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Response Surface Optimization for Waste Water from Textile Industry

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Abstract: The findings of the study showed that at optimum conditions of the operating parameters i.e., current density = 14.17 mA/cm^2, t = 102 min, and pH = 6.25, 63.41% of COD removal, 90.93% of dye removal and 0.0035 kWh/kg of energy consumption, were observed. Kinetic studies showed that EC based treatment of STW followed first order kinetics and the kinetic constants at 30°C for each response parameter i.e., % COD removal and % dye removal were 0.0205 min^{-1} and 0.0097 min^{-1}, respectively. Similarly, at 50°C the kinetic constants for % COD removal and % dye removal were 0.037 min^{-1} and 0.011 min^{-1}, respectively. Further, it was also observed that the amount of Al in the treated STW, sludge and scum was observed to be 25.16 mg/l, 0.50778g and 0.06006 g, respectively.
Keywords: Waste water, Response Surface plots and optimization

I. INTRODUCTION

Water is one of the basic necessities of the life and therefore humanity should be more concerned about its depletion as compared to that of oil or money. Water level in all its sources whether it is ground or surface is depleting at high rate and it is projected that by the year 2030 water will be major political and social issue among the developed countries. Therefore, priority should be given to the storage, efficient usage and recycling of the water. Industries of many developing countries generate a lot of waste water which is disposed into the fields and remains wasted. Therefore, efficient treatment technologies need to be developed to treat the waste water and reuse it. Global usage of fresh water in different sectors such: industries, agricultural, domestic etc., introduce a lot of toxic chemicals in the water. These toxic chemicals are not easily degradable and they stay in the water system for a long time. Disposal of untreated water in the water bodies and lands affect the living beings as well. These toxic chemicals are ingested by fishes and also absorbed by plants. In this way, these toxic chemicals become part of our food chain and living beings also come in contact with these toxic chemicals. Therefore, treatment of wastewater has become a global concern. In earlier years, primitive technologies were used for the treatment of wastewater coming from textile industries. They were mostly based on the biological treatment of the complex dyes. These techniques have shown poor efficiency as most of the dyes were recalcitrant in nature. Afterwards, physic-chemical processes were also used along with biological processes for the degradation of dyes. The various physic-chemical processes include: floatation, electro flotation, flocculation, membrane filtration, electro-kinetics, coagulation, electrochemical destruction, ion exchange, irradiation, precipitation etc. These treatment techniques have shown some reliable results however there still remain certain disadvantages such as high operation cost, sludge disposal, inefficiency in treatment of certain dyes such as: sulphonated azo dyes. Later on dyes were treated using chemical oxidants such as sodium hypochlorite which showed good efficiency however the production of carcinogenic amines during the treatment decreased its usage. Investigations have also been made to treat the wastewater from textile industry using the biodegradation. In this process, microbes utilizes the recalcitrant capacity of dyes to adhere them on their surface. Many dyes have been treated using this process however no specific methodology could still be figured out for this process. Therefore, there still exists a problem of handling the contents in this treatment process. In recent years, an approach of using the electrochemical treatment (ECT) is being studied and efficient results have been observed. With the motive of pacing this research present study has also been designed to treat the effluent of textile industries using the electrochemical treatment process.

II. MATERIALS AND METHODS

The Broad objective of the study is to treat the effluent generated from a textile industry using a lab setup of electrochemical treatment. So The STW prepared in this study was prepared by mixing reactive black dye and other chemical in distilled water (DW). The STW, of 200 mg/L dye concentration, prepared in this way, was observed to have 3148 mg/l of COD. Experiments were designed on the basis of the five level central composite (CC) design in combination with response surface methodology (RSM).

The operating parameters chosen for the present investigation were, pH = 4–10; current density = 14.17–308.64 mA/cm^2 and reaction time = 30– 180 min. The impacts of these operating parameters on three response parameters i.e., percentage removal of COD and dye and amount of energy consumption, were estimated. Further, to maintain the desirability function of the treatment = 1, the multi response optimization was performed.

III. RESPONSE SURFACE PLOTS AND OPTIMIZATION

After validation of the models, Design Expert software was used to plot 3-Dimensional surface plots for all the operating and response parameters. RSM approach was used to draw these plots and they are shown in Figure 1 through Figure 3.

