Fractional factorial design modelling on degradation of Direct Red 81 dye by advanced oxidation process – ozonation: reaction kinetics

Abaranjitha Muniyasamy, Gayathri Sivaporul, Abarna Gopinath, Juliana John, Anant Achary and Padmanaban Velayudhaperumal Chellam

ABSTRACT
In the present work, the degradation of Direct Red 81 by ozonation was studied. The interactive effects of the influencing factors (dye concentration = 500–2,000 mg/L; time = 10–30 min; pH = 7.0–11.0) on degradation efficiency was critically examined through experimental design optimization by central composite design under the response surface methodology. The high correlation coefficients ($R^2 = 0.976$ & adjusted $R^2 = 0.958$) obtained by analysis of variance (ANOVA) demonstrated close fit between the experimental and the predicted values. Optimized conditions under specified cost-driven restraints were obtained for the highest desirability (i.e. degradation of 1,210.59 mg/L dye) at pH = 11.0, initial dye concentration = 2,000 mg/L and ozone exposure time of 27.16 min. The degradation of Direct Red 81 was confirmed through Fourier transform infrared spectroscopy (FTIR) analysis and UV-Vis spectrometry.

Key words | advanced oxidation process, central composite design, Fourier transform infrared spectroscopy, ozonation, response surface methodology

INTRODUCTION
The effluents released from the textile industry pose a great threat to the environment and the associated ecosystems. The textile effluent is loaded with refractory chemical components which render detrimental effects to human health. The discharged effluents are not amenable to degradation owing to the presence of aromatic and benzidine compounds, which impose pernicious effects on living systems. It is substantially evident that 60–70% of the dyes used in the textile industry are azo compounds (Rawat et al. 2016). The industrial dye effluent remains toxic due to its complex aromatic rings with amino and sulphonic functional groups (Yagub et al. 2014). It has been reported that conventional treatment methodologies (physical, chemical, biological) result in the generation of secondary waste and compounds that render harmful effects to human health. Employing an emerging treatment methodology, the advanced oxidation process (AOP) can help us to get rid of the limitations confronted by the conventional methods (Robinson et al. 2001; Kušić et al. 2007). The characteristic feature of the advanced oxidation process is the generation of highly oxidizing hydroxyl radicals by ozone ($O_3$) (Sharma et al. 2013), hydrogen peroxide ($H_2O_2$) (Arslan et al. 1999), high energy electron beam (Paul et al. 2011), radiations like gamma rays (Chen et al. 2008) and UV-coupled AOPs (Amini et al. 2008; Tehrani-Bagha et al. 2010). In an oxidation process, oxidants are selected based on their oxidation potential. The oxidation potentials of various oxidizing species are given in Table 1 (Al-Kdasi et al. 2004).

Among various AOPs, ozonation has been proven to be an excellent oxidation technology for the treatment of textile effluents (Buthiyappan et al. 2016). During the process of ozonation, ozone and hydroxyl radicals generated in the aqueous solution open up the aromatic rings in the dye molecule and result in the cleavage of the chromophore, C-C double bonds and other functional groups (Chu & Ma 2000). Ozone oxidizes the organic dye molecule via a direct oxidation pathway as molecular ozone or by an indirect/radical oxidation pathway, which involves the formation of the hydroxyl radical (Gül & Özcan-Yıldırım 2009). The direct oxidation pathway dominates at acidic pH, whereas...
at alkaline pH the radical oxidation reaction with comparatively higher mineralization efficiency is predominant. This is because, at higher pH, hydroxide ion acts as a catalyst and facilitates the decomposition of ozone into hydroxyl free radical with oxidation potential greater than that of ozone (Chu & Ma 2000; Ulson et al. 2010).

