parameter such as pH, coagulant concentration for conventional chemical coagulation and voltage, electrolysis time, pH, dye concentration and conductivity for EC process in dye and COD removal efficiency has been looked into.

2. Materials and Methods

2.1. Materials

To simulate a textile wastewater, 1000mg/L of synthetic wastewater was prepared using required amount of RR 196 dye by dissolving it in distilled water, which was purchased from Bayer (Germany). The chemical structure and other characteristics of this dye are shown in table 1.
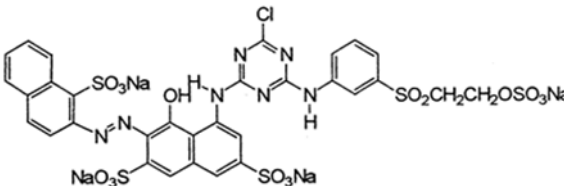
2.2. Experiments

At first, a six beaker jar-test was used to simulate the chemical coagulation process. Each beaker contained 500 ml of the dye solution. Alum and ferric chloride were added as a coagulant at different dosages (25-500 mg/L) with a fixed dye concentration (50 mg/L) in different pH values in the range of 5-10 to determine the optimum efficiency of coagulation and flocculation process. In coagulation a period of 90 min was allowed with 120 rpm, flocculation with 30 rpm about 20 min and sedimentation of about 30 min. The EC cell was fitted with four iron electrodes (Dimension was: 10cm*10cm*1mm and the space between two electrodes was 1cm in all experiments), rectangle scale Plexiglas with an effective volume of 2 L. The electrodes were connected to DC power supply (5to 20 V). Before each run, electrodes were washed out in 0.01 MHCl and rinsed with water. For preventing the demolition of the flocks during their formation, stirring was performed at 20 rpm in the middle of the cell near the electrodes. Settling was conducted without stirring for 30 min before filtration by bag filter. Electrolysis time varied between 5 to 60 min. pH (3 to 10), conductivity (3 to 20 mS/cm), different concentrations of dye (25-300mg/L) were other parameters being followed during EC experiment. The pH of the solutions was measured by a pH meter adjusted by adding NaOH or H_2SO_4.

The conductivity was also adjusted by the addition of KCl and measurement was carried out using conduct meter. Experiments were carried out at room temperature (20±10C).

2.3. Analysis

UV- vis spectrophotometer was employed for determining dye concentration with the calibration method and remaining dye was measured at a

Table 1: Characteristics of reactive red 196.

Dye scientific name	Reactive Red 196
Chemical formula	$C_{31}H_{20}CIN_7Na_4O_{16}S_5$
Molecular weight	1034.27
Maximum absorption wavelength	530 nm
Structure	

Wavelength comparable to the maximum absorbance for RR196 dye. The maximum absorbance was 530nm. Calibration curve based on absorbance measurements was set up and was linear in the range of 5-50 mg/L of standard answer. Dye removal efficiency after experiments was found using the following formula (I):

$$Removal\ (\%) = \frac{c_0 - c}{c_0} \times 100$$

Where C_0 and C are concentrations of dye in front and later experiments in mg/L, respectively. The chemical oxygen demand (COD) of dye solutions was evaluated according to the standard method for examining water and wastewater (10).

3. Results
3.1. Conventional chemical coagulation
3.1.1. Effect of initial pH

The chemical coagulation process was investigated under different pH ranges between 5-1, while the dosage of both coagulant and dye concentration were kept constant at 100 mg/L and 50 mg/L, respectively. The result illustrated that the highest removal efficiency was observed at pH 9 for alum and at pH 8 for ferric chloride with related results in 79.63% and 84.83%, respectively. Figure 1 shows the performance of two coagulants in different pH's. The result indicates that the effectiveness of coagulation in removing dye is highly dependent on initial pH.

After reaching the optimal point, efficiency has slightly diminished.

3.1.2. The effect of coagulant concentration

The section was studied in optimum condition (pH=9 for alum and pH=8 for ferric chloride) and dye concentration was kept 50 mg/L. The effect is presented in figure 2. For this purpose different amounts of coagulants (25-500 mg/L) were added. Add-on (200 mg/L of alum and 300mg/L of ferric chloride) led to dye removal of approximately 79.63% and 84.83%, respectively. The results indicate that with the increase of coagulants concentration, the removal efficiency increased. It is important to note that the decolorization was decreased slightly after reaching the high point. From this result, it became clear that restabilization of particles was occurring.

