International Journal of Industrial Chemistry (IJIC)
a SpringerOpen Journal

RESEARCH Open Access

Decolorization of organic dye solution by ozonation; Optimization with response surface methodology

Masoud B Kasiri*, Nasser Modirshahla and Hasan Mansouri

Abstract

Background: Ozone was used as a strong oxidant for decolorization of solution containing organic dyes. Three azo dyes, CI acid black 1 (AB1), CI acid yellow 19 (AY19) and CI acid orange 7 (AO7) which are widely used colorants in leather dyeing and finishing processes, were quantified with colorimetry. The effects of influential parameters including the ozone dosage, initial concentration of the dyes, initial pH of the solution, and temperature on the decolorization efficiency were studied. Central composite design (CCD) was applied to the optimization of decolorization of the dye solution by ozonation, and a second-order polynomial equation was proposed to predict the process efficiency.

Results and discussion: Predicted results were found to be in good agreement with experimental values (R^2 = 0.9365, 0.9643, and 0.9296 for AB1, AY19, and AO7 respectively), which proves the suitability of the model employed and the success of CCD in optimizing the conditions of ozonation process. The variation of process efficiency as a function of independent variables was shown by graphical response surfaces.

Conclusions: It was found that response surface methodology could effectively predict and optimize the performance of ozonation process for decolorization of solution containing organic dyes, AB1, AY19, and AO7. Also, the optimum values of the process variables to achieve the maximum decolorization efficiency could be calculated and verified experimentally.

Keywords: Color removal, Modeling, Central composite design, Ozonation, Response surface methodology

Background

There are more than 10,000 chemicals used as colorants and among them, organic dyes are the most used and important ones. The properties of organic dyes, such as brightness, visible color at low concentrations, chemical structure, and resistance to light and chemical attack, make them fairly resistant to degradation [1]. Leather industry consumes widely organic dyes where large quantities of them remain in the effluent after dyeing and finishing processes. Different classes of dyes are used for different types of leather including the sole, upholstery, garment, gloves, and bags. But azo dyes come on the top of this list [2].

Due to the toxicity and slow degradation, the azo dyes are classified as environmentally hazardous materials [3]. These dyes are the major cause of both surface and ground water bodies contamination because of their carcinogenicity and toxicity to aquatic life, and they are also easily detected and with undesirable aesthetic aspects [4,5].

A broad range of physicochemical methods has been proposed for treatment of dyeing effluents including biological [6], adsorption [7,8], membrane [9], coagulation-flocculation [10], oxidation-ozonation [11], and advanced oxidation processes (AOPs) [12,13].

Ozonation, one of the most used AOPs, is an oxidative process in which the oxidizing agent used is ozone (O_3). Interest in the use of ozone in wastewater treatment has increased considerably in recent years due to the numerous advantages of this process. Among them is the high oxidation potential of ozone

* Correspondence: m_kasiri@tabriziau.ac.ir
Department of Chemistry, Tabriz Branch, Islamic Azad University, P.O. Box 5157613613, Tabriz, Iran

(2.08 V), even at low concentrations, with its high efficiency in the decomposition of organic matter and in the addition of oxygen to water [14]. In addition and unlike in other oxidizing agents such as Cl_2, oxidation with O_3 leaves no toxic residues that must be removed or disposed [15].

Degradation process with ozone proceeds in two different ways: direct and radical reaction. At acidic pH, molecular ozone selectively attacks specific parts of organic molecules like double bonds or aromatic systems of reactive dyes in direct reaction. At alkaline pH, hydroxide radicals coming from ozone decomposition react unspecifically with organic compounds [16]. The alkaline to neutral pH of dyeing wastewater favors the unspecific radical reaction. However, the pH of the solution may decrease around the dye molecules due to the formation of organic acids such as the ozonation products. Therefore, the reaction mechanism shifts towards the selective direct oxidation [17].

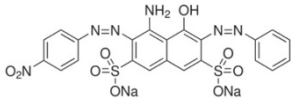
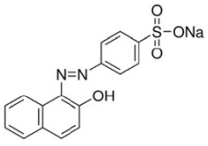
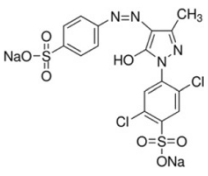
The mechanism of O_3 reaction was studied by Hoigne [16]. Ozone reacts directly with pollutants via ozonolysis and through radical chain reaction. The reaction of ozone with hydroxide anions to intermediate radicals and to hydroxyl radicals is important for the oxidation of saturated organic compounds where no molecular ozonolysis is possible [18].

As it has been previously shown [19], the efficiency of color removal by ozone is dependent on various parameters such as the ozone dosage, initial dye concentration, initial pH, reaction time, and temperature of the solution. In conventional methods used to determine the influence of each one of these parameters, experiments were carried out by varying systematically the studied parameters and keeping constant the others. These should be repeated to all the influencing parameters, resulting in an unreliable number of experiments. In order to optimize the value of effective parameters with the minimum number of experiments, central composite design - the most widely used form of response surface methodology (RSM) - was employed to find improved or optimal process settings in an efficient use of the experimental data. Using RSM, it is possible to estimate linear, interaction, and quadratic effects of the factors and to provide a prediction model for the response.

