PROCESS DEVELOPMENT FOR THE DEGRADATION OF TEXTILE AZO DYES (MONO-, DI-, POLY-) BY ADVANCED OXIDATION PROCESS - OZONATION: EXPERIMENTAL & PARTIAL DERIVATIVE MODELLING APPROACH

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Abstract:

The present study focuses on the process development for degradation of reactive azo dyes (Reactive Orange 16, Reactive Red 120 and Direct Red 80) by Ozonolysis. The process was optimised using One Variable At a Time (OVAT) approach followed by Response Surface Methodology (RSM). The operational parameters influencing the process of degradation, i.e. initial dye concentration (mg/L), pH and ozone exposure time were modelled using Central Composite Design (CCD). Under the optimal condition (Initial dye concentration = 2000 mg/L, pH = 11.0, Ozone exposure time = 10 mins), the highest desirable response (i.e. Concentration of the degraded dye) for the degradation of RO 16, RR 120 and DR 80 are 1289.35 mg/L, 1224.98 mg/L and 1039.87 mg/L, respectively. The high correlation coefficients, 0.9814 (RO 16), 0.9815 (RR 120) and 0.9685 (DR 80) indicates the closeness of the results predicted by RSM with the experimental results. The rate of degradation for all the three dyes at the optimal condition followed pseudo-first order kinetics. The predicted model was also evaluated by partial derivative-based equation modelling and experimental approach. The reliability and applicability of the developed process were confirmed by degrading the synthetic mixed dye effluent.

***Key words***: *Ozonolysis, Central Composite Design, Textile dyes, Reactive Orange 16, Reactive Red 120 and Direct Red 80.*

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1. Introduction

Industries play a major role in gearing up the economy of a nation and hence they are recognized as the "*engine of economic growth*". Textile industries belong to the subsector of the manufacturing industry that has a major contribution to the economy of many countries such as China, Bangladesh, India, Vietnam, Turkey and Nigeria [1]. India accounts 63% of the market share of textiles and garments. The Textile and Apparel (TA) industry in India, contributes to 14% of total industrial production, 4% of gross domestic product and 15% of total export earnings (2016-17) (Textile Ministry, Make in India, TechSci Research). Despite being the major contributor to the global economy, textile industries impose a strong negative environmental impact associated with water pollution [2]. The textile processing units consume large quantity of water for various operations such as washing, dyeing, rinsing and finishing [3]. Everyday around 3.7 million litres of wastewater is produced worldwide by the textile industries [4]. An estimation shows that 7×10^5 metric tonnes of synthetic dyes are produced annually, in which the global consumption by the textile industrial sector is more than 10,000 tonnes/year [5]. Azo dyes represent 60% of the commercially available synthetic dyes and they are extensively used in the textile industries [6]. Azo dyes are of different classes, based on their charge, they are classified as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) [5]. Owing to the demand for fabric with bright colours, usage of reactive dyes containing azo based chromophores with reactive groups such as chlorotriazine, vinyl sulfone, trichloropyrimidine, and dichlorofluoropyrimidine has increased [7, 8]. The fixation rate of these reactive dyes to the cotton fabric is about 60-90%; the unfixed residual dyes along with large amount of water used in the dyeing process are disposed as textile effluents [9]. The untreated or partially treated textile effluent released into the environment and natural water bodies is of great concern, since it affects the photosynthetic activity of the aquatic biota and also results in a bio-magnification. In addition, these dyes with bright colour, complex chemical structure and

78   recalcitrant property may induce carcinogenic, mutagenic or teratogenic effects in the living

79   system [10-12]. The conventional treatment methodologies such as adsorption on activated carbon,

80   flocculation, coagulation, ultrafiltration and reverse osmosis are inappropriate for the industrial

81   application, since they generate large quantity of sludge ,which requires post-treatment and makes

82   the process expensive [13, 14]. In the recent years, Advanced Oxidation Process, which employs