3.2. EC process
3.2.1. Effect of voltage

Applied voltage directly affects process Performance and controlling costs. Figure 3 depicts the dye removal percentage against voltage applied to the electrodes in the EC process. The event of voltage was investigated using various voltages. The optimum voltage (20 V) caused 99.65% dye removal since the other parameters such as pH, conductivity and dye concentration (7,12ms/cm, 50 mg/L) were kept constant, Also, the influence of electrolysis time is presented in
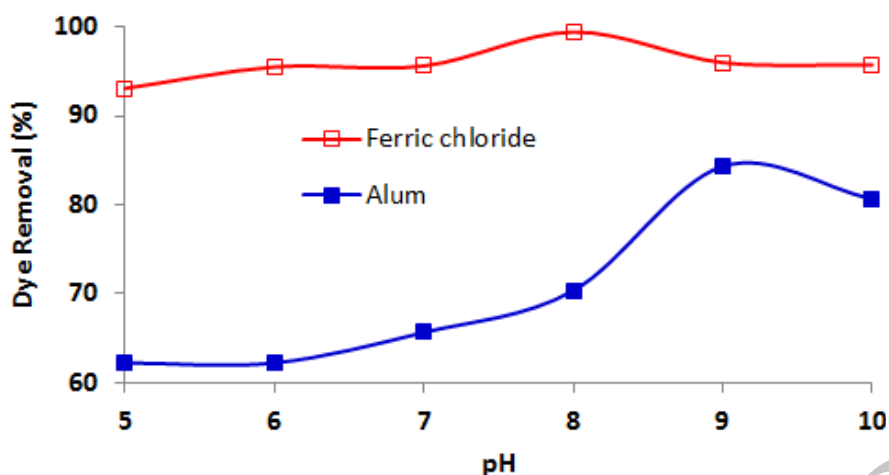
Fig.1: Effect of initial pH on the dye removal at chemical coagulation (C_0 =50 mg/L, coagulant dose =100 mg/L).
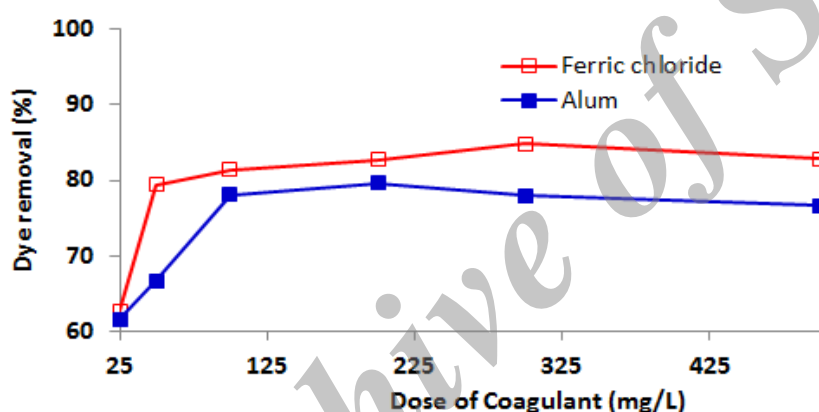
Fig.2: Effect of different coagulant concentration on chemical coagulation (C_0=50mg/L, pH=9 for alum and pH=8 for ferric chloride).

Fig.3. Decolorization efficiency was achieved to a plateau region in almost 60 min.

An increase in time from 5 to 60 min causes an increase in concentration of hydroxyl and metal ion production on the electrodes. The highest efficiency of dye removal in 60 min was 99.65%.

3.2.2. Effect of pH

The pH is an important parameter in determining the application of EC technology. Figure 4 shows the dye removal percentage with

Various initial pH's. The dye solution was adapted to the desired pH by adding sodium hydroxide or sulfuric acid solution. The answers disclosed that by pH increasing up to 8, dye removal of 99.65% was achieved.