This method has been used for modeling and optimization of decolorization process by advanced oxidation processes [20,21]. However, to the best of our knowledge, decolorization of organic dye solutions by ozonation and the effect of interaction of effective parameters using central composite design have not been studied.

In this work, the central composite design has been applied to the modeling and optimization of decolorization of dye solutions containing acid black 1 (AB1), acid orange 7 (AO7), or acid yellow 19 (AY19) by ozonation have been studied. These three dyes are comprehensively used in Iran's tanneries for leather dyeing and finishing. The influencing factors (variables) investigated were the dye and ozone initial concentration, initial pH of the solution, and the temperature and decolorization efficiency was monitored as the process response. Counter plots and response surfaces

Table 1 Chemical structure and characteristics of the dyes

Name	Chemical structure	Molecular formula	Color index number	λ_{max} (nm)	M_w (g/mol)
Acid black 1		$C_{22}H_{14}N_6Na_2O_9S_2$	20470	618	616.49
Acid orange 7		$C_{16}H_{11}N_2NaO_4S$	15510	484	350.32
Acid yellow 19		$C_{16}H_{10}Cl_2N_4Na_2O_7S_2$	18965	401	551.29

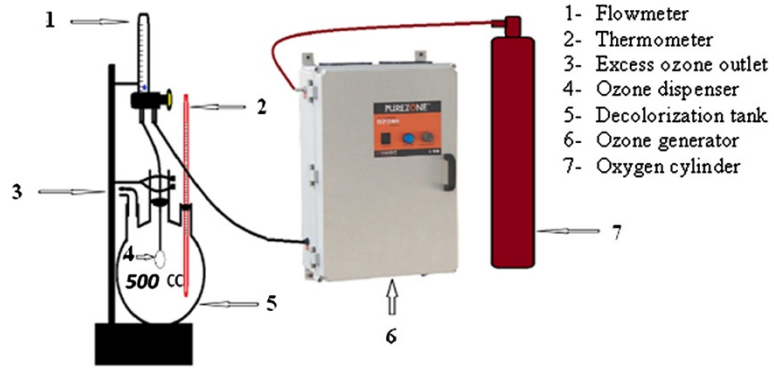


Figure 1 Experimental setup for ozonation batch experiments.

were drawn to predict the efficiency of the decolorization process under different values of the independent parameters.

Methods

Reagents

Ozone was continuously produced by an ozone generator (model 1000 mg/L, Nano Paak Sayyal, Iran). The dyes, AB1, AO7, and AY19, were obtained from Azar Paints Company, Tabriz, Iran. Their structure and characteristics are given in Table 1. Sulfuric acid and sodium hydroxide were of laboratory reagent grade and were obtained from Merck Inc., Darmstadt, Germany.

Ozonation experimental setup

For decolorization process, ozonation was carried out in a batch reactor, 500 ml in volume, equipped with a magnetic stirrer and a thermometer. Experimental setup for ozonation batch experiments is shown in Figure 1.

Experimental design

In this work, central composite design, which is a widely used form of RSM, was employed for the optimization of decolorization process. In order to evaluate the influence of operating parameters on the decolorization efficiency of the dyes, four independent factors were chosen: ozone concentration (X_1), initial dye concentration (X_2), initial pH of the solution (X_3), and temperature (X_4). A total of 31 experiments were done in this work, including 2^4 = 16 cube points, 2 × 4 = 8 axial points and seven replications at the center point.

Experimental data were analyzed using the response surface regression procedure of a statistical analysis system (NemrodW version 2000 LPRAI, Marseille, France). For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (1)$$

where X_0 is the value of X_i at the center point and δX presents the step change [22]. The experimental ranges and the levels of the independent variables for dye removal are given in Table 2.

Results and discussion

Second-order polynomial model

In this work, a central composite design was used to propose a mathematical model of the process behavior. This method involves the performing of the experiments according to the design, factors, and levels selected, estimating the coefficients of the mathematical model to predict the response and finally, check the adequacy of the model obtained [23]. The central composite design (CCD) matrix and experimental results obtained during the ozonation process are presented in Table 3.

A second-order polynomial response equation (Equation 2) was proposed to correlate the dependent and independent

Table 2 Experimental ranges and levels of the independent test variables

Variable	Range and level				
	−2	−1	0	+1	+2
Ozone concentration (mg/L) (X_1)	200	400	600	800	1000
Initial dye concentration (mg/L) (X_2)	10	20	30	40	50
Initial pH (X_3)	3.0	4.5	6.0	7.5	9.0
Temperature (°C) (X_4)	25	30	35	40	45

Table 3 The 4-factor central composite design matrix and the value of response function (CR%)