83   hydroxyl radicals for the oxidation of a wide range of recalcitrant pollutants, has attracted the

84   attention of environmental engineers for development of a zero discharge technology [15]. AOPs

85   based on the ozonation method has been reported as a promising remediation technology for the

86   removal of dyes, which involves oxidative cleavage of the organic dye molecule by direct and

87   radical oxidation pathway [16]. For direct oxidation [17]:

88      $$O_3 + dye \rightarrow dye_{oxid}(\text{oxidation product of dye}) \tag{1}$$
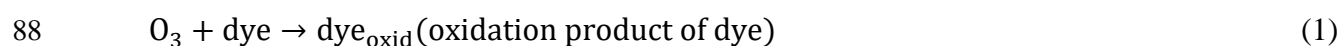
89   For indirect/radical oxidation [17]:

90      $$O_3 + H_2O \rightarrow HO^{\circ} + O_2 \tag{2}$$

91      $$HO^{\circ} + dye \rightarrow dye_{oxid} \tag{3}$$

92   The advantages of ozonation are decomposition of residual ozone to oxygen [18, 19], no

93   sludge generation, color and organic reduction in a single step, requirement of less space and on-

94   site installation [4, 20]. Moreover, the main source of ozonation is air, which is ubiquitous hence

95   development of such a process for a real-time application in textile effluent treatment is of great

96   significance. Large-scale implication of the potent oxidative technology such as ozonation remains

97   an issue due to the lack of control in the complex multivariate operating system, which encompass

98   the following factors: ozone mass transfer ratio, mechanism of reaction and ratio of hydroxyl

99   radical produced [21]. To address the problem, there is a need to adopt an efficient and systematic

100   approach in the process control and development. Conventional or statistical methods can be

101   employed for process optimization. OVAT (One Variable At a Time) approach is a conventional

method of process optimization, in which the influence of the individual variable on the process is examined by variation of one parameter, while the others are maintained constant. The conventional methods are time consuming and do not provide adequate information for effective optimization of the process. Response Surface Methodology (RSM), a powerful statistical experimental design tool, overcomes the limitations of the conventional methods and considers the interactive effect between the variables. RSM involves optimization of a complex, unknown noisy function into a simple function, for a small region under designed experimental conditions [7, 22, 23].

The present work aims to develop an Ozonolytic process for the degradation of industrially used textile dyes namely Reactive Orange 16 (RO 16 - Mono azo), Reactive Red 120 (RR 120 Di-azo) and Direct Red 80 (DR 80 - Poly azo). The dyes were selected based on the industrial usage of reactive and direct azo dyes [8]. The linear effect of the process parameters like pH, initial dye concentration (mg/L) and ozone exposure time on the degradation of RO 16, RR 120 and DR 80 were studied by OVAT (One Variable At a Time) approach. Three Factor level Box-Wilson face centered Central Composite Design (CCF) based Response Surface Methodology (RSM) was used to study the interactive effect between the process parameters on the response (concentration of dye degraded-mg/L) and the process was statistically optimized. The reaction kinetics for the degradation of all the three dyes was established. The effectiveness of the developed process was also evaluated for the simulated synthetic mixed dye effluent containing RO 16, RR 120 and DR 80 dyes. The process was mathematically modeled using partial derivative equation and was experimentally compared and verified with the CCD experiments.

2. Materials and methods

2.1. Materials Used:

127   Reactive Orange 16 (RO-16), Reactive Red 120 (RR-120) and Direct Red 80 (DR-80) were

128 used as the model dyes in this study. These dyes were purchased from Sigma- Aldrich, India. The

129 physicochemical properties of these dyes are available in Table 1. The dye solutions of different

130 concentrations (100, 200, 400, 600, 800, 1000 mg/L) were prepared using deionized water. Ozone

131 (500mg/h) was generated using an ozone generator (principle of corona discharge) purchased from

132 Ozone Engineers Pvt.Ltd., India. The pH of the ozonised and non–ozonised samples were

133 measured by pH meter (Elico, LI 617). Other chemicals such as sodium hydroxide and sulphuric

134 acid were obtained from Spectrum reagents and chemicals Pvt. Ltd, India.