3.2.3. Effect of dye

According to figure 5, the EC process was carried out using different Initial carried out using different initial dye concentrations in the range of 25-300mg/L in optimized current density, time
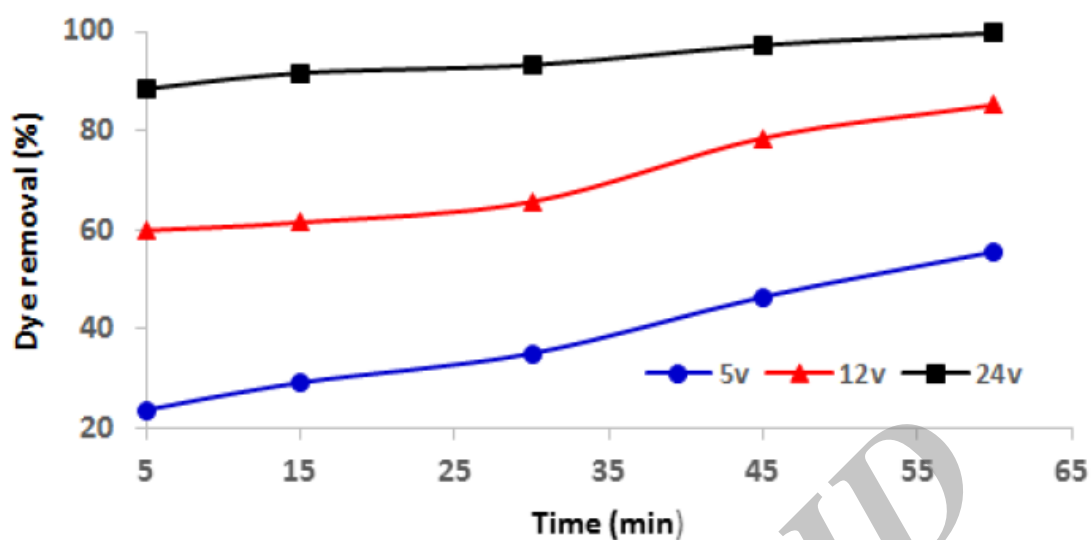
Fig.3: Effect of different voltages on the performance of an EC process (pH= 7, C_0= 50mg/L, conductivity = 12ms/cm).

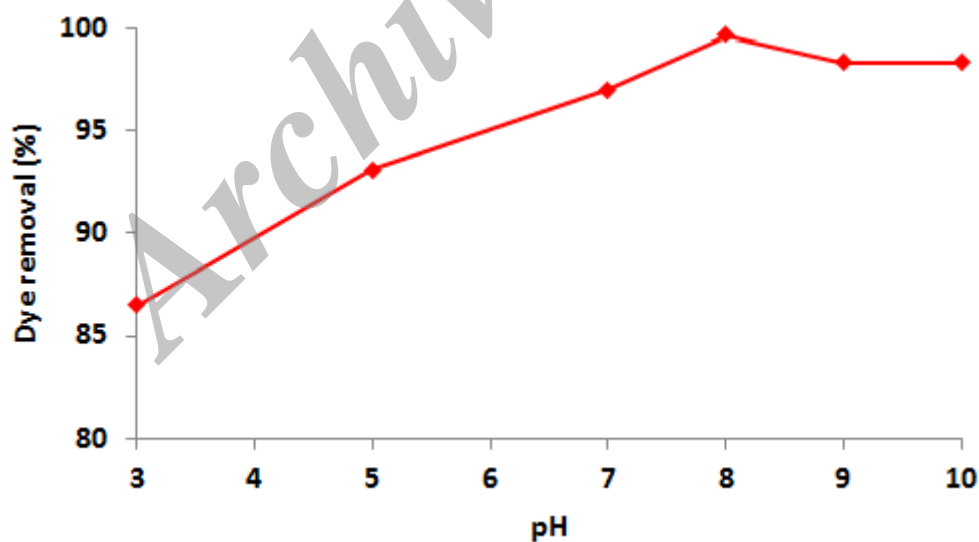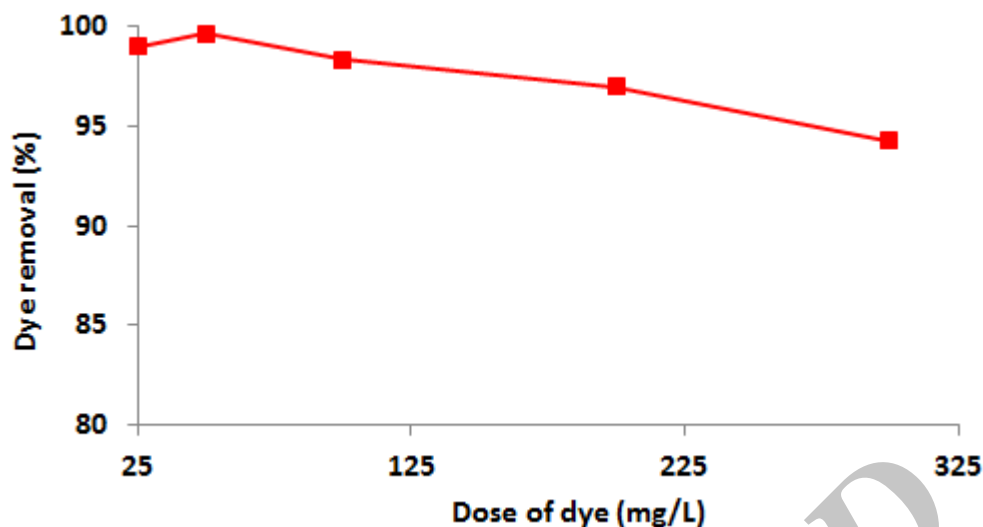*Fig. 4: Effect of initial pH on dye removal (C_0=50 mg/L, current density 62.5 A/m², time =60min, conductivity =12mS/cm).*