Mechanism of direct and indirect oxidation (Szpyrkowicz et al. 2003; Gül & Özcan-Yıldırım 2009):

Direct oxidation:

\[ \text{O}_3 + \text{dye} \rightarrow \text{dye}_{\text{oxid}} \]  

Indirect oxidation:

\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{HO}^+ + \text{O}_2 \]  

\[ \text{O}_3^+ + \text{H}^+ \leftrightarrow \text{HO}_3^+ \]  

\[ \text{HO}_3^- \rightarrow \text{HO}^+ + \text{O}_2 \]  

The fate of unreacted \( \text{HO}^+ \) radical may end by recombination:

\[ \text{HO}^+ + \text{O}_3 \rightarrow \text{HO}_4^- \]  

\[ \text{HO}_4^- \rightarrow \text{HO}_2^- + \text{O}_2 \]  

\[ \text{HO}_4^- + \text{HO}_4^- \rightarrow \text{H}_2\text{O}_2 + 2\text{O}_3 \]  

\[ \text{HO}_4^- + \text{HO}_3^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{O}_3 \]

Although there are several reports that prove ozonation as an effective method for the treatment of textile effluent, fewer works have been reported on optimization and process development, which is very essential to take up the process for large scale commercialization. The present work is aimed at establishing the degradation attributes of Direct Red 81 (DR 81), the model dye used in the study. The effect of process parameters like pH, concentration of dye and ozone exposure time on the degradation of Direct Red 81 were examined and the interactive effects between the variables and the response were also established through response surface methodology by the central composite design (CCD) approach. Fourier transform infrared spectroscopy (FTIR) analysis was performed to confirm the degradation of DR 81.

MATERIALS AND METHODS

Materials

Direct Red 81 (DR 81) of molecular formula \( \text{C}_{29}\text{H}_{19}\text{N}_5\text{Na}_2\text{O}_8\text{S}_2 \) was used as the model dye in this study. It was purchased from Sigma-Aldrich, India. The molecular weight of DR 81 is 675.6 g/mol. DR 81 belongs to the class of direct dyes with two sulfonated and two azo groups. The dye has maximum absorbance (\( \lambda_{\text{max}} \)) at 512 nm. Sodium hydroxide and sulphuric acid were obtained from Spectrum reagents and chemicals Pvt. Ltd, India. The aqueous solution of dye was prepared for 2,000 mg/L (stock) using distilled water.

Ozone-reactor setup

The ozone reactor consists of an Ozone generator (MOS – Ozone Engineers Pvt Limited, Tamil Nadu, India), a reaction vessel, a TDS meter (WT018-1NO, Himedia) and a pH meter (Elico, LI 120). Ozone was purged at the constant rate of 500 mg/hr. The block diagram and top view of the ozone reactor are shown in Figure 1(a) and 1(b) respectively.

Table 1 | Oxidation potential of the oxidants (Al-Kdasi et al. 2004)

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation potential (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.8</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1</td>
</tr>
<tr>
<td>Oxygen (atomic)</td>
<td>2.42</td>
</tr>
<tr>
<td>Oxygen (molecular)</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Figure 1 | (a) Block diagram of ozone reactor. (b) Top view.
Ozonolysis of DR 81 dye and instrumental analysis

The ozone was purged into the aqueous dye solution of concentration (100 mg/L) at the constant rate of 500 mg/h at pH of 11.0. The spectral graph of DR 81 solution (treated and untreated) and the molecular structure of the dye is shown in Figure 2(a) and 2(b) respectively. The treated samples were taken at different intervals and the absorbance was measured using a UV-Visible spectrophotometer (Eppendorf-Kinetic, Germany). The degradation efficiency was estimated by Equation (4) and the residual dye concentration (mg/L) was evaluated from these data:

\[
\% \text{ dye removal} = \left(\frac{C_0 - C}{C}\right) \times 100
\]

(4)

where \(C_0\) and \(C\) are the initial and final concentration of dye respectively.

