REMOVAL OF CRYSTAL VIOLET DYE FROM WATER USING ELECTROCOAGULATION PROCESS

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Abstract-

Electrocoagulation (EC) is the most efficient processes that utilized to remove the color and organic pollutants from water and wastewater, which decreases the sludge generation. In this research, electrocoagulation process has been utilized for the removal of color from aqueous solutions containing crystal violet dye. The study was produced by using iron electrodes as anode and cathode for electrocoagulation. An L9 orthogonal array of the Taguchi method was used to evaluate the effects of experimental conditions on the electrocoagulation process. Completely nine experiments were carried based on L9 orthogonal array highlighted by Taguchi's method and the optimum levels were forecasted on the basis of the average S/N graph method. Throughout the experiments, initial dye concentration, pH of solution, as well as treatment time were considered to be the process variables, and thus considering the removal efficiency as the response variable. Furthermore, the analysis of variance has been implemented to identify the most significant factor that has a great impact on the response.

Index: Electrocoagulation, Taguchi, crystal violet, iron electrodes

I. INTRODUCTION

Textile wastewater has actually a high content of pollutants, the sources of which tend to be the all-natural impurities, dyes and processing chemical compounds. The textile industry uses a lot of water during dyeing and completing operations. Dye pollutants out of this industry tend to be the source that is major of contamination. Considerable amounts of these dyes stay in the effluent after the achievement of dying process. The discharge of this wastewater to the environment creates aesthetic problems due to the color and additionally damages the quality of the collecting water simply because numerous of dyes introduced and their breakdown products are toxic, carcinogenic or mutagenic to life forms [1]. Electrochemical technology and its applications on wastewater treatment have become increasingly interesting; because of its advantage especially for color removal [2.3]. Electrochemical techniques are believed is means that tend to be powerful the therapy of dyeing wastewater. Thus, electrochemical technique happen effortlessly tested and shown considerable benefits such as easy operation and paid down price that is operating [4–6]. Electrochemical process requires considerably less equipment than traditional biological treatment processes [7].

Electrocoagulation equipment is simple and easy to operate. Short reaction time and low sludge production are two other advantages of the technique [8]. It is extremely required to enhance the electrochemical process for the efficient dye removal. Design of experiment (DOE) is tried to study the effect of variables and their responses to a minimum wide range of experiments. The experimental design of the Taguchi method of orthogonal array (OA) is the collection of statistical procedures which used for increasing, developing and optimizing processes. The Taguchi method uses to learn the impact of specific factors, selecting the relationship between variables and operational conditions. This method additionally determines the performance in the levels which can be optimum with few numbers of experiments [9].

The most widely utilized electrode material in electrocoagulation process is iron. Whenever iron is employed as anodes, upon oxidation in the system that is electrolytic, it creates iron hydroxide, Fe(OH)n where n = 2or 3. There are two mechanisms proposed for the production of the metal hydroxide [10,11]: In the case of iron, the main reactions are as follows:

$$Mechanism 2 \begin{cases} Anode \begin{cases} 4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{+2} + 8e^{-} \\ 4Fe_{(aq)}^{+2} + 10H_{2}O_{(1)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^{+} \\ Cathode: 8H_{(aq)}^{+} + 8e^{-} \rightarrow 4H_{2(g)} \\ Overall: 4Fe_{(s)} + 10H_{2}O_{(1)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \end{cases}$$

The removal of dye molecules can be done by surface complexation or electrostatic attraction, when the insoluble metal hydroxides of iron is used in the process. In surface complexation, the assumption is that pollutant can act as a ligand to bind a hydrous iron moiety with both precipitation and adsorption mechanisms [12–14]:

 $\begin{array}{l} \mbox{Precipitation:} \left\{ \begin{array}{l} DYE + \mbox{monomeric Fe} \rightarrow [DYE_\mbox{monomeric Fe}]_{(s)} \\ \\ DYE + \mbox{Polymeric Fe} \rightarrow [DYE_\mbox{Polymeric Fe}]_{(s)} \end{array} \right. \\ \mbox{Ad sorption:} \left\{ \begin{array}{l} DYE + \mbox{Fe} (\mbox{OH})_{n(s)} \rightarrow [\mbox{Sludge}] \\ \\ \\ [DYE_\mbox{Polymeric Fe}]_{(s)} + \mbox{Fe} (\mbox{OH})_{n(s)} \rightarrow [\mbox{Sludge}] \end{array} \right. \end{array}$

II. AIMS AND OBJECTIVES

In this study, the removal of crystal violet through electrocoagulation process has been examined. These dyes are soluble in water. The aim of this study work is determining the effectiveness of removing crystal violet dye using electrocoagulation and to study the effects of various experiments parameters (treatment time, pH and initial dye concentration) on removal process, and investigate potential use of Taguchi's technique and to find out the conditions for improved performance of electrocoagulation in removing dye.