Fig.5: Effect of initial dye concentration on dye removal (current density =62.5   A/m², time =60min, pH=8, conductivity =12mS/cm).

and pH with steady conductivity (12mS/cm). The decolonization efficiency displayed a plateau region From 25 mg/L up to 50 mg/L, the adsorption capacity of flocs was not exhausted and the rate of dye removal was relatively constant. After that the decolonization efficiency falls from 96.20 to 95% with an increase in concentration of the dye from 50 to 300 mg/L. This is probably due to the formation of sufficient number of ferric hydroxide complex produced at first steady dye removal.

3.2.4. Effect of conductivity

Functioning of dye solution conductivity on dye removal efficiency has been shown in figure 6. The conductivity was adjusted in different values by the addition of KCl. The effect of conductivity was investigated between 3-20mS/cm. These results indicated that increasing solution conductivity resulted in the increase of dye removal.

In the optimum scope of another parameter achieved from past examination, the phylogeny of

The dye removal displayed a slight increase from 95.62% to 99.98%. It is ascertained that by adding KCl, potential of anode to produce more ion was extended.

3.3. COD reduction

The COD removal efficiency in the optimized shape for both conventional chemical coagulation and EC was determined. Both the COD removal increased steadily with increasing the dye removal. The COD was reduced to 88.86% for EC process and 55% and 53% for alum and ferric chloride, respectively. Figures 7-9 show the relationship between the dye removal efficiency and COD removal efficiency for two processes.

4. Discussion and Conclusion

As the functional groups of reactive dyes are anionics such as sulphonics, hydroxyls and amines allowing a negative charge when dissolved in water, it appears that their negative charge must be neutralized with decreasing pH. Equally it can be visualized in figure 1. Optimum pH for both coagulants was >7. Hence, sludge apparently
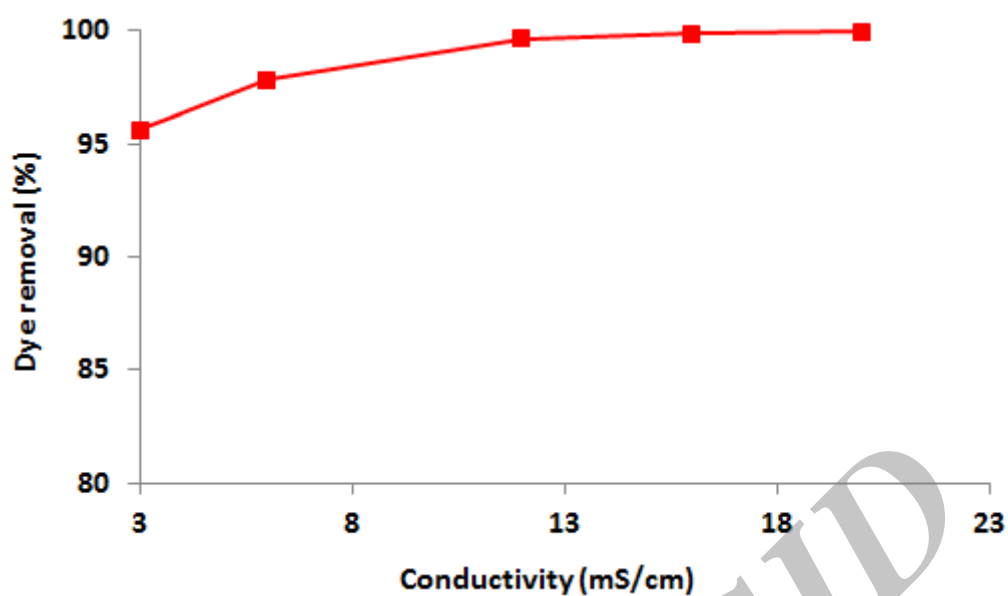
Fig.6. Effect of conductivity on dye removal (C_0=50mg/L, current density = 62.5A/m^2,time =60 min, pH=8).