FTIR spectrum of ozone treated samples

The ozone treated and untreated samples of DR 81 were analysed using FTIR - spectroscopy to identify the functional groups. IR spectra for the ozone treated and untreated dye samples were recorded in the range of 400–4,000 cm\(^{-1}\).

The effect of process parameters on the degradation of DR81 by Ozonation – OVAT

The effect of process parameters such as concentration of dye (200–2,000 mg/L), pH (7.0–11.0) and exposure time of ozone (10–30 min) on the degradation of DR 81 was studied by varying one variable at a time (OVAT). The effect of concentration of dye was studied by exposing DR81 dye of varying concentrations (200–2,000 mg/L) to ozone (500 mg/h) at constant time of exposure as 30 min and at pH of 11.0. To study the influence of pH on the degradation, the dye solution of various pH ranging from 3.0 to 11.0 of 500 mg/L concentration was exposed to ozone for 30 min. The effect of exposure time (10–60 min) was studied by treating aqueous dye solution of concentration 500 mg/L prepared at pH 11.0.

Kinetic analysis of degradation of DR 81 dye by Ozonation

The process of degradation of DR 81 dye is attributed by either the ozone molecule (direct oxidation) or by release of hydroxyl radicals (indirect). The rate of the whole reaction could possibly be calculated, if the rate of ozone mediated and the rate of the hydroxyl radical mediated process is known (Pachhade et al. 2009). Alternatively, the rate of the whole reaction could be calculated by the fitting the experimental data in zero order, pseudo first order and pseudo second order rate Equations (5)–(7) for its maximum regression co-efficient. The pattern of degradation of DR81 by Ozonation at optimised process conditions (OVAT) was recorded to find the order of reaction and related kinetic parameters. The experiments were carried out at pH = 11.0, initial dye concentration of 500 mg/L.
concentration of 500 mg/L and exposure time of 30 min:

\[
\frac{-dC_A}{dt} = k \quad \text{(or)} \quad C = C_0 - kt \quad \text{(Zero order)} \quad (5)
\]

\[
\frac{-dC_A}{dt} = k'C \quad \text{(or)} \quad \ln \frac{C_0}{C_t} = k't \quad \text{(Pseudo 1st order)} \quad (6)
\]

\[
\frac{-dC_A}{dt} = k'^2C^2 \quad \text{(or)} \quad \frac{1}{C_t} = \frac{1}{C_0} + k''t \quad \text{(Pseudo 2nd order)} \quad (7)
\]

where \( C_0, C_t, k, k', k'' \) are initial, final concentration of dye, zero order, pseudo first order and pseudo second order rate constants respectively.

**Experimental design and optimization based on CCD**

To study the effect of linear parameters and their interaction, the process of degradation of DR81 was statistically modelled and optimised using the response surface methodology (RSM). This is a combination of mathematical and statistical methods that employs basic principles such as randomization, replication and blocking for designing experiments; evaluating the interactive effects of dependent and independent parameters and predicting the optimized condition for achieving the highest desirability (Körbahti 2007; Cavazzuti 2012; Myers et al. 2016).

Central Composite Design, the most effective class of second order RSM design was employed in the experimental design. Central composite design with three factors at two coded levels consists of 20 experimental runs was applied using Stat Ease – Design-Expert 7.0.0. The number of experiments was determined through Equation (8):

\[
N = 2^k + 2k + x_0 \quad (8)
\]

where \( N, k \) and \( x_0 \) are the number of required experiments (facts), the number of parameters and the number of central points respectively (Soltani et al. 2014).

Each independent variable was coded at two levels (high and low levels) and the ranges were determined by the preliminary experiments (OVAT) carried out at room temperature. The independent variables used in this study were initial dye concentration (500–2,000 mg/L), pH (7.0–11.0), ozone exposure time (10–30 min) as shown in Table 2. The parameters \( (X_i) \) were coded as \( x_i \) using the following equation:

\[
x_i = (X_i - X_0)/\delta X \quad (9)
\]

where \( X_0 \) and \( \delta X \) are the values of \( X_i \) at the centre point and step change, respectively (Soltani et al. 2013).

