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Optimisation of ozone treatment for colour and COD removal of acid dye effluent using central composite design experiment

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Abstract

Central composite design experiment is used to study the effect of ozone treatment for acid dye effluents and to optimise the variables such as salt concentration, pH and time, which influence the efficiency of colour and COD removal of dye effluents. Acid Red 88 dye is used for this study and the salt additive sodium sulphate is varied between 5 and 15 g/l, pH is between 3 and 11 and the treatment time is varied between 30 and 360 s. It is observed from the results that the treatment time plays a major role in decolouration and COD removal of the dye effluent. The increasing decolouration efficiency is obtained with increasing treatment time. At neutral pH, the efficiency of ozone is low in terms of decolouration when compared with that at acidic and alkaline pH. Lower salt concentration gives faster decolouration of the effluent while increasing the salt concentration interferes with the decolouration efficiency. Maximum COD removal of 64% is obtained at lower salt concentration in about 195 s at alkaline pH.

Keywords: Acid dyes; Ozonation; Colour removal; Experimental design; Chemical oxygen demand

1. Introduction

Textile industries produce large volume of effluents, which are very toxic, resistant to physico-chemical treatments and not easily biodegradable. The non-biodegradability of textile wastewater is due to the high content of dyestuffs, surfactants and other additives, which are generally organic compounds of complex structure [1]. Use of variety of dyes and chemicals in the dyeing processes causes considerable variation in the wastewater characteristics like pH, colour and chemical oxygen demand (COD).

Ozone is very effective for decolourising dye wastewater because it attacks conjugated double bonds and these are often associated with colour [2,3]. Ozone demand for the decolouration is greatly reduced by eliminating suspended solids. Since these are the ingredients of COD that consume large amount of ozone [4] it has been reported that the ozonation is relatively ineffective

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in reducing the COD concentration especially for the medium and high strength waste effluents. However, in conjunction with the chemical coagulation, the COD reduction is as high as 70% [5,6].

The objective of the present work is to study the decolouration and COD removal of Acid Red 88 dye effluent by using Box–Hunter design experiment. The design experiments are an alternative and more efficient approach, which are increasingly being used in biological studies. The design experiments were already used in design of dyes of high technical properties for silk [7], in structure optimisation of thiadiazole disperse dyes [8] and also for different decolouration processes [9,10]. Basically the optimisation process involves three major variations namely performing the statistically designed experiments, estimating the coefficient in a mathematical model, and predicting the response and checking the adequacy of the model. The response surface methodology is used in the Box–Hunter design of experiments [11] to develop a mathematical correlation between the salt concentration, pH and time variations for colour and COD removal of Acid Red 88 dye effluents.

2. Methodology and design of experiment

A class of five level central composite design for the estimation of parameters in a second order model was developed by Box–Hunter [11–13]. The behaviour of the system is explained by the following second-degree polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i \geq j}^{k} \sum_{i=1}^{k} \beta_{ij} x_i x_j \quad (1)$$

where $Y =$ predicted response, $\beta_0 =$ offset term, $\beta_i =$ linear effect, $\beta_{ii} =$ squared effect, $\beta_{ij} =$ interaction effect.

Several factors influence colour and COD removal of acid dye effluent, of which salt concentration, pH and time have a significant effect. Hence, these critical variables were chosen and designed as X_1, X_2, and X_3, respectively, in our model. The low, middle and high levels of each variable were designated as -1.682, 0 and $+1.682$, respectively, and the corresponding actual values for each variable are listed in Table 1. The actual design experiment is listed in Table 2. The three significant independent variables X_1, X_2 and X_3 and the mathematical relationship of the response Y on these variables can be approximated by the quadratic/(second-degree) polynomial equation as shown below,

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (2)$$

where $Y =$ predicted response, $\beta_0 =$ constant, β_1, β_2, and $\beta_3 =$ linear coefficients, β_{12}, β_{13}, and

Table 1
Actual values of the variables for the coded values

Variables	Actual values for the coded values				
	−1.682	−1.000	0	+1.000	+1.682
Salt conc., g/l (X_1)	5	7	10	13	15
pH (X_2)	3	4.6	7	9.4	11
Time, s (X_3)	30	97	195	293	360

Table 2
The central composite design for the three independent variables

Trail no.	Coded values of the variables		
	Salt conc. (X_1)	pH (X_2)	Time (X_3)
1	−1	−1	−1
2	+1	−1	−1
3	−1	+1	−1
4	+1	+1	−1
5	−1	−1	+1
6	+1	−1	+1
7	−1	+1	+1
8	+1	+1	+1
9	−1.682	0	0
10	+1.682	0	0
11	0	−1.682	0
12	0	+1.682	0
13	0	0	−1.682
14	0	0	+1.682
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

β_{23} = cross product coefficients, β_{11}, β_{22}, and β_{33} = quadratic coefficients.