.

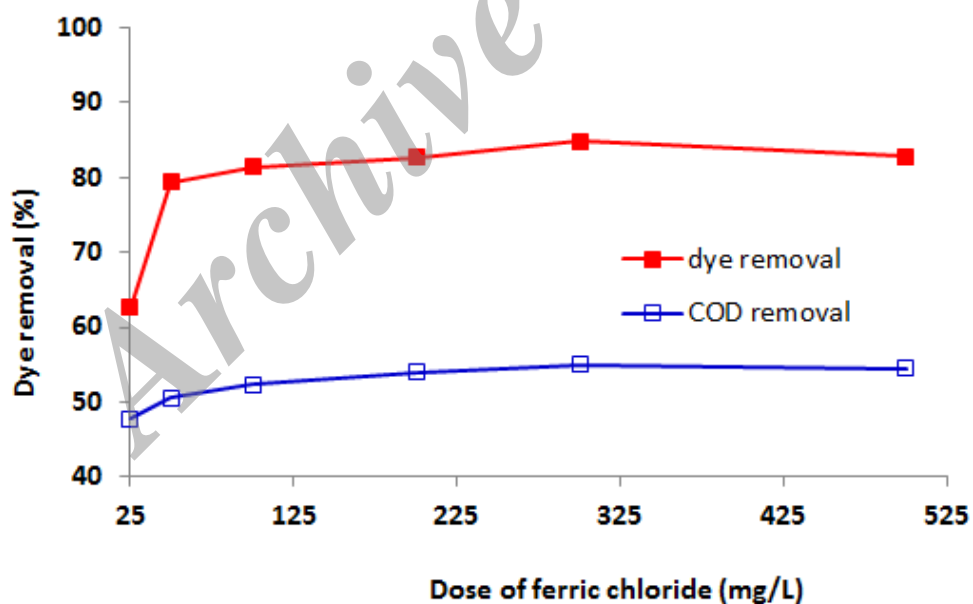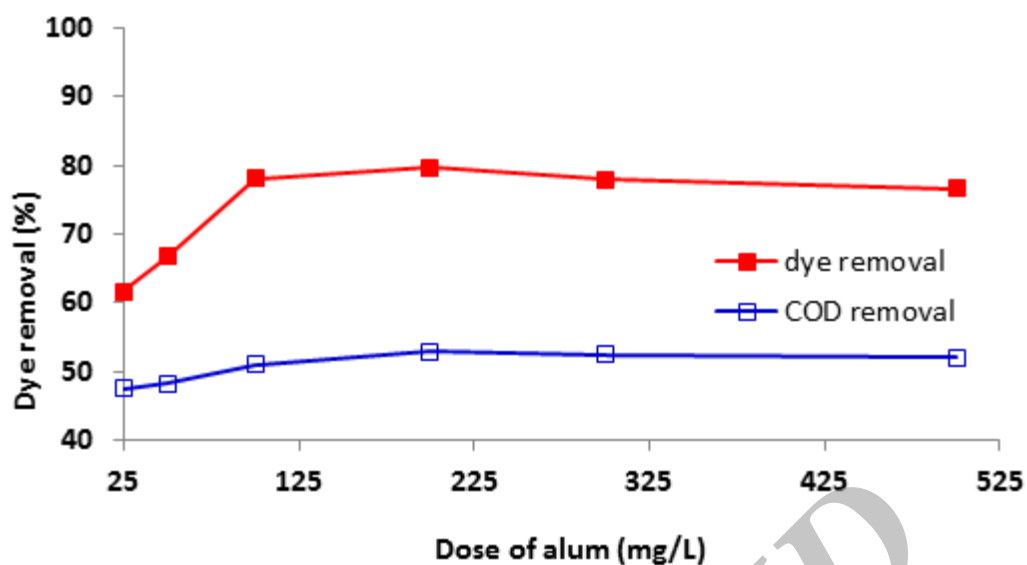*Fig.7: Initial concentration of ferric chloride effect on dye and COD removal (C_0=50 mg/L, pH=8).*

Fig.8: Initial concentration of alum effect on dye and COD removal (C₀=50 mg/L, pH=9).