These reactions involved in this treatment process are initiated at Al electrode. As an anode, oxidation takes place and ions such as, Al^{3+} and OH^-, are produced. The reactions involved during this process are shown in Eq. (4.4) and Eq. (4.5).

$$Al_{(s)} \rightarrow Al^{3+}_{aq} + 3e^- \tag{4.4}$$

$$3H_2O_{(l)} + 3e^- \rightarrow \frac{3}{2}H_{2(g)} + 3OH^- \tag{4.5}$$

The products of these reactions further react among themselves, to generate several types of hydroxides. These hydroxides are: $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, $Al_6(OH)^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)^{4+}$, $Al_{13}O_4(OH)^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ (Bayramoglu et al. 2003). The generation of these monomeric and polymeric species of hydroxides is largely dependent on the concentration of aluminum ions in the reaction mixture and its pH. During the on-going reaction, the proportional concentration of different types of the aluminum hydroxides can be estimated from hydrolysis constants, as mentioned in the following equations (Duan et al., 2003).

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad pK_1=4.95 \tag{4.6}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad pK_2=5.6 \tag{4.7}$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad pK_3=6.7 \tag{4.8}$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad pK_4=5.6 \tag{4.9}$$

From the Eq. (4.6) through Eq. (4.9), it can be depicted that the range of hydrolysis constant may vary within a large limit, however, it majorly falls within the pH values of 5 to 6. It could also be observed that major aluminum hydroxide species reported in these reactions were Al^{3+} and $Al(OH)_4^-$. These species of aluminum hydroxide i.e., Al^{3+} and $Al(OH)_4^-$, exist during low and high pH, respectively.

The response surface plots for %COD removal (Y_1) and %dye removal (Y_2) are shown in Figure 1 and Figure 2. From these figures, it can be depicted that at constant value of current, the % removal of COD increased with increasing pH of the reaction mixture.

This scenario was followed till the pH of the reaction mixture reached ~ 7 pH. After pH = 7, the change in % removal of COD was observed to be very limited. Hence, it can be depicted that maximum % removal of COD occurred within the pH range of 4 to 7. In case of % removal of dye, the inverse phenomenon was reported. % removal of dye was reported to decrease with increasing the pH from 4 to 7.

However, changes in % removal of dye after pH = 7, was minimal, as also observed in case of % removal of COD.

Precipitation of the salts and their adsorption are two ways which influence the COD removal during the ECT-based treatment of synthetic wastewater. At lower pH i.e. < 7, the different types of hydroxides of aluminum were generated. With the passage of time, when the reaction proceeds the concentration of these hydroxides increased significantly. This further lead to precipitation of hydroxides and sludge is formed which started the adsorbing process. Moreover, the electrodes were also reported to be covered with these precipitates and further reactions were halted. Hence, with increasing pH the % removal of COD decreased.

The trend shown in above mentioned figures can also be corroborated with the Faraday's Law, which explains the relationship between the current, time and the dissolving of anode into the reaction mixture. This relationship can be explained as following:

$$w = \frac{MJt}{ZF} \tag{4.10}$$

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Where, w depicts the amount of ions generated after passing a *J* amount of current through the anodes for *t* time; Z shows the number of e^- transferred during the oxidation/reduction reaction(s). However, F defines the Faraday's constant and M is the atomic weight of the material from which anode is made up of. Therefore, it can be depicted that the factors such as, anode, current density, time of reaction etc., are inter-related and impact each other. The number of ions produced by the anode defines the rate of degradation of the pollutant, which is also directly related to current density and time of reaction. For an instance, an increase in values of current density and time, increase the number of ions produced from the anode and subsequent, floc formation. Therefore, it can be said that time and current density, positively impact the removal efficiency of the reaction. Consequently, from the response surface plots, it could be seen that values of Y_1 and Y_2 increases upto a certain value till t < 100, after which the further change in these values is very limited. Efficiency of the reaction system,could have been fulfilled by the time reached 100 min, after which its efficiency decreased and removal of COD and dye was minimal.

In case of electric current (X_1), the removal of COD and dye i.e, Y_1 and Y_2, respectively, was very slow till $X_1 \leq 16$, after which significant increase in Y_1 and Y_2 was observed. Increase in generation of ions and subsequent hydroxides, from the anode, with increase in current passing through, could be the plausible cause for such a trend. Faraday's law also supports this argument and hence, it accepted for explaining the trend observed in this study.

A linear trend was observed in case of the Y_3 i.e., the amount of energy consumed during the reaction process. The Y_3 was observed to have direct relation with all the operating parameters. At constant value of current and lower pH, lesser energy was observed to be consumed. However, with increasing the value of current passing through the system, the increase in energy consumption was observed. At higher t, the energy consumption was also reported to increase with increased supply of current.