The three-factor designed experiments were assigned with six replicates at the design centre to provide degrees of freedom for evaluating experimental error and also to determine the precision of the response variable near the centre. Response of the process i.e. concentration of the degraded dye was evaluated and analysed to determine the process performance. The response can be correlated with the factors under consideration by linear or quadratic models. A quadratic model is depicted by the following equation:

\[
\eta = \beta_0 + \sum_{j=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ij} x_i^2 + \sum_{i<j=2}^{k} \beta_{ij} x_i x_j + e_i \quad (10)
\]

where \( \eta \) is the response, \( x_i \) and \( x_j \) are variables, \( \beta_0 \) is constant coefficient, \( \beta_i's, \beta_{ij}'s \) and \( \beta_{ij}'s \) are interaction coefficients of linear, quadratic and the second-order terms, respectively, and \( e_i \) is the error (Körbahti 2007). In the present study, the response is concentration of degraded dye and it is computed for Equation (10) including ANOVA to obtain the interactive effect between the process parameters and the

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Experimental design for Direct Red 81 dye degradation by ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Name</td>
</tr>
<tr>
<td>A</td>
<td>pH</td>
</tr>
<tr>
<td>B</td>
<td>Dye concentration</td>
</tr>
<tr>
<td>C</td>
<td>Time</td>
</tr>
<tr>
<td>Response</td>
<td>Name</td>
</tr>
<tr>
<td>Y</td>
<td>Concentration of dye degraded</td>
</tr>
</tbody>
</table>
response. The fitness of the polynomial model is expressed by the correlation coefficients $R^2$ and the adjusted $R^2$; statistical significance is interpreted from the F-test executed by the program.

**RESULTS AND DISCUSSION**

**Effect of process parameters on degradation of DR 81**

The effect of initial dye concentration on the degradation of DR81 is studied under the experimental conditions as mentioned in the Materials and methods section. The study involves variable initial concentration of dye, the percentage of degradation will not give an exact efficiency, and hence the response was taken as the concentration of dye degraded. From the results, it is observed that there is a reduction in the percentage of degradation with the increase in the initial dye concentration. The complete degradation of DR 81 is observed till 500 mg/l, beyond which the rate of degradation decreases with respect to increase in the initial concentration. Although the decrease in percentage is more than 38% from 200 mg/L to 2,000 mg/L, the concentration of dye degraded increases with an increase in initial dye concentration. This may be attributed to the scavenging effect rendered by the intermediates formed during the process of ozonation and also due to the decrease in the ratio of ozone to dye molecules in the solution (Tehrani-Bagha et al. 2010). The effect of pH on the degradation of DR81 is studied in the experimental conditions as mentioned in the Materials and methods section. It is observed that the concentrations of dye degraded at pH 3.0, 5.0, 7.0, 9.0 and 11.0 are 241.5 mg/L, 291 mg/L, 316.3 mg/L, 339.6 mg/L and 463.6 mg/L respectively. From the results, it is inferred that the concentration of dye degraded increases as the pH of the solution moves towards alkaline range and it is found to be high at pH 11.0. This is because at alkaline pH, ozone decomposes into hydroxyl radical with higher oxidation potential whereas at acidic pH it remains as molecular ozone with relatively less oxidation potential (Sevimli & Sarikaya 2002). As mentioned in the Materials and methods section, the effect of ozone exposure time on the degradation of DR81 is studied. The concentrations of dye degraded were 343.3 mg/L, 456.1 mg/L and 496.6 mg/L at 10, 20, 30 min respectively and the complete degradation was observed at the 40th minute of exposure. A difference of 4 mg/L was observed between the 30th and 40th minute of exposure and so for further studies the 30th minute of exposure was used.