Run	[Ozone] (mg/L)	$[Dye]_0$ (mg/L)	Initial pH	Temperature (°C)	Decolorization efficiency (%)					
					Experimental			Predicted		
					AB1	AY19	AO7	AB1	AY19	AO7
1	−1	1	1	1	76	80	58	78.03	79.20	59.83
2	1	−1	1	−1	80	93	52	82.20	92.04	57.33
3	2	0	0	0	76	86	56	72.41	87.37	53.00
4	1	1	−1	1	57	50	32	59.20	51.20	36.16
5	0	0	0	0	76	85	61	74.30	83.42	58.00
6	1	1	−1	−1	54	63	39	55.54	62.04	41.00
7	0	0	0	−2	71	89	47	71.00	87.60	43.00
8	1	−1	−1	−1	78	81	50	77.20	81.04	52.16
9	−1	−1	−1	1	75	80	47	73.00	78.00	51.66
10	1	−1	−1	1	75	90	48	79.87	85.00	50.00
11	0	0	0	2	79	77	55	74.30	78.00	58.00
12	−1	1	1	−1	75	86	44	71.37	90.45	44.83
13	−2	0	0	0	67	85	58	68.08	83.00	54.00
14	0	0	0	0	73	82	56	74.30	83.42	58.00
15	−1	1	−1	−1	52	65	33	54.37	60.54	36.66
16	−1	−1	1	1	85	89	74	84.70	93.00	74.83
17	0	−2	0	0	92	92	75	90.41	92.00	71.00
18	0	0	0	0	77	86	57	74.30	83.42	58.00
19	0	0	0	0	74	85	59	74.30	83.42	58.00
20	0	0	0	0	71	82	55	74.30	83.42	58.00
21	−1	1	−1	1	59	46	40	58.03	48.20	37.66
22	0	0	−2	0	61	43	42	56.75	46.00	38.33
23	1	1	1	1	78	81	57	76.20	77.70	57.33
24	1	1	1	−1	67	89	46	69.45	90.54	45.33
25	0	2	0	0	63	61	48	62.08	61.00	45.00
26	0	0	0	0	74	81	57	74.30	83.42	58.00
27	−1	−1	−1	−1	68	70	48	71.04	74.54	50.66
28	−1	−1	1	−1	80	92	57	79.04	90.04	56.33
29	0	0	2	0	80	92	61	81.75	88.24	61.66
30	1	−1	1	1	89	89	75	87.87	93.00	72.33
31	0	0	0	0	75	83	61	74.30	83.42	58.00

variables:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} b_{ij} x_i x_j \qquad (2)$$

where Y is a response variable of decolorization efficiency; b_i, the regression coefficients for linear effects; b_{ii}, the regression coefficients for quadratic effects; b_{ij}, the regression coefficients for interaction effects; x_i are coded experimental levels of the variables.

Based on the experimental results, the value of the coefficients was estimated and the second-order equation for predicting the efficiency of the process for each dye was expressed as follows (Equations 3, 4, and 5):

$$\begin{aligned}(\mathrm{AB1})\, Y = {} & 74.286 + 1.083\, x_1 - 7.083\, x_2 + 6.250\, x_3 \\ & + 2.333\, x_4 - 1.250\, x_1 x_2 - 0.750\, x_1 x_3 \\ & + 0.000\, x_1 x_4 + 2.250\, x_2 x_3 + 0.250\, x_2 x_4 \\ & + 0.750\, x_3 x_4 - 1.009\, x_1^2 + 0.491\, x_2^2 \\ & - 1.259\, x_3^2 - 0.134\, x_4^2 \end{aligned} \qquad (3)$$

$$(\mathrm{AO7})Y = 58.000 - 0.250\,x_1 - 6.500\,x_2 - 6.833\,x_3 + 3.250\,x_4 + 0.000\,x_1x_2 - 0.250\,x_1x_3 - 0.750\,x_1x_4 - 0.250\,x_2x_3 - 0.750\,x_2x_4 + 4.250\,x_3x_4 - 1.125\,x_1^2 - 0.000\,x_2^2 - 2.500\,x_3^2 - 2.625\,x_4^2 \quad (4)$$

$$(\mathrm{AY19})Y = 83.429 + 1.250\,x_1 - 7.750\,x_2 + 10.500\,x_3 - 2.417\,x_4 - 1.000\,x_1x_2 - 1.125\,x_1x_3 + 0.125\,x_1x_4 + 4.375\,x_2x_3 - 3.625\,x_2x_4 - 0.500\,x_3x_4 + 0.455x_1^2 - 1.795\,x_2^2 - 4.045\,x_3^2 - 0.170\,x_4^2 \quad (5)$$

The decolorization efficiencies (CR%) have been predicted by Equations 3, 4, and 5 and presented in Table 3. Based on the results indicated in this table, there are good agreements between the experimental and predicted values of decolorization efficiency.

Second-order polynomial models validation

The predicted values of decolorization obtained using models (Equations 3, 4, and 5) are plotted against the experimental results and shown in Figure 2. The coefficient of determination (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. This coefficient belongs to the line that best fits on the data of the scatter plot with equation $Y = ax + b$ and it is obtained with regression analysis based on the minimization of the squared errors. When this factor is closer to 1 and also, the coefficients of the line equation are closer to 1 and 0, respectively, the model is better. As can be seen in this figure, the predicted values match the experimental results reasonably well with R^2 of 0.936, 0.964, and 0.929 for AB1, AY19, and AO7.

The values prove the good adjustments of the predicted values to the experimental results, since those indicate that 0.936, 0.964, and 0.929 values of the variability in the response could be explained by the models. These values imply 93.6%, 96.4%, and 92.9% of the variations for AB1, AY19, and AO7 dyes, respectively; removal efficiency are explained by the independent variables. This also means that these models do not explain only about 6.4%, 3.6%, and 7.1% of variations for the removal of AB1, AY19, and AO7, respectively.