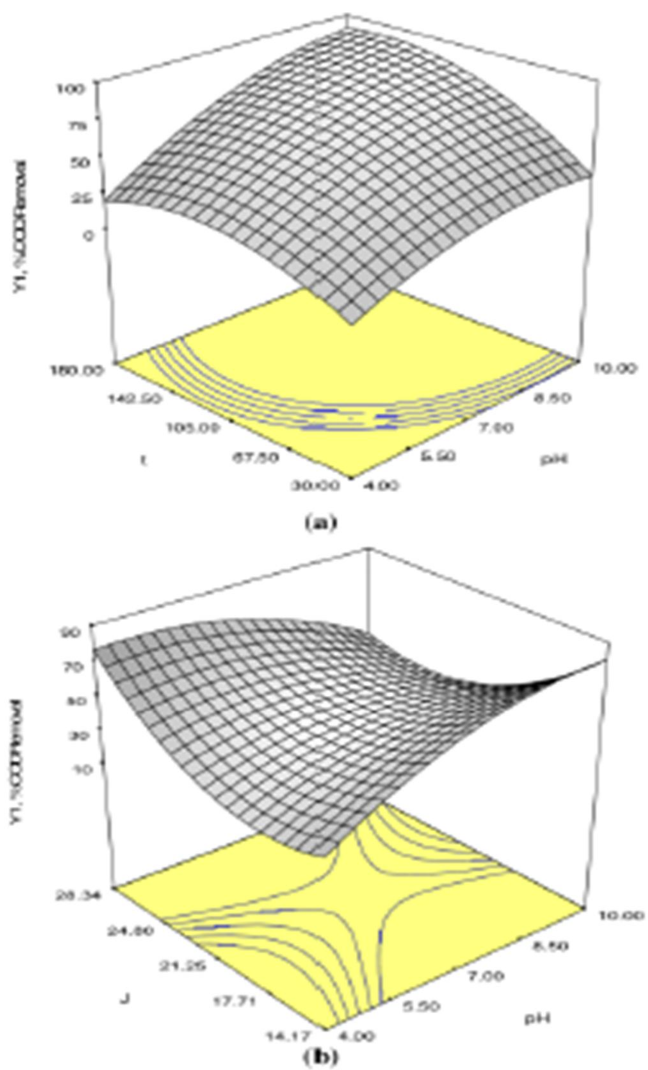

Fig – 1 Response surface plots for COD removal: (a) t v/s pH at *current* = 14.17 mA/cm^2; (b) pH v/s current at *t* = 102 min