**Reaction kinetics**

The degradation pattern of DR81 by ozonation was studied by carrying out the experiments as mentioned in the Materials and methods section. The results are shown in Table 3. From the results, it is inferred that the regression co-efficient is maximum ($R^2 = 0.9695$) for pseudo first order kinetics. The rate of dye degradation is 90 mg/L.min. The rate of degradation is much higher when compared with the studies reported earlier, as shown in Table 4. It has also been reported in certain studies that the

<table>
<thead>
<tr>
<th>Order of reaction</th>
<th>Rate constant $k'$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>$k = 12.285$</td>
<td>0.7209</td>
</tr>
<tr>
<td>Pseudo 1st</td>
<td>$k' = 0.181$</td>
<td>0.9695</td>
</tr>
<tr>
<td>Pseudo 2nd</td>
<td>$k'' = 0.009$</td>
<td>0.8539</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dye used</th>
<th>Dye concentration (mg/L)</th>
<th>pH range</th>
<th>Rate constant ($k'$)</th>
<th>$R^2$</th>
<th>Rate of the reaction (mg/L.min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Yellow 4</td>
<td>20</td>
<td>Acidic (5.5)</td>
<td>0.273</td>
<td>0.994</td>
<td>5.46</td>
<td>Shu &amp; Huang (1995)</td>
</tr>
<tr>
<td>Acid Black 1</td>
<td>20</td>
<td>0.438</td>
<td>0.957</td>
<td>8.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid Orange 10</td>
<td>20</td>
<td>0.695</td>
<td>0.941</td>
<td>13.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid Red 14</td>
<td>20</td>
<td>0.957</td>
<td>0.989</td>
<td>18.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Procion Red MX-5B</td>
<td>100</td>
<td>Alkaline (11.0)</td>
<td>0.112</td>
<td>0.9008</td>
<td>11.2</td>
<td>Pachhade et al. (2009)</td>
</tr>
<tr>
<td>250</td>
<td>0.0982</td>
<td>0.9044</td>
<td>24.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.059</td>
<td>0.9386</td>
<td>29.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct Red 81</td>
<td>500</td>
<td>Alkaline (11.0)</td>
<td>0.181</td>
<td>0.9695</td>
<td>90</td>
<td>Current study</td>
</tr>
</tbody>
</table>
degradation rate of azo dyes elevates with the increase in pH due to the predominance of the radical oxidation pathway (Chu & Ma 2000; Sevimli & Sarikaya 2002).

Processing and optimization by RSM

RSM results for degradation of DR 81

An empirical expression depicting the mutual relationship between the dependent variable (concentration of the degraded dye) and the independent variables involved in the ozonation process was established using fractional factorial design modelling; that is, RSM based on CCD. In the initial experiments, the initial concentration of dye taken was 500 mg/L but, based on the reaction kinetics, the initial concentration of dye was increased to 2,000 mg/L in RSM. The mathematical expression in turn would be explored to determine the significance of the model. Based on the experimental results, the mathematical expression to relate the process parameters and the response is given as follows:

\[
\text{(Concentration of the degraded dye)} \ Y = -3418.435 
+ 708.4046 \ A + 0.0128 \ B + 28.646 \ C - 39.2194 \ A^2 
- 0.000116505 \ B^2 - 1.65266 \ C^2 + 0.02496 \ AB 
+ 3.778 \ AC + 0.015655 \ BC
\] (11)

As the ratio between the maximum and minimum experimental response is above 10, the model has been transformed and reduced to log10 as suggested by Box-Cox plot. The reduced transformed equation is as follows:

\[
\log_{10} (\text{concentration of the degraded dye}) \ Y 
= -2.11287 + 0.76688A + 0.000692B + 0.05095C 
- 0.035319A^2 - 0.00000146B^2 - 0.0012C^2 
- 0.0000299AB + 0.000007376BC
\] (12)