Analysis of variance and fitting the quadratic model

Analysis of variance (ANOVA) is a mean to test the significance and adequacy of the model [24]. Table 4 indicates the results of the quadratic response surface model fitting in the form of analysis of variance. The values of R^2 show that the proposed models predict the performance of the

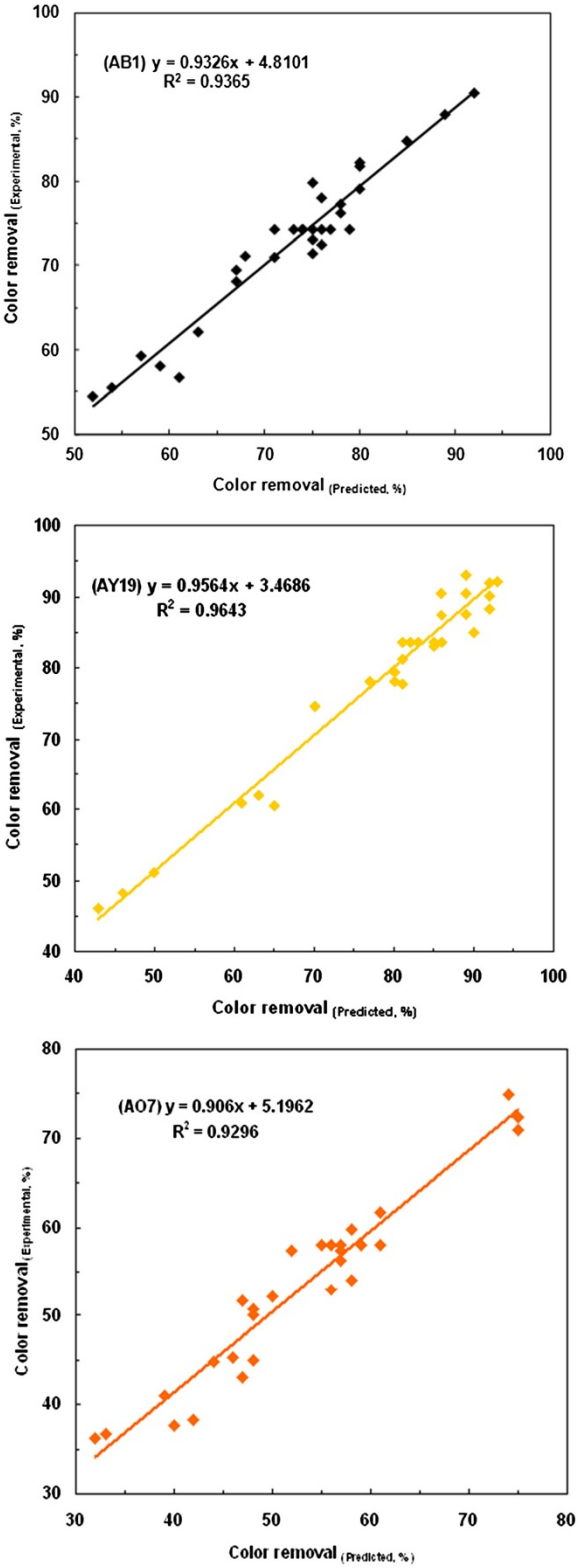


Figure 2 Comparison of experimental results and the predicted values of the response variable (CR%). Top image, AB1; middle, AY19; bottom, AO7.

Table 4 ANOVA for fit of the dye decolorization efficiency from central composite design

Source of variations	Regression			Residual			Total		
	AB1	AY19	AO7	AB1	AY19	AO7	AB1	AY19	AO7
Sum of squares	2507.66	5376.69	3058.86	149.17	236.79	331.33	2656.84	5613.48	3390.19
Degree of freedom	14	14	14	16	16	16	30	30	30
Adjusted mean square	179.11	384.04	218.49	9.32	14.79	20.70	-	-	-
***F* value**	19.21	25.96	10.55	-	-	-	-	-	-

AB1, R^2 = 0.944; adjusted R^2 = 0.895; AY19, R^2 = 0.958; adjusted R^2 = 0.921; AO7, R^2 = 0.902; adjusted R^2 = 0.817.

decolorization process with high accuracy. Adjusted R^2 is also a measure of goodness of a fit, but it is more suitable for comparing models with different numbers of independent variables. It corrects the R^2 value for the data counts and the number of terms in the model by using the degrees of freedom on its computations, so if there are many terms in a model and not very large sample size, adjusted R^2 may be visibly smaller than R^2 [25,26]. In this study, adjusted R^2 values (0.895, 0.921, and 0.817 for AB1, AY19, and AO7 respectively) were very close to the corresponding R^2 values (see Table 4).

ANOVA shows whether the variation from the model is significant or not when compared with the ones associated with residual error [27,28]. The F value, which is the ratio between the mean square of the model and the residual error, performs this comparison. If the proposed model be a good predictor of the experimental results, the F value should be greater than the tabulated value of the F distribution for a certain number of degrees of freedom in the model at the level of significance α. The F values obtained, 19.21, 25.96, and 10.55 for AB1, AY19, and AO7, respectively, are clearly greater than the tabulated F (2.352 at 95% significance) confirming the adequacy of the model fits. The experimental error (1.98%, 1.90%, and 2.38% for AB1, AY19, and AO7 respectively) due to uncontrolled factors was calculated from the replicates of the center point.