The degree of experiments chosen for this study has central composite design [11,14] of three independent variables. The design is applicable to the critical variables that have been identified and it is preferred because relatively few experimental combinations of the variables are needed to estimate potentially complex response functions [15,16]. Twenty experiments are needed to estimate the 10 sets of coefficients for colour and COD removal of the model using multiple linear regression analysis. The above equation was solved using the design expert (State-Ease Inc. Statistics Made-Easy, Minneapolis, MN, Version 3.1, 1985) to estimate the response of the independent variables. All experiments were performed in duplicate. To obtain the optimum values of the independent variables, the regression equation was optimised following an iterative method [16].

3. Materials and methods

3.1. Materials

The chemical structure of Acid Red 88 dye used is given in Fig. 1. The dye used is as received from the manufacturer (Atul Limited, India). The sodium sulphate salt used is of analytical grade. The experimental set up consists of an oxygen concentrator (Sim O_2 plus, Italy) ozone generator (Ozonetek Ltd., India), ozonation chamber and ozone destructor (Ozonetek Ltd., India). A controlled flow rate of 2 l min^{-1} of oxygen is used to produce 2 g/h of ozone. The concentration of ozone is analyzed using an ozone analyzer (BMT 201, Berlin). The ozonation chamber consists of 850 mm of glass column with 50 mm of inner diameter having a capacity of 1500 ml of effluent. It is provided with a sample port at various points, an ozone gas inlet at the bottom with a ceramic diffuser over the inlet port to diffuse the oxygen/ozone gas mixture through the column. It is also provided with a closed top with a collection port to collect the unreacted ozone gas for analysis and to the thermal vent ozone destructor before venting it out. A PTFE tube is used for connecting the ozone outlet port from the ozone generator and the ozone reaction chamber.

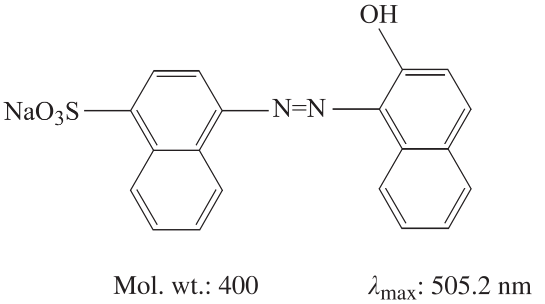

Fig. 1. Chemical structure of the dye used.

3.2. Preparation and analysis of acid dye effluents

Five hundred millilitres of effluent having a concentration of 500 μM of Acid Red 88 dye is used. Effluent is subjected to decolouration in the ozonation chamber and it is determined through absorbance at maximum wavelength (λ_{max}) of the dye by using Hitachi UV–visible spectrophotometer (U-3210), Japan. The pH of the effluent is determined by using μ pH system 361 (Systronics, India) before and after treatment. Chemical oxygen demand (COD) is analyzed by open reflux method [17].

4. Results and discussion

Response surface methodology is an empirical modelling technique, which is used to evaluate the relationship between a set of controllable experimental factors and observed results. Several factors influence colour and COD removal of acid dye effluents of which, salt concentration, pH and treatment time play a vital role. In order to study the effect of these variables central composite design is used. Treatments are carried out based on the design experiment given in Table 2. The experimental and predicted values are given in Table 3. The regression equations given below are

Table 3
Experimental and theoretically predicted values for colour and COD removal of Acid Red 88 dye effluent