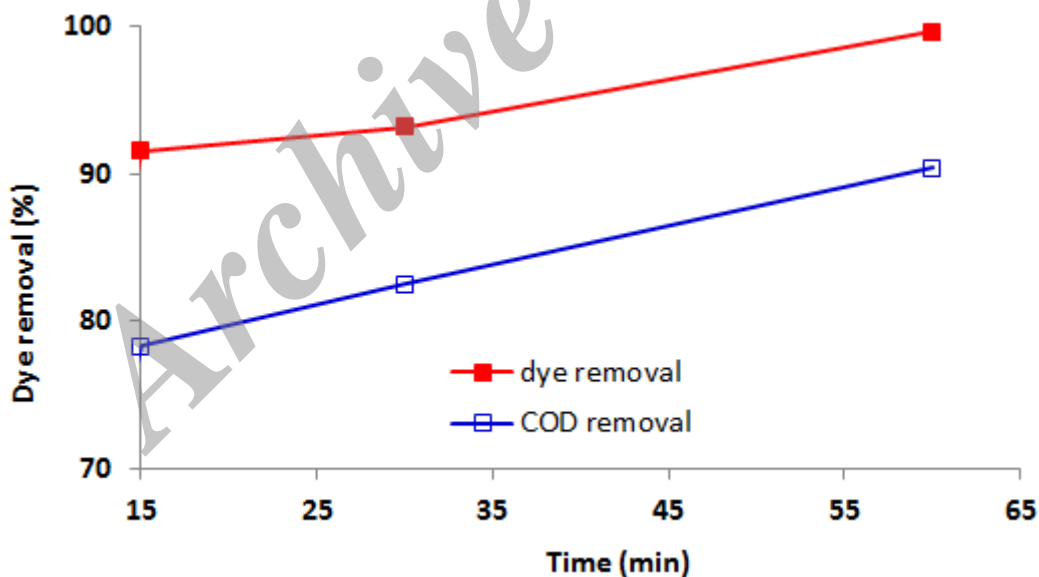***Fig.9: Trend of dye and COD removal in the EC process (C₀=50mg/L, pH=8, conductivity =12mS/cm).***

Served as condensation nuclei, and dye particle was enmeshed as the precipitate was settled. A similar outcome was reported by other researchers. They recorded 89% and 90% Reactive Blue 19 (RB19) removal efficiency for alum and ferric chloride respectively in pH =7 (11). It is defined by increasing voltage and time the faster chemical reaction takes place at the anode and cathode electrodes, resulting in more ions and hydroxides produced to get the dye pollutant. Moreover, bubble generation rate increases and their size decreases by increasing of cell voltage, resulting in a quicker removal of pollutant by H2 floatation. In other fields, researchers have progressed to the same result (12-15). The results of another study showed that the removal efficiency was 97% of 32 V and 60 min reaction time for Reactive Red 198 (RR198) dye by EC process using iron electrodes. Jafarzadeh and Daneshvar applied the EC process for the treatment of textile wastewater, and reported the removal efficiency of 94% of the basic dye solution. They reason the removal rate increased with increasing the applied electric potential and response time (17). The optimal term for the maximum removal efficiency of Levafix O range dye for textile solution using EC process (with aluminum electrodes) was achieved at current density =100 A/m^2, electrolysis time =12min and pH=6. 4. It was also shown that by increasing current density and electrolysis time removal efficiency increased. Hence, the quantity of aluminum ions depends on the electromotive force (current density in this subject area) and electrolysis time. An increment in any of these parameters caused an increase in the formation of coagulant and higher dye removal (18). The issue of pH on the process performance is excused as the following: Kinetic conversion of Fe^{2+} to Fe^{3+}exteremly depends on pH. Moreover coagulant charge is altered by different pH. In other words the pH changes during EC depending on, the initial pH. The raw pH of synthetic dye solution between 6 and 6.5. Hence, as seen in figure 4, in neutrals and slight alkalinity (pH=7-9) condition, we expected more Fe(OH)$_3$ production than Fe(OH)$_2$which is more stable and proper to precipitate. Dye removal was slightly decreased in pH=9 because of establishment of another cationic hydroxide or metal hydroxide formed and precipitated as Fe(OH)$_4$ accumulation around

anode electrodes resulting in consuming OH$^-$ ions, H$^+$ release and decreasing pH. Moreover, as Al(OH)$_4^-$ does not exhibit any decolorization capacity, a reduction is noted also in the removal efficiency above pH 9 according to equations II and III.A pH increase occurs when the solution pH is down as mentioned by another investigation (19-21). Therefore, when the solution pH is above 9, a pH decrease occurs. In other words, EC can act as a pH neutralizer (22).