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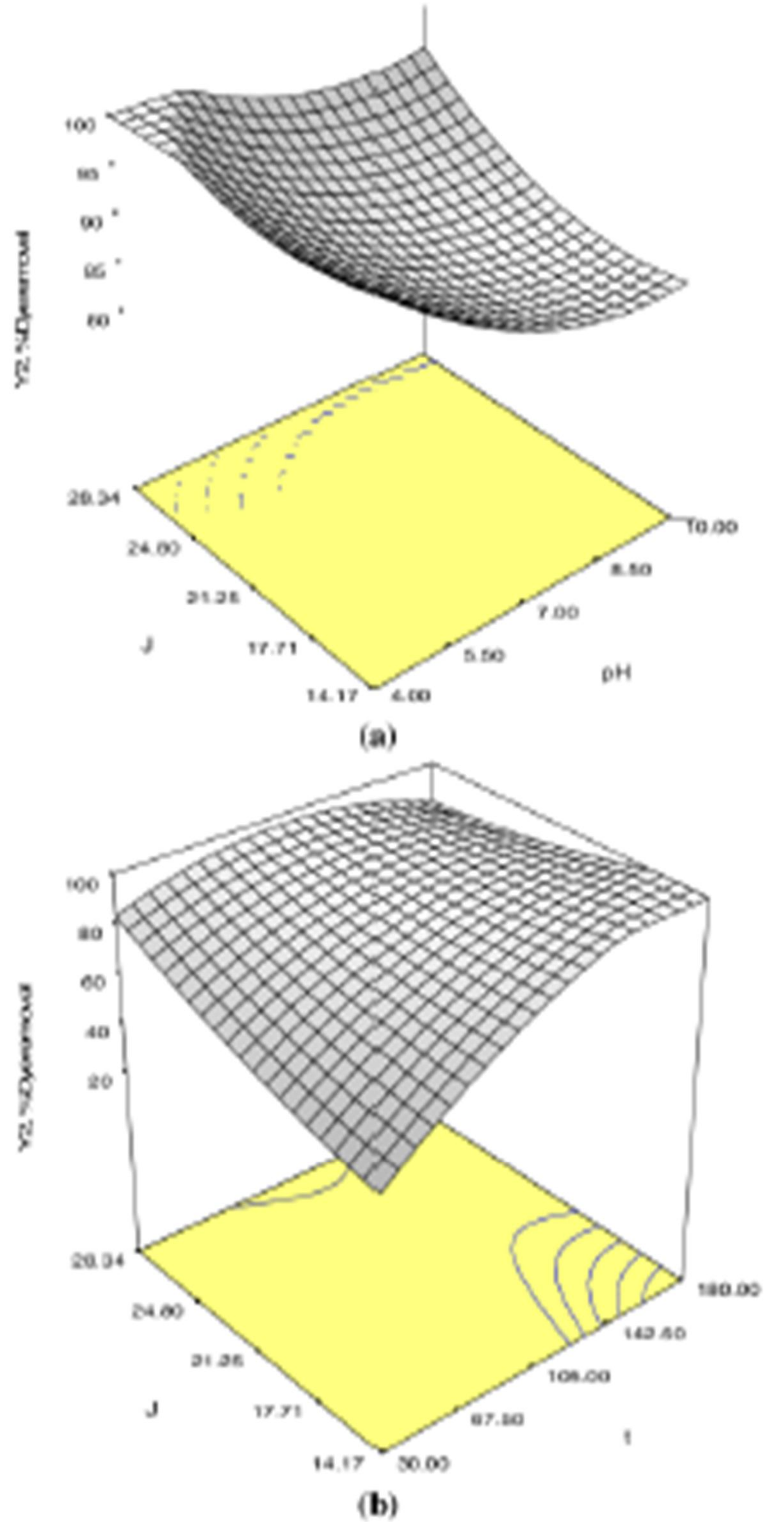

Fig – 2: Response surface plots for COD removal: (a) current v/s pH at t = 102 min; (b) current v/s t at pH = 6.25