Table 1. Physico-chemical properties of Azo dyes

Properties	RO-16 (Mono Azo)	RR-120 (Di Azo)	DR-80 (Poly Azo)
λ_{max}	494 nm	536 nm	528 nm
Molecular Formula	$C_{20}H_{17}N_3Na_2O_{11}S_3$	$C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$
Molecular wt. (g/mol)	617.54	1469.98	1373.07
No of azo bonds	1	2	4
No of Sulfonated groups	2	6	6

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2.2. Ozonolysis of aqueous dye solution:

137   Ozonolysis of aqueous dye solutions (RO-16, RR-120 and DR-80), concentration

138 500mg/L, were carried out at pH 11.0 by purging ozone into a closed container of 11.3 cm height

139 and 2.8 cm diameter. The absorption spectra were monitored using UV-Visible Spectrometer

140 (Eppendorf - Kinetic, Germany) for the ozonised and non–ozonised samples. The percentage of

141 degradation and changes in the concentration of dye during Ozonolysis was calculated using the

142 equation 4,

143 % of dye degradation $= \left(\frac{C_b - C_f}{C_b}\right) \times 100$ (4)

144   where C_b and C_f are the maximum absorbance of the dye solution before and after

145   irradiation respectively.

146

147   **2.2.2. Influence of process parameters on the degradation of azo dyes – OVAT:**

148   The linear effects of the process variables (Initial dye concentration, pH and ozone

149   exposure time) on the response (concentration of dye degraded) by Ozonolysis was studied through

150   One Variable at a Time Approach (OVAT). The effect of ozone exposure time (10 to 30 mins) on

151   the degradation of the (RO-16, RR-120 and DR-80) azo dyes was studied by treating aqueous dye

152   solution of concentration 500 mg/L prepared at pH 11.0. The influence of pH on the degradation

153   was studied in the dye solutions of various pH ranging from 3.0 to 11.0 of 500 mg/L initial dye

154   concentration were exposed to ozone for 20 mins. The effect of initial dye concentration on the

155   degradation of RO 16, RR 120 and DR 80 azo dyes was studied by exposing dye solutions of

156   varying concentration (200-1000 mg/L) to 500 mg/h ozone for a constant time period of 20 mins,

157   at a pH11.0.

158

159   **2.2.3. Process optimization by RSM**

160   Conventional optimization method such as One Variable At a Time Approach provides

161   information only about the linear effect of the operational parameters and hence Response Surface

162   Methodology, has been adopted to study the linear, interactive and quadratic influence of the

163   process parameters on the response [7, 24]. Box-Wilson Central Composite Design (CCD) method

164   is extensively used in process optimization since it helps in acquiring sufficient information to test

165   lack of fit with minimal design points [9]. In the present study, three factor-five level Box-Wilson

166   Face Centred Central Composite Design (CCF) algorithm was used in Design-Expert 7.0.0., Stat-

167   Ease, USA. The entire experimental design with 20 runs is divided into three components such as

168   factorial points, axial points and centre points.

169    $[(\mathbf{N} = 20) = \mathbf{2^{k=3}}$ (8 factorial points) $+ \mathbf{2k}$ (6 axial points) $+ \mathbf{x_0}$ (6 Centre points)]   (5)

170   where, N, k and x_0 are the number of required experiments, the number of parameters and the

171   number of central points respectively [25]. The factorial points represent the design points coded

172   at low and high levels of each factor. The star or axial points located at the centre of each face of

173   the factorial space allows estimation of the curvature of the model. These points are dispensed in

174   such a way that the standard error of the response variable remains the same at any point of the

175   response surface. The centre points in the design space provides degrees of freedom for estimating

176   experimental error and also helps in the determination of precision of the response variable near

177   the centre [7]. The dependent and independent variables in the current study are pH, initial dye