The regression coefficient values, standard deviation, t value, and P value are given in Table 5. The Student's t test was used to determine the significance of the regression coefficient of the parameters. The P values were also used as a tool to check the significance of each of the coefficients, which, in turn, are necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of t value and smaller P value, the more significant is the corresponding coefficient [29].

b_3 is significant at a level less than 5% for all the dyes studied. The interaction coefficient b_{23} for AB1 and AY19 and the interaction coefficient b_{34} for AO7 are also significant at a level less than 5%. Therefore, the

Table 5 Estimated regression coefficients and corresponding *t* and *P* values from the data of central composite design experiments

Coefficient	Parameter estimate			*t* value			*P* value		
	AB1	AY19	AO7	AB1	AY19	AO7	AB1	AY19	AO7
b_0	74.286	83.429	58.000	64.37	116.03	64.46	< 0.01	< 0.01	< 0.01
b_1	1.083	1.250	−0.250	1.74	3.22	−0.51	10.1	1.82	62.5
b_2	−7.083	−7.750	−6.500	−11.36	−19.96	−13.38	< 0.01	< 0.01	< 0.01
b_3	6.250	10.500	6.833	10.03	27.04	14.06	< 0.01	< 0.01	< 0.01
b_4	2.333	−2.417	3.250	3.74	−6.22	6.69	0.177	0.0796	0.0542
b_{11}	−1.009	0.455	−1.125	−1.77	1.28	−2.53	9.6	24.8	4.48
b_{22}	0.491	−1.795	−0.000	0.86	−5.04	−0.00	40.2	0.235	100.0
b_{33}	−1.259	−4.045	−2.500	−2.20	−11.37	−5.62	4.25	< 0.01	0.136
b_{44}	−0.134	−0.170	−2.625	−0.23	−0.48	−5.90	81.8	65.0	0.106
b_{12}	−1.250	−1.000	0.000	−1.64	−2.10	0.00	12.1	8.0	100.0
b_{13}	−0.750	−1.125	−0.250	−0.98	−2.37	−0.42	34.0	5.6	68.9
b_{23}	2.250	4.375	−0.250	2.95	9.20	−0.42	0.946	< 0.01	68.9
b_{14}	0.000	0.125	−0.750	0.00	0.26	−1.26	100.0	80.1	25.4
b_{24}	0.250	−3.625	−0.750	0.33	−7.62	−1.26	74.8	0.0266	25.4
b_{34}	0.750	−0.500	4.250	0.98	−1.05	7.14	34.0	33.4	0.0380

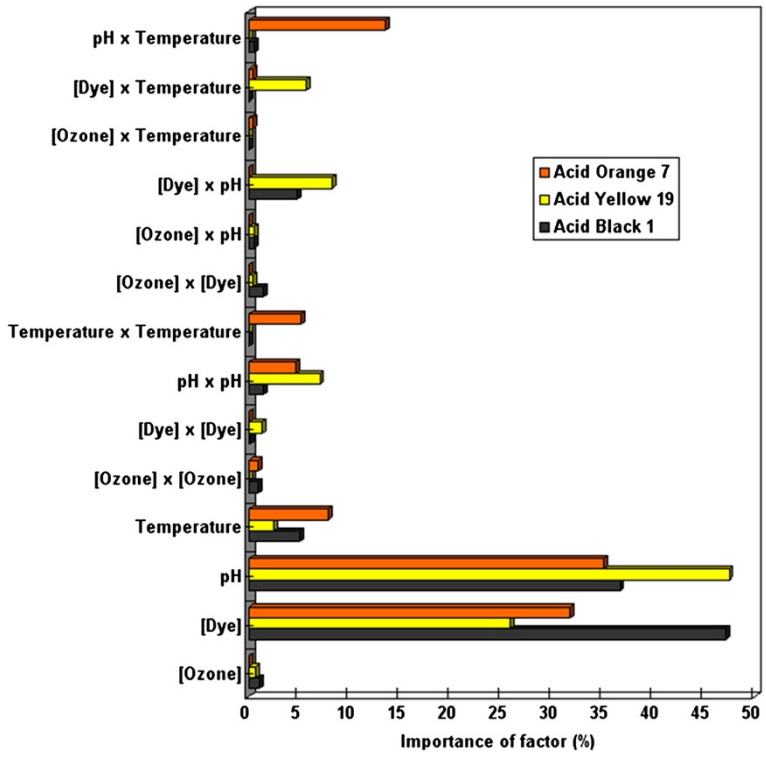


Figure 3 Pareto graphic analysis of the factors.

initial pH for all the dyes (coefficient b_3), the interaction of the dye concentration and initial pH for AB1 and AY19 removal (coefficient b_{23}), and the interaction of initial pH and the temperature for AO7 removal (coefficients b_{34}) are the most influential factors. The significance of these quadratic and interaction effects between the variables would have been lost if the experiments were carried out by conventional methods.