III. LITERATURE REVIEW

The electrocaogulation process was helpful in eliminating of phosphorus, nitrogen and organics as compared with biological treatment. Beck et al.(1974) [15] studied the process of electrocoagulation for the wastewater treatment from food industry. The authors have made a comparison between electrocoagulation and chemical treatment accompanied by dissolved air flotation. The formation of Floc for both processes was fast. The electrocoagulation process has produced a floc in (2-3) min. and compacted it in (3-10) min., while the dissolved air flotation required (10-20) min. to do that. Weitraub et al. (1983)[16] showed that electroflocuulation and electrocoagulation make use of the direct introduction of flocculent ions into the emulsion suspension by means of electrical dissolution of sacrificial electrode (eg Fe \rightarrow Fe⁺³). The authors also, pointed out that if insufficient flocculent ions are produced insignificant effect on the process of oil separation. When the correct dosage of ions is introduced the process of flocculation occurs with good oil separation.

Zhu et al.(1991)[17] studied the efficiency of the electrocoagulation process in COD removal. They concluded that the method of electrocoagulation was very efficient in the removal of COD and decoloration at low energy consumption.

Balkan and Kolesnikova(1996) [18] demonstrated the higher efficiency of iron electrodes in treating wastewater containing impurities such as cyanides, amines, alcohol, and aldehydes in quantities ranging from 50 to 300 mg/l. They attributed this efficiency to the larger initial particles $(10-30) \mu m$ for trivalent iron versus 0.05 μm for trivalent aluminum.

Lawrence and Louis (2000)[19] performed a field study which deals with the objective of electrocoagulation technology in removing barium and total suspended solids from water-retention ponds. They showed that the average system removed 56.5% of the barium and 84.2% of TSS, and the average reductions of 10% to 30% were recorded for TOC, COD, and BOD.

With the objective of treating effluents industrial liquid wastes by electroflotation, K.A.Matis in 1980 [20] performed some advanced laboratory tests to remove the paint from a liquid by floating them with finely – dispersed bubbles of hydrogen and oxygen, that are formed as a result of electrolysis of the liquid. He has used batch tests to give preliminary information on the flotation characteristics, whilst continuous – flow experiments were used to give the final design data. The Voltage used was about (13 Volt) at a current density of (100 amperes/m²) with an interelectrode spacing of (3 mm). Results which were found from the separation of a paint water suspension, showed a retention period of (55 min.) in continuous operation, was enough to remove paint concentration in about (90%) with current density of (300 amperes/m²).

The main purpose of Perkins et al.(1995) [21] study is to discover and develop a method to reduce the pollution load that was generated in textile wastewater plant. One of the methods that were suggested by the authors is to treat textile wastewater was the electrochemical treatment as a viable mechanism for removal of color from textile dyeing wastewater. They have selected four reactive dyes. Another study conduced by Lin et al. (1994) [22] that used the electrochemical treatment to remove textile dye samples which were conducted on a laboratory scale. The authors have discovered that the elimination is good of organic substances in various operating conditions. A study presented by Faynshteyn et al.(1970) [23] deals with the influence of pH value on the effectiveness of electroflotation in purification of effluents. They have found that the effectiveness of purification depends so much on the quantity and ratio of the reagents, as on the resulting pH value. Lewin and Forster (1974) [24] have conducted experiments to show the effect of pH on the process of electrocoagulation in the field of protein recovery. They have demonstrated that the most effective pH was 4. Vik et al.(1984)[25] showed that the value of pH was increased through the electrocoagulation process due to the formation of hydrogen gas at cathode. Also, as the charge increases the values of pH tend to increase, the results of their study showed that the pH value of the raw water does not have any impact on the removal of organics at different chemical dosages when the pH value was held between (3.9 and 6.0).

IV. METHODOLGY

A. Materials

Crystal violet dye with molecular mass of 407.99 g/mol, and the wavelength of 584 nm which corresponds to maximum absorbance. The crystal violet used in this work was the analytical grade one. The pH of the solution is managed by using 0.1M hydrochloric acid and 0.1M sodium hydroxide.

B. Preparation of stock solutions

The solution of dye in this study was prepared by dissolving an accurately weighted of the selected dye in distilled water with a concentration of 0.1 gm in 1000 ml of water (100 ppm). The dye structure was shown in Fig.1. The solution is more diluted 10 times to prepare 10 ppm of solution. The concentration of dye solution had been determined by a spectrophotometer working in the visible range on absorbance mode. Absorbance values were recorded during the corresponding maximum absorbance wavelength and the dye solution was initially calibrated for the concentration in terms of absorbance units.