178   concentration (mg/L), ozone exposure time (mins) and concentration of dye degraded (mg/L),

179   respectively. The levels of the independent variables (Table 2) were determined by the screening

180   experiments (OVAT) at 37°C. The relation between the response variable and the independent

181   variables was established by the quadratic or linear model. An empirical equation depicting the

182   quadratic model along with the linear model is as follows:

183    $$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} x_i x_j \qquad (6)$$

184   where, Y is the predicted response, x_i and x_j are variables, β_0 is constant coefficient, β_j, β_{jj}

185   and β_{ij} are interaction coefficients of linear, quadratic and the second-order terms, respectively.

186   The significance of the model was determined by Analysis of Variance (ANOVA). Quality of the

187   model and statistical significance of the model terms were evaluated using Fischer's or F-Test and

188   correlation coefficient R^2 [26].

Table 2. Experimental design for degradation of RO 16, RR 120 and DR 80 azo dyes by

ozonolysis

Factor	Units	Low Actual	High Actual	Mean	Std. Dev.
A = pH	–	7	11	7	2.828

B = Dye Concentration	mg/L	500	2000	1250	530.330
C = Exposure Time	mins	10	30	20	7.071
Response	**Units**	**Model**	**Transformation**	**Mean**	**Ratio**
Y_1 = Concentration of RO 16 degraded	mg/L			884.90	4.957
Y_2 = Concentration of RR 120 degraded	mg/L	Quadratic	Base 10 log	862.40	4.394
Y_3 = Concentration of DR 80 degraded	mg/L			818.79	7.429

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2.2.4 Partial differential derivative based model:

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191   The degradation of azo dyes (mono-, di-, poly-) by ozonation is represented in

192 mathematical expressions shown in the equations 9, 10, 11. The partial differential expression with

193 respect to A, B & C was derived and the response was calculated by solving those equations at

194 specific constraints. The experimental response, i.e. concentration of dye degraded (mg/L), is

195 compared with model predicted response and equation based response.

2.2.5. Kinetics of ozonolytic degradation

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197   The reaction kinetics was determined for the degradation of RO 16, RR 120 and DR 80 at the

198 optimal condition from the CCD method (initial dye concentration= 2000 mg/L, pH= 11 and

199 Ozone exposure time = 10 mins). The rate of degradation was calculated by fitting the

200 experimental data approximated to pseudo-first order rate equation (with respect to dye) in

201 equation (7 & 8).

202     $\frac{dC}{dt} = k_d'[C]$ (7)

203      $\ln \frac{[C_0]}{[C]} = k'_d t$ *(pseudo-first order)*   (8)

204   where $k'_d = k[O_3]$ represents pseudo-first order rate constant [27, 28]. The rate of

205 degradation thus obtained at the optimal condition of RSM was critically analysed.

2.2.6. Degradation of simulated industrial dye effluent

207   A mixture of synthetic dye effluent (RO 16 (666.3 mg/L) + DR 80 (666.3 mg/L) + DR 80

208 (666.3 mg/L)) was prepared and ozonated at the optimal condition obtained from CCD of RO 16,

209 RR 120 and DR 80 (initial dye concentration = 2000 mg/L, pH = 11 and ozone exposure time =

210 10 mins). The process of degradation was monitored within the time interval by measuring the

211 absorbance of the synthetic mixed dye effluent at 0th min, 5th min and 10th min of ozone exposure.