Moreover, the Pareto analysis is a mean that gives more significant information to interpret the results. It calculates the percentage effect of each factor on the response, according to the equation [30]:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} b_{ij} x_i x_j \qquad (6)$$

where P_i is the relative importance of factor. Figure 3 shows the Pareto graphic analysis. As can be seen in this figure among the variables, initial dye concentration and

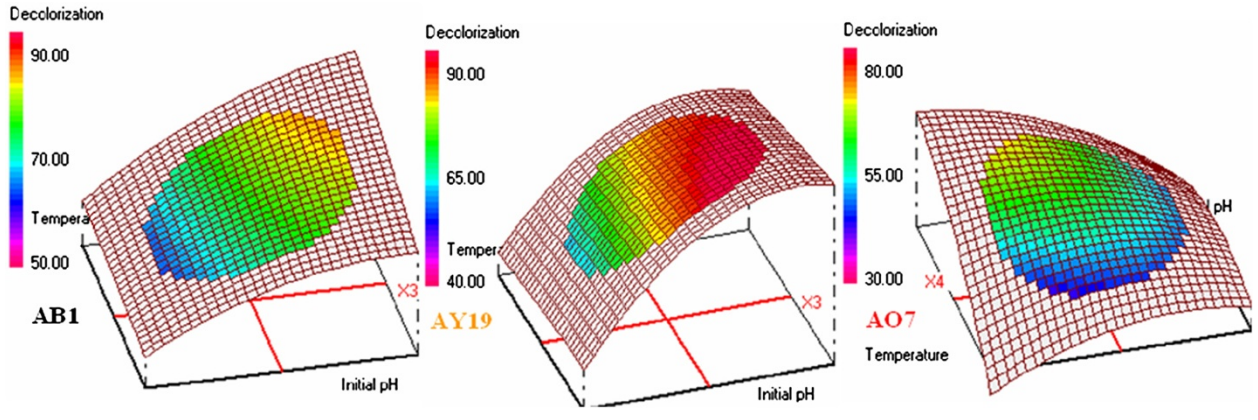


Figure 4 Response surfaces for decolorization process as a function of temperature and initial pH of the solution.

pH of the solution have the more influential effect on the decolorization process efficiency.

So, the insignificant terms can be removed from the RSM models, and the reduced and best fitted models for decolorization efficiencies (CR%), developed from the regression procedure and supported by ANOVA and Pareto analysis, could be presented as (Equations 7, 8, and 9)

$$(\mathrm{AB1})Y = 74.286 + 1.083\,x_1 - 7.083\,x_2 + 6.250\,x_3 + 2.333\,x_4 - 1.250\,x_1x_2 + 2.250\,x_2x_3 - 1.009x_1^2 - 1.259x_3^2 \quad (7)$$

$$(\mathrm{AO7})Y = 58.000 - 0.250\,x_1 - 6.500\,x_2 - 6.833\,x_3 + 3.250\,x_4 - 0.250\,x_2x_3 + 4.250\,x_3x_4 - 1.125x_1^2 - 2.500x_3^2 - 2.625x_4^2 \quad (8)$$

$$(\mathrm{AY19})Y = 83.429 + 1.250\,x_1 - 7.750\,x_2 + 10.500\,x_3 - 2.417\,x_4 - 1.000\,x_1x_2 - 1.125\,x_1x_3 + 4.375\,x_2x_3 - 3.625\,x_2x_4 - 0.500\,x_3x_4 - 1.795x_2^2 - 4.045x_3^2 \quad (9)$$

Effect of variables as response surface and counter plots

The response surfaces were drawn with two variables kept constant at their zero level and the other two varying within the experimental ranges. These surface plots provide a method to predict the decolorization efficiency for different values of the tested variables.

In Figure 4, the response surfaces were developed as a function of temperature and initial pH, while the ozone concentration and the dye concentration were kept constant at 600 and 30 mg/L, respectively, being the central levels. The efficiency of the process increased with an increase in solution temperature, showing that the overall ozonation reaction is endothermic. This could be due to the increasing collision frequency of the dye molecules on the surface of the ozone bubbles as a result of the increasing temperature. On the other hand, the fraction of molecules that possesses energy in excess of activation energy also increases; consequently, the decolorization efficiency of the ozonation process increases accordingly. Lin and Lai [31] have also generalized a kinetic model consisting of multiple steps for ozonation and adsorption of dye molecules in the textile wastewater, where the increasing of temperature enhances the process efficiency.

Table 6 Decolorization efficiency at optimum values of the process parameters

Variable	Optimum value (predicted)			Experimental value		
	AB1	AY19	AO7	AB1	AY19	AO7
Ozone concentration (mg/L)	739	829	556	740	830	560
Initial dye concentration (mg/L)	13	15	14	13	15	14
Initial pH	6.3	6.2	7.5	6.2	6.2	7.6
Temperature (°C)	39	38	39	38	39	39
Decolorization efficiency (%)	91.28	96.89	77.91	93.00	98.00	80.00

The response surfaces also show that the ozonation process efficiency in alkaline pHs is the optimum. This could be explained by the fact that at alkaline pH, hydroxyl radicals coming from ozone decomposition react unspecifically with organic compounds. Lu et al. [32] have reported the same findings for treatment of wastewater containing azo dye by ozonation. They have mentioned that the removal rate of color is enhanced under the alkalinity condition due to the formation of hydroxyl radicals which has stronger oxidation ability.