Trail no.	For colour removal		For COD removal	
	Actual value (%)	Predicted value (%)	Actual value (%)	Predicted value (%)
1	61.88	60.08	42.6	40.54
2	53.28	53.59	38.5	35.55
3	58.29	57.88	52.6	49.56
4	55.85	54.67	46.4	44.17
5	97.26	102.19	55.7	57.1
6	96.21	100.36	56.8	59.02
7	98.25	101.69	52.2	54.32
8	97.58	103.13	54.6	55.84
9	95.92	94.05	55.8	56.33
10	93.26	89.81	52.8	53.41
11	97.85	95.13	55.6	56.02
12	98.2	95.6	60.2	60.93
13	11.18	14.8	18.4	24.1
14	99.92	90.97	52.4	47.84
15	94.38	94.31	55.4	54.03
16	96.92	94.31	54.2	54.03
17	93.38	94.31	54.2	54.03
18	92.92	94.31	52.8	54.03
19	94.25	94.31	52.4	54.03
20	93.12	94.31	55.4	54.03

obtained after the analysis of variance gives the level of percent colour and COD removal:

$$\begin{aligned}\%\ \text{Colour removal} = {} & 94.3130 - 1.2618X_1 \\ & + 0.1412X_2 + 22.6428X_3 \\ & - 0.8412X_1^2 + 0.3729X_2^2 \\ & - 14.6405X_3^2 + 0.8175X_1X_2 \\ & + 1.1650X_1X_3 \\ & + 0.4225X_2X_3 \qquad (3)\end{aligned}$$

$$\begin{aligned}\%\ \text{COD removal} = {} & 54.0339 - 0.8673X_1 \\ & + 1.4597X_2 + 7.0571X_3 \\ & + 0.2974X_1^2 + 1.5698X_2^2 \\ & - 6.3831X_3^2 - 0.1X_1X_2 \\ & + 1.725X_1X_3 - 2.95X_2X_3 \qquad (4)\end{aligned}$$

To test the estimated regression equation for the goodness of fit, Fisher's F-test is employed and the multiple correlation coefficient R^2 is calculated. Square regression is significant at a level of 98% and 94% for colour and COD removal, respectively. The fitted regression equation shows a good fit of the model.

4.1. Effect of time

The time required for complete decolouration is considered only for the analysis of the variables, such as salt concentration and pH on decolouration. The time required for complete decolouration of the effluents is found out by determining X_3 from the regression equation (3) by substituting $Y = 100\%$ for different values of X_1 and X_2. The complete decolouration time for various conditions is calculated and given in Table 4. It is observed from the results that the time taken for complete colour removal is low at pH 3 and 11 and it is high at pH 7. This indicates that the reaction between ozone and substrate occurs by means of molecular ozone and hydroxyl radicals, which are highly reactive species. Therefore higher colour removal rate is obtained at both acidic and alkaline pH.

The result of the effect of pH and salt concentration on percent COD reduction with respect to time is given in Table 5. It can be seen from the table that at a given pH and salt concentration the percent COD reduction increases with time and then decreases. The increase in the COD reduction may be due to the reduction in organic content of the effluent caused by ozonation. Lopez et al. [18] have observed that a reduction of COD on ozone treatment of industrial textile effluents is due to the reduction of total organic carbon (TOC) and partial oxidation of organic substrates. Koynnchu and

Table 4
Time taken for complete decolouration of Acid Red 88 dye effluents

Salt conc. (g/l)	Time (s)				
	pH				
	3	5	7	9	11
5	211	223	234	231	230
7	211	220	226	225	225
10	222	226	226	223	216
13	240	247	250	230	219
15	248	254	268	242	226

Table 5
Percent COD reduction of Acid Red 88 dye effluents on ozone treatment

Time (s)	Salt conc. (g/l)																								
	pH																								
	5					7					10					13					15				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
30	25	27	31	38	47	22	24	28	35	44	18	20	24	31	39	14	16	21	27	36	13	14	19	25	34
97	43	43	46	51	58	40	41	43	48	55	38	38	41	45	52	36	36	38	43	50	34	35	37	42	49
120	47	47	49	54	60	45	45	47	52	58	43	43	45	49	56	41	41	43	47	54	41	40	42	46	52
195	58	56	56	59	64	57	55	55	58	62	56	54	54	56	61	56	53	53	56	60	56	53	53	56	60
270	61	57	56	56	59	61	57	56	56	59	62	57	56	56	59	62	58	56	57	59	63	59	57	58	60
293	61	56	54	54	56	61	56	54	54	56	62	57	55	55	57	63	58	56	56	58	64	60	57	57	59
360	55	49	45	44	44	56	50	46	44	45	58	52	48	46	46	61	54	50	48	49	63	56	52	50	50

Afsar [19] and Perkins et al. [20] have also observed a similar trend in the treatment of reactive dye and acid dye effluents, respectively. The decrease in percent COD reduction at the end of treatment may be attributed to the formation of certain persistent substances occurring due to ozonation.