The relation between the experimental and predicted results of degradation is given in Table 5. The coefficients of determination \( R^2 = 0.976 \) and adjusted \( R^2 = 0.958 \) as shown in Table 5 are found to be relatively high, which demonstrates the significance of the model. A, B, C, AB, BC, \( A^2 \), \( B^2 \) and \( C^2 \) were found to be the significant model terms, with \( P \) values as low as \(< 0.0001\), \(< 0.0001\), \(< 0.0001\), 0.0337, 0.0123, 0.0009, 0.0245 and 0.0028 respectively. From the model equation, it is also inferred that A, B, C, and BC are having positive effects and \( A^2 \), \( B^2 \), \( C^2 \), and AB are having negative effects respectively. The signal to noise ratio can be determined from the ‘Adequate precision’ and the desired value should be greater than 4 (Mannan et al. 2007; Soltani et al. 2013); the present study depicts its suitability with the ratio of 26.129 (Table 4). The model’s reliability is manifested by the relatively low coefficient of variation (1.89%). Apart from this, the adequacy of the model in turn can be interpreted from the residuals obtained by calculating the difference between the experimental and predicted response. The relation between the predicted and experimental response can be interpreted from Figure 3(a). Figure 3(b) is a graphical representation of the

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1.205703</td>
<td>8</td>
<td>0.150713</td>
<td>54.95604</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>A-pH</td>
<td>0.351278</td>
<td>1</td>
<td>0.351278</td>
<td>128.0903</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>B-Concentration</td>
<td>0.23588</td>
<td>1</td>
<td>0.23588</td>
<td>86.01154</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>C-Time</td>
<td>0.139116</td>
<td>1</td>
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<td>50.72747</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>AB</td>
<td>0.01614</td>
<td>1</td>
<td>0.01614</td>
<td>5.885199</td>
<td>0.0337</td>
</tr>
<tr>
<td>BC</td>
<td>0.024487</td>
<td>1</td>
<td>0.024487</td>
<td>8.929117</td>
<td>0.0123</td>
</tr>
<tr>
<td>( A^2 )</td>
<td>0.054886</td>
<td>1</td>
<td>0.054886</td>
<td>20.01376</td>
<td>0.0009</td>
</tr>
<tr>
<td>( B^2 )</td>
<td>0.018618</td>
<td>1</td>
<td>0.018618</td>
<td>6.788899</td>
<td>0.0245</td>
</tr>
<tr>
<td>( C^2 )</td>
<td>0.040238</td>
<td>1</td>
<td>0.040238</td>
<td>14.67235</td>
<td>0.0028</td>
</tr>
<tr>
<td>Residual</td>
<td>0.030167</td>
<td>11</td>
<td>0.002742</td>
<td>79.28692</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>0.029853</td>
<td>6</td>
<td>0.004975</td>
<td>79.28692</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Pure Error</td>
<td>0.000314</td>
<td>5</td>
<td>0.00006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1.235869</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R²: 0.97559; Adj R²: 0.95784; Adeq Precision: 26.1293; C.V%: 1.89.
normal probability for the concentration of the degraded dye versus the internally studentized residuals. From the figure, it can be interpreted that there is no dispersal since the obtained data points were found to be unwavering and appeared on a straight trend line. Besides this, random dispersal of the residuals was being witnessed in the following plots wherein residuals were plotted against predicted concentration of the degraded dye (Figure 3(c)) and the run number (Figure 3(d)).