Figure 5 shows the response surfaces of the decolorization efficiency as a function of initial dye concentration and the temperature of the solution while the two other variables were kept constant. Increasing the initial concentration of the dye provides more dye molecules in contact with oxidant species and consequently, the efficiency of the removal process increases. As the process efficiency did not decrease

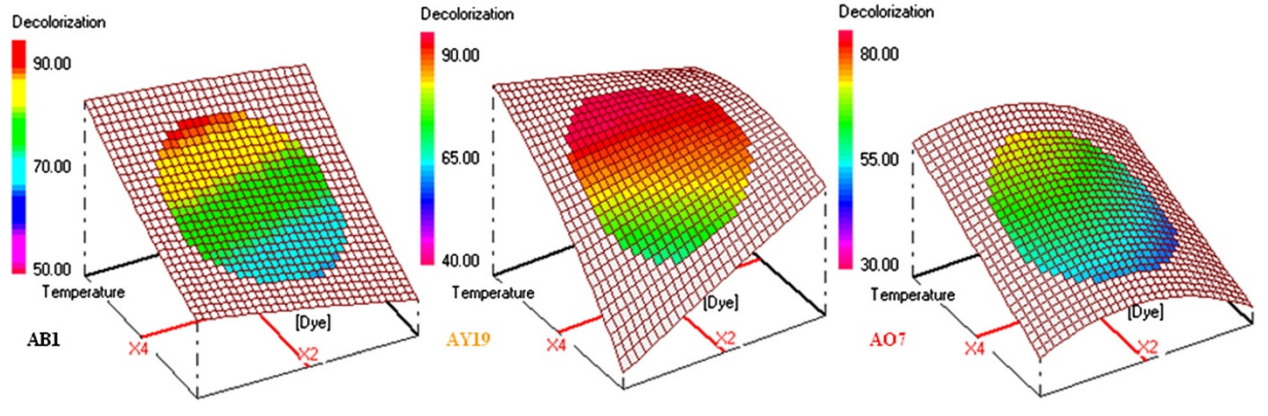


Figure 5 Response surfaces for decolorization process as a function of initial dye concentration and temperature of the solution.

in high concentration of the dye (up to 50 mg/L), the amount of the oxidant (O_3) must be enough. This means that the applied amount of ozone could oxidize even more concentrated dyes. The efficiency of the process increased with an increase in the solution temperature, and the reason of this trend was explained in the previous paragraph.

Model optimization and confirmation

The value of independent variables was optimized to achieve the highest performance of the decolorization process. The desired goal in term of decolorization efficiency was defined as 'maximize' to reach the highest efficiency. The optimum values of the process variables for the maximum decolorization efficiency and the maximum values of decolorization that were verified experimentally are shown in Table 6. This shows that the strategy to optimize the decolorization process and to obtain the maximal efficiency by CCD for the decolorization of these organic dyes during ozonation process is successful.

Experimental

The desired concentration of the dye with a defined pH value was fed into the Pyrex reactor. The pH of the solution was measured by pH meter (Hanna pH211, Hanna Instruments, Cluj-Napoca, Romania) and was not monitored during the experiment. During the injection of the ozone, agitation was done at maintained speed to keep the solution homogeneous. The concentration of ozone injected was determined by a flow meter. At different intervals proposed by the experimental design, 2-ml sample were taken and the remaining dye concentration was determined using Ultrospec 2000 (Biotech Pharmacia, UK, model 80-2106-00) UV–vis spectrophotometer, at wavelength of the maximum absorption and calibration curve. Using this method, the percent color removal could be obtained. The percent color removal (CR%) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one.

Conclusions

It was found that response surface methodology could effectively predict and optimize the performance of ozonation process for decolorization of solution containing organic dyes, AB1, AY19, and AO7. High color removal (>75%) was obtained under optimal value of process parameters for dye solutions in the first 5 min of the removal process. Analysis of variance showed the high coefficient of determination values (R^2 = 0.9365, 0.9643, and 0.9296 for AB1, AY19, and AO7 respectively), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The Pareto analysis of the model terms showed that the initial concentration of the dye and pH of the solution are the most influential variables. The variation of process efficiency as a function of independent variables was shown by graphical response surfaces. Also, the optimum values of the process variables for the maximum decolorization efficiency were calculated and then verified experimentally.

Competing interest

The authors declare that they have no competing interests.

Authors' contributions

MK carried out the RSM studies, participated in the sequence alignment, and drafted the manuscript. NM conceived of the study and participated in the design of the study. HM carried out the experiments and coordination as an industrial advisor. All authors read and approved the final manuscript.

Acknowledgment

The authors thank Islamic Azad University, Tabriz Branch, Iran for all the supports provided.