4.2. *Effect of salt concentration*

Fig. 2 shows the extent of colour removal against the salt concentration and time. It is observed from the plot that at any given salt concentration the colour removal increases with increasing treatment time. It is also observed from the same figure that at a given treatment time, with increasing salt concentration the percent colour removal is not significantly increased. However, the time taken for complete decolouration increases with increasing salt concentration. The reason for this may be due to increasing the solid content in the dye bath effluent, which interferes with the reaction of ozone. It is reported that the sulphonic acid group present in the dye and salts of sodium sulphate produce sulphate radicals during its decomposition [21]. The sulphate radical

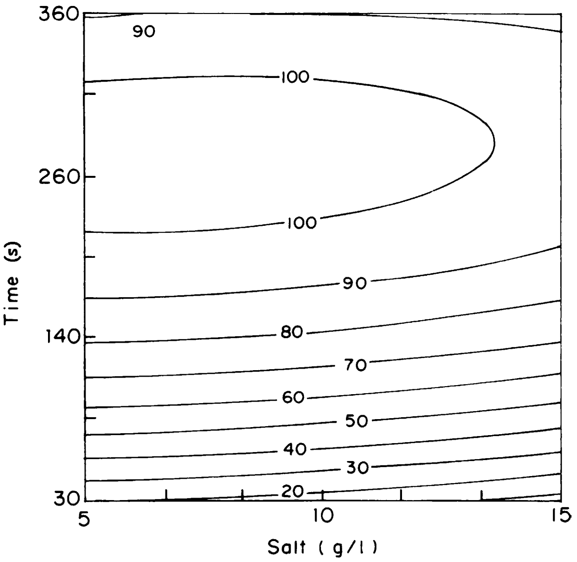

Fig. 2. Effect of salt concentration on percent colour removal of Acid Red 88 dye effluents at pH 3.

has the unique nature of attacking the dye molecule at various positions resulting in rapid fragmentation of the dye molecules [22]. The optimum condition for complete decolouration is calculated from the regression equation (3) by solving the inverse matrix. It is found that at 5 g/l of salt concentration and at pH 3 the dye decoloured completely at 211 s.

Fig. 3 represents the extent of percent COD removal of Acid Red 88 dye effluent. At a given time, by increasing the salt concentration, the percent COD removal decreases. However at a given salt concentration, the percent COD removal increases with time up to a particular level and then decreases. The probable reason behind this is may be the structured polymer dye molecules in this effluent are oxidised by ozone resulting in the production of small molecules such as acetic acid, aldehydes and ketones instead of CO_2 and water [23]. These small molecules increase the COD content in the effluent rather than decreasing it. The maximum COD removal is obtained at 5 g/l of salt concentration. The optimum value is obtained by the derivation of the regression equation (4) and by solving the inverse matrix. The optimum condition for maximum percent COD removal occurs when the salt concentration is 5 g/l at pH 11.

4.3. *Effect of pH*

The solubility of ozone is readily affected by pH, temperature, ionic strength and presence of radical scavengers in the liquor. The influence of pH is the result of the relationship between oxidation potential and decomposition behavior of ozone. In acidic pH, the ozone is available as molecular ozone and in alkaline pH it decomposes into secondary oxidants such as $OH^\bullet$, $HO_2^\bullet$, $HO_3^\bullet$ and $HO_4^\bullet$. Among these, $OH^\bullet$ is an important one and has the highest oxidation potential of 2.8 V. The oxidizing potential of ozone decreases from 2.08 V at acidic pH to 1.4 V in alkaline solutions [24]. This indicates that the ozone stability decreases with increasing pH resulting in generation of secondary oxidants. Fig. 4 shows the percent colour removal of selected dye effluents against pH versus time at 5 g/l of salt concentration. It is observed from the plot that at a given pH, the percent colour removal increases with increasing treatment time. However, the time taken for complete colour removal increases with

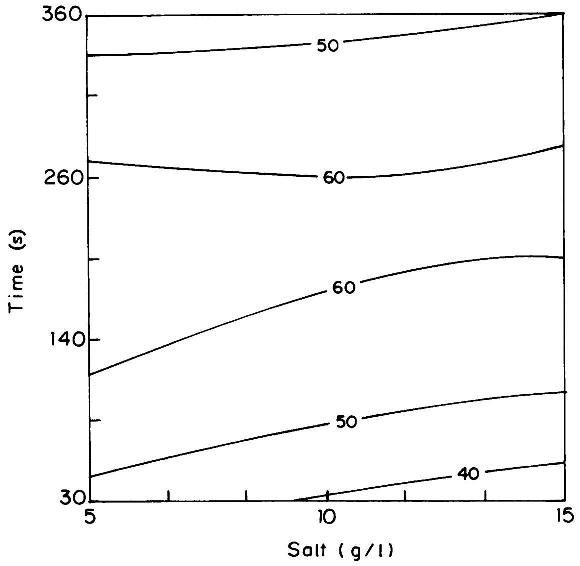

Fig. 3. Effect of salt concentration on percent COD removal of Acid Red 88 dye effluents at pH 11.