**Interactive influence of process parameters on degradation efficiency**

2D contour plots and 3D response plots were used to study the interaction between the process parameters. This facilitates the visual representation of the system behaviour (Olmez-Hanci et al. 2011; Soltani et al. 2013; Soltani et al. 2014). From the reduced model, it is observed that pH (A) and ozone exposure time (C) did not have significant interactive effect on the response (i.e. concentration of the degraded dye). Two independent parameters were varied within the experimental ranges and the third parameter was held constant. The interactive effect (AB) of pH (A) – initial dye concentration (B) and interactive effect (BC) initial dye concentration (B) – ozone exposure time (C) is shown in Figure 4(a)–4(d) respectively. From the results, it is inferred that at pH 10.08, 1,145.5 mg/L of dye could be degraded out of 1,835.72 mg/L of initial dye concentration at 20 min (Figure 4(a) and 4(b)). The concentration of dye degraded increases as the pH increases from 7.0 to 11.0 irrespective of dye concentration. Similarly, in the interactive effect of BC, at a constant pH of 11.0, for degrading 1,957.6 mg/L of dye 26.90 min of ozone exposure is required (Figure 4(c) and 4(d)). Alkaline pH had an appreciable impact on degradation efficacy than acidic pH, this is because at acidic pH ozone is available as molecular oxygen and at alkaline pH it decomposes into secondary radicals such as OH•.
OH₂, OH³ and OH⁴ thus providing a more favourable microenvironment for the degradation of the dye molecule (Muthukumar et al. 2005). It was visualized that increased exposure time resulted in higher degradation efficiency. This might be due to the increase in exposure time enhancing the mineralization of the effluent (Somensi et al. 2010).

Optimization using RSM and confirmation

The process parameters were optimized for obtaining the highest desirable response (concentration of dye degraded) under specified constraints. The optimal conditions were generated by setting goals for each response within the studied experimental range. Some optimal solutions were generated, the highest desirable response obtained was 1,210.59 mg/L at initial pH 11.0 and exposure time of 27.16 min. Additional experiments were performed to confirm and validate the degradation response. The response (concentration of the degraded dye) obtained from the experiment performed under optimal condition is 1,217.2 mg/L, which is compared with the response generated by the model (i.e. 1,210.59 mg/L). The residuals is about 7 mg/L, which proved the accuracy of the model.

FTIR analysis and change in pH:

The FTIR spectra of DR81 dye solution and after degradation are shown in Figure 5(a) and 5(b). The broad peaks obtained in the spectrum (Figure 5(b)), ranging from 3,600–3,900 cm⁻¹, are attributed to OH stretching vibrations. The spectral peak obtained at 2,359.67 cm⁻¹ signifies NH stretching vibration. The spectral peaks 1,631.38 and 1,501.87 can be imputed to the N-H deformation vibrations. The peaks obtained in the range of 1,529.59 and 1,572.1 cm⁻¹ may be attributed to the N = N stretching vibrations. The peak at 1,478.75 signifies C-H deformation vibration. The substantial decrease in the intensity of peaks at 3,315.17 cm⁻¹ and 1,631.88 cm⁻¹ (Figure 5(a)) might be attributed to the partial oxidation of the organic compounds. These variations and shifts in the FTIR spectrum may be attributed to the oxidation and mineralization of the organic dye molecule. The change in pH is also observed in the process of degradation of DR 81. The decrease in pH is observed
in solution from pH 3.0 to 2.71, 5.0 to 3.84, 7.0 to 5.34, 9.0 to 6.36, 11.0 to 7.56. The possible reason for the decrease in pH is the formation of acids due to degradation of aromatic rings. From the results of FTIR and change in pH, it is partially evident that the complete elimination of the dye is possible through ozonation.

CONCLUSION

In the present study, the degradation of Direct Red 81 dye by ozonation is studied by assessing the effect of operational parameters and its interactions through CCD. The regression coefficients $R^2 = 0.976$ and adjusted $R^2 = 0.958$ prove the accuracy and adequacy of this mathematical model. Under optimized conditions of pH 11.0, with an exposure time of 27.16 min, 60% degradation is observed for 2,000 mg/L of initial concentration of dye. The degradation is also partially confirmed through FTIR and change in pH of solution after degradation. The complete mineralisation of dyes is also possible by augmenting the process with the addition of $\text{H}_2\text{O}_2$ or other chemical oxidants.

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