Received: 20 August 2012 Accepted: 5 December 2012
Published: 9 January 2013

References

1. Eremektar G, Selcuk H, Meric S (2007) Investigation of the relation between COD fractions and the toxicity in a textile finishing industry wastewater: effect of preozonation. Desalination 211:314–320
2. Zollinger H (1987) Color chemistry, syntheses, properties and applications of organic dyes and pigments. Wiley-VCH, Zurich
3. Khataee AR, Zarei M, Pourhassan M (2010) Bioremediation of malachite green from contaminated water by three microalgae: neural network modeling. Clean - Soil Air Water 38:96–103
4. Patnaik P (2006) Azo dyes, a comprehensive guide to the hazardous properties of chemical substances, 3rd edition. Wiley, Hoboken
5. Hai FI, Yamamoto K, Fukushi K (2007) Hybrid treatment systems for dye wastewater. Crit Rev Environ Sci Tech 37:315–377
6. Khataee AR, Kasiri MB (2011) Modeling of biological water and wastewater treatment processes using artificial neural networks. Clean - Soil Air Water 39:742–749
7. De Clercq J (2012) Removal of mercury from aqueous solutions by adsorption on a new ultra stable mesoporous adsorbent and on a commercial ion exchange resin. Int J Ind Chem 3:1
8. Sheibani A, Shishehbor MR, Alaei H (2012) Removal of Fe(III) ions from aqueous solution by hazelnut hull as an adsorbent. Int J Ind Chem 3:4
9. Harrelkas F, Azizi A, Yaacoubi A, Benhammou A, Pons MN (2009) Treatment of textile dye effluents using coagulation - flocculation coupled with membrane processes or adsorption on powdered activated carbon. Desalination 235:330–339
10. Salari D, Niaei A, Khataee AR, Zarei M (2009) Electrochemical treatment of dye solution containing C. I. Basic Yellow 2 by the peroxi-coagulation method and modeling of experimental results by artificial neural networks. J Electroanal Chem 629:117–125
11. Sarayu K, Swaminathan K, Sandhya S (2007) Assessment of degradation of eight commercial reactive azo dyes individually and in mixture in aqueous solution by ozonation. Dyes Pigm 75:362–368
12. Rasoulifard MH, Majidzadeh H, Torkian Demneh F, Babaei E, Rasoulifard MH (2012) Photocatalytic degradation of tylosin via ultraviolet activated persulfate in aqueous solution. Int J Ind Chem 3:16
13. Kasiri MB, Khataee AR (2012) Removal of organic dyes by UV/H_2O_2 process: modelling and optimization. Environ Technol 33:1417–1425
14. De Souza S, Bonilla K, De Souza A (2010) Removal of COD and color from hydrolyzed textile azo dye by combined ozonation and biological treatment. J Hazard Mater 179:35–42
15. Liakou S, Cornaros M, Lyberatos G (1997) Ozonation of azo dyes. Water Sci Technol 36:155–163
16. Hoigne J (1998) Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes. In: The handbook of environmental chemistry, Part C, quality and treatment of drinking water, 2nd edition, vol 5. Springer, Berlin
17. Kornmuller A, Karcher S, Jekel M (2001) Cucurbituril for water treatment. Part II: ozonation and oxidative regeneration of cucurbituril. Water Res 35:3317–3324

18. Chu L, Xing X, Yu A, Sun X, Jurcik B (2008) Enhanced treatment of practical textile wastewater by microbubble ozonation. Process Saf Environ Prot 86:389–393
19. Bernal-Martinez L, Barrera-Diaz C, Solis-Morelos C, Natividad R (2010) Synergy of electrochemical and ozonation processes in industrial wastewater treatment. Chem Eng J 165:71–77
20. Khataee AR, Kasiri MB, Alidokht L (2011) Application of response surface methodology in the optimization of photocatalytic removal of environmental pollutants using nanocatalysts. Environ Technol 32:1669–1684
21. Kasiri MB, Aleboyeh H, Aleboyeh A (2010) Mineralization of C.I. acid red 14 azo dye by UV/Fe-ZSM5/H_2O_2 process. Environ Technol 31:165–173
22. Myers RH, Montgomery DC (2002) Response surface methodology. Wiley, New York
23. Aleboyeh A, Daneshvar N, Kasiri MB (2008) Optimization of C.I. acid red 14 azo dye removal by electrocoagulation batch process with response surface methodology. Chem Eng Process 47:827–832
24. Khataee AR, Dehghan G, Ebadi E, Pourhassan M (2010) Central composite design optimization of biological dye removal in the presence of Macroalgae *Chara* sp. Clean - Soil Air Water 38:750–757
25. Santos SCR, Boaventura RAR (2008) Adsorption modelling of textile dyes by sepiolite. Appl Clay Sci 42:137–145
26. Box GEP, Behnken DW (1960) Some new three level designs for the study of quantitative variables. J Technometrics 2:455–475
27. Aleboyeh A, Kasiri MB, Olya ME, Aleboyeh H (2008) Prediction of azo dye decolorization by UV/H_2O_2 using artificial neural networks. Dyes Pigm 77:288–294
28. Segurola J, Allen NS, Edge M, Mc Mahon A (1999) Design of eutectic photoinitiator blends for UV/visible curable acrylated printing inks and coatings. Prog Org Coat 37:23–37
29. Bayne CK, Rubin IB (1986) Practical experimental designs and optimization methods for chemists. Wiley-VCH, Deerfield Beach
30. Khataee AR, Fathinia M, Aber S, Zarei M (2010) Optimization of photocatalytic treatment of dye solution on supported TiO_2 nanoparticles by central composite design: intermediates identification. J Hazard Mater 181:886–897
31. Lin SH, Lai CL (2000) Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds. Water Res 34:763–772
32. Lu X, Yang B, Chen J, Sun R (2009) Treatment of wastewater containing azo dye reactive brilliant red X-3B using sequential ozonation and upflow biological aerated filter process. J Hazard Mater 161:241–245

doi:10.1186/2228-5547-4-3
Cite this article as: Kasiri *et al.*: Decolorization of organic dye solution by ozonation; Optimization with response surface methodology. *International Journal of Industrial Chemistry* 2013 **4**:3.