C. Experiment setup

The experiments were performed in a 1000-mL glass beaker, in the operation of batch mode. The dye solutions of various initial concentrations of dye were prepared with the dissolving of the dye in distilled water to prevent with impurities. Iron plates dimensions of 120 mm \times 60 mm \times 2 mm (length \times width \times thickness) were utilized as electrodes. The electrode was dipped 6.5 cm into the solution with the submerged area of the electrode in the solution equal to 39 cm^2 . The electrodes had been connected to a DC power supply that provide 0-30 V. The whole contents in the beaker were agitated by using a magnetic stirrer to keep uniform concentration in the beaker. After the electrolysis period, the dye solution was permitted to settle for a fixed retention time. After the fixed retention time, the sludge was separated and the dye concentration in the supernatant liquid was measured to determine the color removal efficiency. The schematic diagram of the experimental setup is shown in Fig. 2.



Fig. 1. Dye structure



Fig. 2. Experimental setup

The dye concentration in the solution was determined using the standard method of photoelectric by a spectrophotometer (APHA 1998). The maximum absorption wavelength of crystal violet dye was 584 nm. At the wavelength of 584 nm, a linear relationship was noticed between the absorbance and concentration of the crystal violet dye in the studied solution. The color removal performance had been computed using the following equation:

Dye Removal Efficiency (%) = $100*(C_0-C_i)/C_0$ (1)

Where: Co and C_i = initial concentrations of dye and concentration at any time "t" in mg/l, respectively.

D. Apparatus

UV–Vis spectra were recorded using UV–Vis spectrophotom (SpectroDirect) from Lovibond that equipped with a quartz cell. SD 300 pH meter from Lovibond, was used to measure the pH of the solutions. A magnetic stirrer (78-1) from China was employed for stirring the dye solution and an analytical scale was used for weighting the used materials.

E. Taguchi orthogonal array (OA) experimental design

In recent years, Taguchi method has been used extensively for the optimization and experimental design. The method employs the systematic orthogonal arrays (OA) in the designing of experiments. The OA is a case of experiment where the columns for the independent variables are "orthogonal" to one another. The result of designed experiment can be examined by using both the analysis of variance (ANOVA) and the signal-to-noise ratio (S/N). Hence, the important parameter that contributes to the process can be identified. This research investigates the removal of crystal violet dye using electrocoagulation process. The main purpose of this work is to discover the optimum conditions to maximize dye removal efficiency with minimum number of experiments. Hence, the orthogonal arrays of Taguchi method were employed. The signal-to-noise ratio and the analysis of variance were applied to find the optimal levels and to examine the effect of process parameters on dye removal efficiency. At last, a confirmation test utilizing the optimal levels of parameters was carried out to demonstrate the performance of Taguchi's optimization method.

V. RESULTS AND DISCUSSIONS

A. Statistical Analysis

In this work, the optimizing of experimental variables for crystal violet dye removal, three factors (initial dye concentration, pH and treatment time) in three levels each factor were studied by fractional factorial design leading to nine experiments. To see the influence of electrocoagulation process parameters (variables) on the response (final dye removal), the three parameters of the electrocoagulation process had three levels each, as shown in Table 1.

rable 1. Electrocoagulation parameters and then levels	Table 1: Electrocoagulation	parameters and their levels.
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F	Demonster (Eester)	TT. 14	Levels .			
Factor	Parameter (Factor)	Unit	1	2	3	Ex _j
А	Initial dye concentration	mg/l	10	30	50	NO
В	pН	-	5	7	9	1
С	Treatment time	min.	5	10	15	2

The advantages of Taguchi technique tend to be: preserving the efforts in performing experiments, saving the experiment's time, decreasing the cost, and quickly exploring factors being significant. To be able to lower time and cost of experiments, nine experiments were conducted according to Taguchi optimization method along with an L9 orthogonal array (Table 2).

Table 2: Taguchi's of L9 (33) orthogonal array.

Dung	Parameters			
Runs	Α	в	С	
1	Level 1	Level 1	Level 1	
2	Level 1	Level 2	Level 2	
3	Level 1	Level 3	Level 3	
4	Level 2	Level 1	Level 2	
5	Level 2	Level 2	Level 3	
6	Level 2	Level 3	Level 1	
7	Level 3	Level 1	Level 3	
8	Level 3	Level 2	Level 1	
9	Level 3	Level 3	Level 2	

Generally, the optimized process in Taguchi method is depending on four main steps, planning, conducting, analysis and validation. These steps can be summarized as follows:

1. Determining the factors becoming optimized, determine the control factors and their levels, and choose an appropriate orthogonal array for design of experiments.

- 2. Carrying out the experiments according to orthogonal array plan.
- 3. Analyzing the data by determining the S/N ratio, evaluating the experimental results by using ANOVA test, and discovering the optimal level for every one of process variables.
- 4. Validation of experiments by performing confirmation experiment.