$$Al_{(aq)}^{3+}+3H_2O\rightarrow Al(OH)_{3(S)}+3H_{(aq)}^+ \qquad (II)$$

$$Al(OH)_3+OH^-\leftrightarrow Al(OH)_4^- \qquad (III)$$
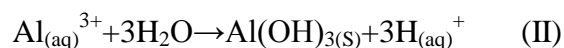
Daneshvar et al., showed optimum efficiency for removing acid red dye 14 from aqueous solution (with iron electrodes)was 93% in pH=6-9 (19). The performance of an EC process for the removal of Reactive black dye 5 from synthetic wastewater was 98% in pH=5-9 in optimum condition (20).The opposite relationship between the initial dye concentration and removal efficiency of dye takes place, because constant voltage and conductivity produce an insufficient number of hydroxide ions to coagulate the greater number of dye particles in high concentration, limiting adsorbing and removal ability. Another study reported similar outcomes for the decolorization of reactive dye solution be an EC process (21). However, in this study as figure 5Shows there is no significant change by increasing dye concentration of 25 mg/L to 50 mg/L, Because of sufficient established hydroxide at this scope. After that we scarcely have seen a slight constant decrease, Probably due to produced oxide layer on iron electrodes was compared to form precipitates, made resistant result in decreasing iron hydroxide. Hence, revealed a little decrease in removing dye efficiency. Granting to the outcomes of this survey, in that location is a substantial relationship between conductivity and dye removal efficiency that is the dye removal efficiency increase with increasing conductivity. The reduction in the dye removal efficiency may be ascribed to a modification in the ionic strength due to the changing conductivity of aqueous medium. Ionic strength affects the kinetic and equilibria of reaction between charge species occurring during the EC. Moreover,

increasingsolution conductivity using KCl has other advantages. Chloride ions could significantly reduce the adverse result of other pairings, such as HCO_3^- and SO_4^{2-} (22). The existence of the carbonate ion would lead to the precipitation of Ca^{2+}ion that forms an insulating layer on the airfoil of the cathode according to following equations. These will increase the ohmic resistance of the EC cell (23).

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (IV)$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (V)$$
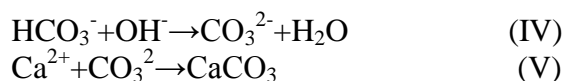
Dalvand et al., reported that the removal efficiency of RR 198 increased from 96% up to 99% in 5 min by adding 3mol NaCl (3).In another study comparison of EC using iron and aluminum electrodes with chemical coagulation for the removal of highly soluble acid dye showed that the development of the decolorization displayed a sharp increase when conductivity increased (24). One of the most significant causes of higher COD removal efficiency is obtained in increasing metal hydroxide. The process of COD removal can be more complicated than it, including electrostatic adsorption and physical particle enmeshment. As dye increased removal efficiency, COD removal increased, Although COD removal efficiency was more depressed than it because of breaking dye and converting to aromatic compound. In other fields, researchers have progressed to the same result. Dalvand et al., reported the COD removal efficiency of 15% in 5min, 20% in 15 min and 66.6% in30 min for RR198 dye (16).

The outcome of this survey showed that, effectiveness of chemical coagulation was sound suitable with 79.63% and 84.83% dye removal for alum and ferric chloride respectively, but also EC showed more strength than it by demonstrating dye removal up to 99.98% in optimum condition. Current density, electrolysis time, initial pH, dye concentration and conductivity were the central parameters of EC (25). As the current density and electrolysis time increased the removal of dye also increased. It was found that the proper voltage and electrolysis time was 20 volts and 60 minutes. Dye removal efficiency increased when the initial pH and conductivity value of the solution increased and should be held at 8 and 12mS/cm,

respectively. Increasing in dye concentration is due to decrease in dye removal efficiency. It is likewise known that, the growth on the current density and conductivity means the growth in energy use.

Acknowledgements

References

1. Vera G, Aleksandra V, Marjans S. Efficiency of the Coagulation/Flocculation Method for the Treatment of Dye Bath effluents. *Dyes and Pigments*. 2005;67: 93-99.