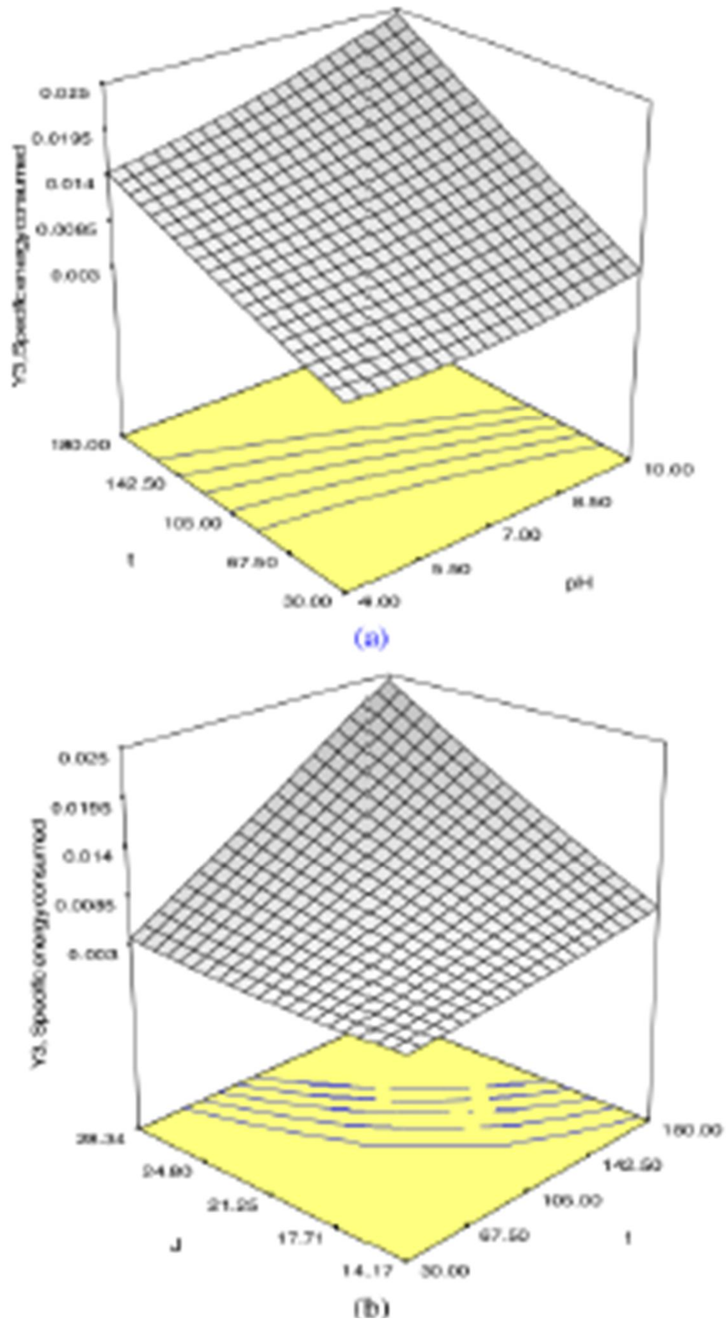

Fig – 3: Response surface plots for COD removal: (a) current v/s t at pH = 6.25; (b) pH v/s t at current = 14.17 mA/cm^2

IV. OPTIMIZATION ANALYSIS

Optimization of ECT-based decontamination of STW was conducted to obtain the maximum value of Y_1 and Y_2, however, maximum value for Y_3. Similarly, desirability functions were set to obtain the maximum value of Y_1 and Y_2 and, minimum value for Y_3. Limits/constraints applied to each response parameters was different and described in Table 1.

After applying the constraints, the optimum values of the response parameters were obtained, which are shown in Table 2. From Table 2, it is evident that the optimum values for the response parameters Y_1,Y_2 and Y_3 were 62%, 89.17% and 0.0047 kWh/litre of effluent treated, respectively. At these optimum conditions the values of the operating parameters X_1, X_2 and X_3 were observed to be 14.17 mA/cm^2, 102 min and 6.25, respectively.

The findings of optimization process were further verified by running three random runs (as shown in Table 3). The findings of these random runs depicted that values of the response parameters i.e., Y_1, Y_2 and Y_3, were observed to be 63.41%, 90.93% and

0.0035 kWh/litre of the effluent treated, respectively. As these values were similar and close to the predicted values therefore, it could be said that the models generated in this study are adequate for treating the textile wastewater.

At optimized conditions, the value of pH was observed to be 6.25 and at this pH of the reaction mixture the species of the aluminum hydroxide which were supposed to dominant are: , $Al(OH)_3$, $Al(OH)_2^+$ and $Al(OH)^{2+}$. Hence, these species further assisted in coagulation and adsorption of the contaminants and reduce the COD of the reaction mixture.

After running the experiments at optimized conditions, the amount of aluminum electrode that was observed to dissolve was of weight 2.6975 g. However, theoretically, as per Faraday's law, it should be 1.129 g. Therefore, the efficiency of the reaction mixture was observed to be 238.9% which is similar to the findings of Gao et al. (2010).

Table 1 Constraints applied for the optimization

Variables	Objective	Lower Limit	Upper Limit
J ($mAcm^{-2}$)	minimize	14.17	28.34
t (min)	minimize	30	180
pH	is in range	5	7

Table 2 Optimum condition identified for ECT of STW

Variables	Optimum values
J ($mAcm^{-2}$)	14.17
t (min)	102
pH	6.25

Table 3 Experimental and predicted values of response parameters

Parameters		Values
D		0.734
Y_1	Pre	62.2%
	Exp	63.41%
Y_2	Pre	89.17%
	Exp	90.93%
Y_3	Pre	0.0047
	Exp	0.0035

V. CONCLUSION

The findings of this study made it evident that electrochemical process may prove to be an prominent technology for the treatment of synthetic textile wastewater. Based on the findings of this study several conclusions were drawn, which are discussed as following:

A. RSM-based optimization of the treatment process proved that at optimum conditions of the response parameters, the values of operating parameters i.e., pH, current density and time were 6.25, 14.17 mA/cm^2 and 102 min, respectively.

B. At optimum conditions of the operating parameters, the values of response parameters i.e., % COD removal, % dye removal and consumption of energy during the treatment process, were observed to be 63.41%, 90.93% and 0.0035 KWh/per litre of the STW treated, respectively.

C. As value of pH was observed to be 6.25 at the optimum conditions, therefore, the species of aluminum hydroxide that were supposed to cause coagulation and adsorption would be $Al(OH)_3$, $Al(OH)_2^+$ and $Al(OH)^{2+}$.

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