The results of nine experiments of electrocoagulation process are presented in Tables 2 and 3, respectively. In order to reduce experimental errors every single response results was tested two times. A range of values from 37.8% to 99% was obtained for removal efficiency. From the average values of the results, run 1 and run 5 showed the lowest and highest removal efficiency for electrocoagulation process, respectively. Experimental data were analysed using the Minitab software (version 17). The settling time of 30 min was used for all the processes because it was found from preliminary experiments that the color removal after this time is virtually constant.

Table 3 The L9 (3^3) orthogonal array for optimization of electrocoagulation process .

Exp. No.	Factor A	Factor B	Factor C	Response (%)
1	10	5	5	80.2
2	10	7	10	94.2
3	10	9	15	97.6
4	30	5	10	93.3
5	30	7	15	99.4
6	30	9	5	90.8
7	50	5	15	80.2
8	50	7	5	37.8
9	50	9	10	94.7

The results of the experiments were assessed by the analysis of variance (ANOVA). The main purpose of the ANOVA was to determine the effect of each parameter on the variance of the results pertaining to the total variance of all the parameters.

Table 4 shows the ANOVA results for crystal violet dye removal efficiency in the electrocoagulation process. The ANOVA results of the electrocoagulation show that the most important factor contributing to the color removal is, treatment time followed by, pH and lastly initial dye concentration. Also, the F-test was performed for all the parameters at 99% confidence level. F value in Table 4 shows that treatment time factor has the most significant effect on dye removal by the electrocoagulation process.

Table 4:	Analysis of	Variance for	experimental	responses	in
	alactro	congulation	process		

		electio	coaguiatioi	i piùcess.		
Factor	DF	Seq	Adj	Adj	F	Р
		SS	SS	MS		
А	2	195.6	195.6	97.80	1.07	0.484
В	2	226.1	226.1	113.03	1.23	0.448
С	2	380.6	380.6	190.29	2.08	0.325
Error	2	183.2	183.2	91.58		

Where 'DF' is the total degrees of freedom, 'Seq SS' is Sequential sum of squares, 'Adj SS' is Adjusted sums of squares, 'Adj MS' is Adjusted mean squares, 'F' is the Fvalue, and 'P' is the P-value

The S/N was used to measure both the mean value (named "signal" represents the desirable effect) and the standard deviation (named "noise" represents the undesirable effect) of a set of data. Higher S/N ratios are desirable in dye removal. The S/N ratio used for this type of response is defined as follows [26]:

Where 'n' is the number of repetitions and 'Y_i' the observed data obtained from present experimental work.

The results of S/N ratio for the designed experiments after ANOVA calculations are shown in Fig. 3 in the electrocoagulation process.



Fig.3 Process parameters results on S/N in electrocoagulation.

According to the Fig. 3, the best S/N was found at pH of 9. There is a general agreement in the literature that confirms the optimal pH. When the pH was decreased from 9 to 5, the S/N ratio decreased significantly. The S/N ratio increased as a consequence of increasing treatment time, that is because, when the time of treatment increase, the rest dye that not treated will have enough time to react and treat. There is a rise in floc production in solution and hence an improvement when looking at the effectiveness of color removal.

Some investigators have actually reported that in electrocoagulation, current density can affect the treatment performance (Pouet M., et al., 1995)[27], while some others have stated that current density has no considerable role on pollutant removal (Chen X. et al., 2000)[28]. Therefore, it stays uncertain that whether the current density influences

the treatment performance or not. For this reason, we used a constant current of 10 V and 2 A for all the experiments.

B. Confirmation Test

Confirmation test is recommended by Taguchi for the verifying the experimental results. The confirmation test in this study was performed in optimal conditions and the color removal efficiency was obtained as 95.6% for electrocoagulation process.

VI. CONCLUSION AND RECOMMENDATIONS

A. Conclusion

In this work, electrocoagulation for crystal violet dye removal has been successfully applied. The electrocoagulation process of dye removal was modeling making use of Taguchi approach to recognize the significance of the variables in the electrocoagulation process. The ANOVA study revealed that the treatment time is the most significant variable in electrocoagulation process of that dye removal. Electrocoagulation is a process that is efficient for the removal of color of synthetic wastewaters containing crystal violet. The efficiency for the process is influenced strongly by the pH, initial dye concentration, and the time of the reaction. The removal of crystal violet dye containing synthetic wastewater was increased from 37.8% to 99.4 % respectively. The treated effluent can now be easily used for economical and conventional biological treatment methods. Optimal electrolysis time of 15 minutes was determined to achieve a removal between 80.2 and 97.6 %. These parameters being functional applied to synthetic wastewater and resulted in satisfactory of color removal additionally enhance of biodegradability.

- B. Recommendations
- 1. Make use of this treatment process for different Dyes.
- 2. Apply this method of treatment for water and wastewater in Basrah city.
- 3. Study other variables in electrocoagulation method and check its effect.

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