2. Slokar YM, Marechal AML. Methods of decoloration of textile wastewaters. *Dyes Pigments*. 1998; 37: 335-56.

3. Daneshvar N, Salari D, Aber S. Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake. *Journal of Hazardous Material*. 2002; 94: 49-67.

4. Daneshvar N, Salari D, Khetaes AR. Photocatalytic degradation of azo dye acid red 14 in water;investigation of the effect of operational parameter. *Journal of Photochemistry and Photobiology*. 2003; 157: 111-16.

5. Kim T, Park C, Shin E, Kim S. Decolorization of disperse and reactive dyes by continuous EC process. *Desalination*. 2002; 150: 165-75.

6. Liang CZ, Sun SP, Li FY, Ong YK, Chung TS. Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. *Journal of Membrane Science*. 2014; 469: 306-15.

7. Comninellis C, Pulgarin C. Anodic oxidation of phenol for waste water treatment. *Journal of applied electrochemistry*. 1991; 21(8): 703-8.

8. Lopes A, Martins S, Morao A, Magrinho M, Goncalves I. Dedredation of textile Dye C.I.Directed Red 80 by Electrochemical Processes. *PortugaliaElectrochimica* **186** 2004; 22: 279-94.

9. Holt P, Barton G, Mitchell C. The future for EC as a localized water treatment technology. *Chemosphere*. 2005; 9:355-67.

10. Federation WE, American Public Health Association. Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA. 2005.

11. Nateghi R, Assadi A, Bonyadinejad GR, Safa S. Effectiveness of coagulation process in removing Reactive Blue 19 dye from textile industry wastewater. *Journal of Color Science and Technology*. 2011; 5(1): 242-35.

12. USEPA. Profile of the Textile Industry, EPA Office of Compliance Sector Notebook Project, 1997.

13. Aoudj S, Khelifa A, Drouiche N, Hecini M, Hamitouche H. Electrocoagulation process applied to wastewater containing dyes from textile industry. *Chemical Engineering and Processing: Process Intensification*. 2010; 49(11): 1176-82.

14. Daneshvar N, Ashassi-Sorkhabi H, Tizpar A, Decolorization of orange II by EC method. *Separation and purification Technology*. 2003; 31(2): 153-62.

15. Zaied M. Bellakhal N. EC treatment of black liquor from paper industry. *Journal of hazardous materials*. 2009; 163(2): 995-1000.

16. Dalvand A, Gholami MI, Joneidi A, Mahmoodi NM. Investigation of electrochemical coagulation process efficiency for removal of reactive red 198 from colored wastewater. *Journal of Color Science and Technology*. 2009; 3: 97-105.

17. Jafarzadeh NA. Daneshvar N. Treatment of textile wastewater containing basic dyes by EC process. *Journal of Water and Wastewater*. 2006; 57: 22-29.

18. Kobya M, Demirbas E, Can OT, Bayramoglu M. Treatment of levafix orange textile dye solution by electrocoagulation. *Journal of hazardous materials*. 2006; 132(2): 183-8.

19. Daneshvar N, Ashassi-Sorkhabi H, Kasiri M. Decolorization of dye solution containing Acid Red 14 by EC with a comparative investigation of different electrode connections. *Journal of Hazardous Materials*. 2004; 112(1): 55-62.

20. Şengil İA, Özacar M. The decolorization of CI Reactive Black 5 in aqueous solution by EC using sacrificial iron electrodes. *Journal of hazardous materials*. 2009; 161(2): 1369-76.

21. Kobya M, Bayramoglu M, Eyvaz M. Techno-economical evaluation of EC for the textile wastewater using different electrode connections. *Journal of hazardous materials*. 2007; 148(1): 311-18.

22. Chen G. Electrochemical technologies in wastewater treatment. *Separation and purification Technology*. 2004; 38(1): 11-41.

23. Mollah MY, Schennach R, Parga JR, Cocke DL. Electrocoagulation (EC)—science and applications. *Journal of hazardous materials*. 2001; 84(1): 29-41.

24. Chafi M, Gourich B, Essadki AH, Vial C, Fabregat A. Comparison of electrocoagulation using iron and aluminium electrodes with chemical coagulation for the removal of a highly soluble acid dye. *Desalination*. 2011; 281: 285-92.

25. Assadi A, Fazli MM, Emamjomeh MM, Ghasemi M. Optimization of lead removal by electrocoagulation from aqueous solution using response surface methodology. *Desalination and Water Treatment*. 2016; 57(20): 9375-82.