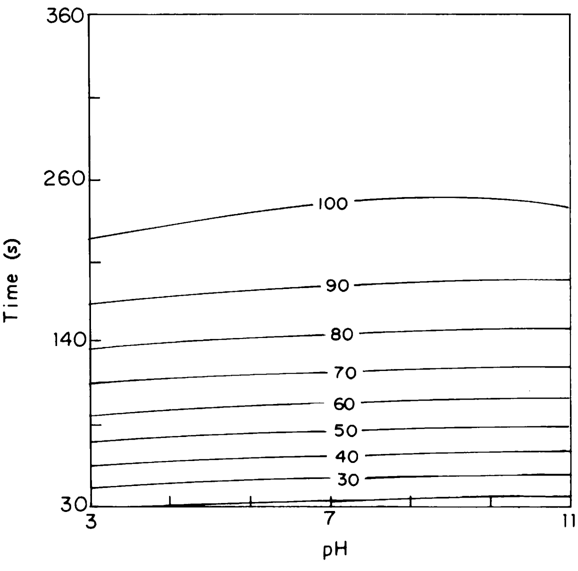

Fig. 4. Effect of pH on percent colour removal of Acid Red 88 dye effluents at 5 g/l salt concentration.

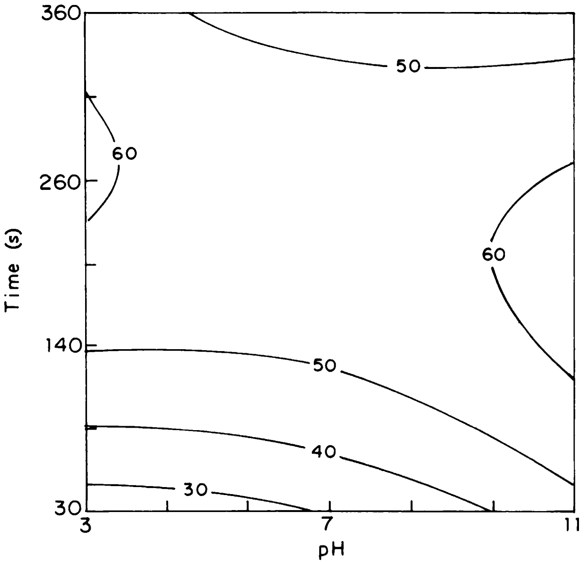

Fig. 5. Effect of pH on percent COD removal of Acid Red 88 dye effluents at 5 g/l salt concentration.

increasing pH up to 7, beyond this level it decreases. This clearly indicates that the two different oxidizing mechanisms i.e., in acidic pH molecular ozone remains as the main oxidant and at alkaline pH it decomposed to produce hydroxyl radical which acts as oxidant. Even though the hydroxyl radical has higher oxidation potential than ozone, its selectivity is very less [25]. The optimum condition for colour removal occurs at pH 3 when the salt concentration is 5 g/l.

Fig. 5 shows the percent COD removal of the dye effluent at 5 g/l of salt concentration. It is observed from the plot that at a minimum treatment time, the percent COD removal increases with pH. However at the maximum treatment time it decreases with pH. The optimum condition for COD removal is calculated from the regression equation (4). Maximum COD removal of 64% is obtained at lower salt concentration in about 195 s at alkaline pH.

5. Conclusions

The effect of ozone treatment on acid dye effluent is studied by using central composite design experiment. The salt concentration, pH and treatment time influence the colour and COD removal of Acid Red 88 dye effluents. It is concluded from this study that the percent colour removal increases with increasing treatment time. Complete decolouration time increases with increasing salt concentration. Acidic and alkaline pH take less time for complete decolouration when compared with that of neutral pH. At minimum treatment time the percent COD reduction increases; however, it decreases at maximum time.

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