3. Results and Discussion

3.1. Characterization of the mono, di and poly azo dyes: RO 16, RR 120 and DR 80

214   The stability of the mono (RO 16), di (RR 120) and poly (DR 80) azo dye solutions at

215 varied pH (3.0 to 11.0) and temperature range (20°C to 60°C) was studied. From the spectral

216 graphs, it was observed that the absorption spectra of the dye solutions at different pH's and

217 temperatures were similar. This shows that the dye molecules are stable at various pH and

218 temperature conditions. The absorption spectra of the untreated and the treated dye solutions of

219 RO 16, RR 120 and DR 80 were given in the figure 1a, 1c and 1e, respectively. The maximum

220 absorbance for RO 16, RR 120 and DR 80 was observed at 494 nm, 536 nm and 528 nm

221 respectively. The decrease in the intensity of the peak in the visible region was observed with

222 respect to increase in the ozone exposure time, whereas new peaks were observed in the ultraviolet

223 region. This might be attributed to the breakage of azo bonds (-N=N-) and formation of
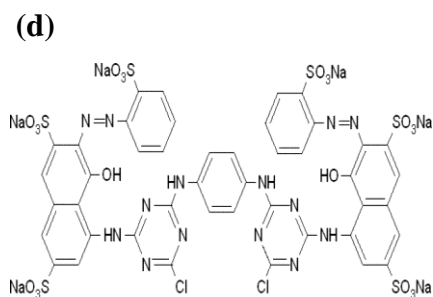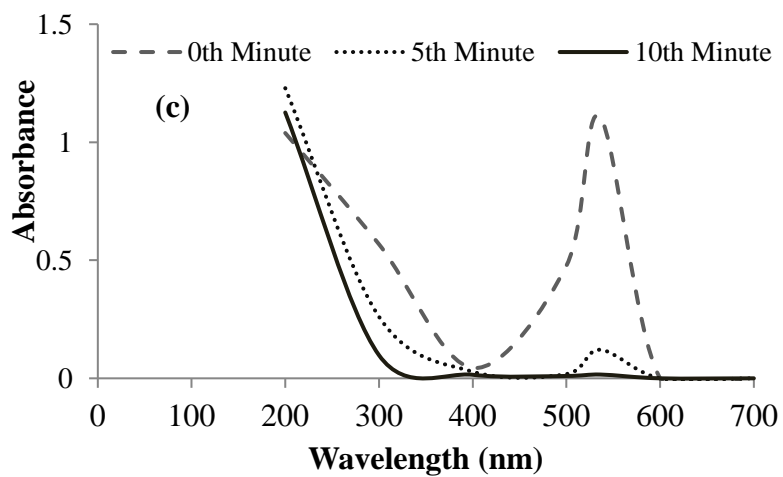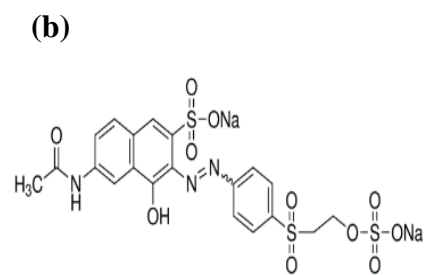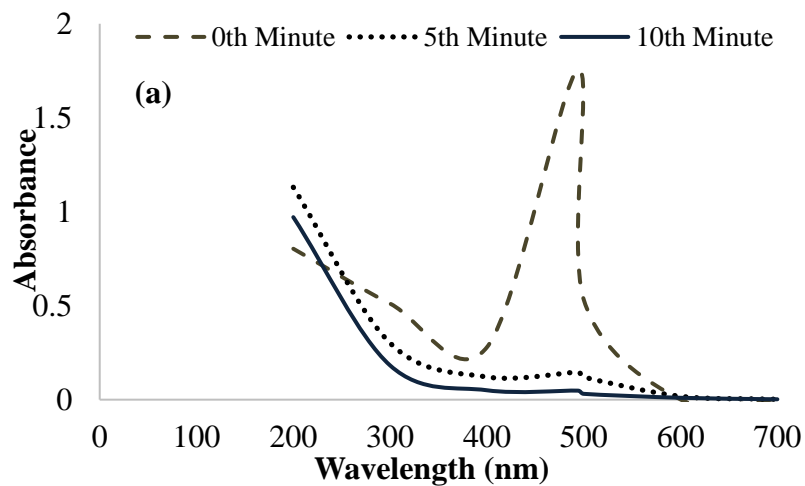
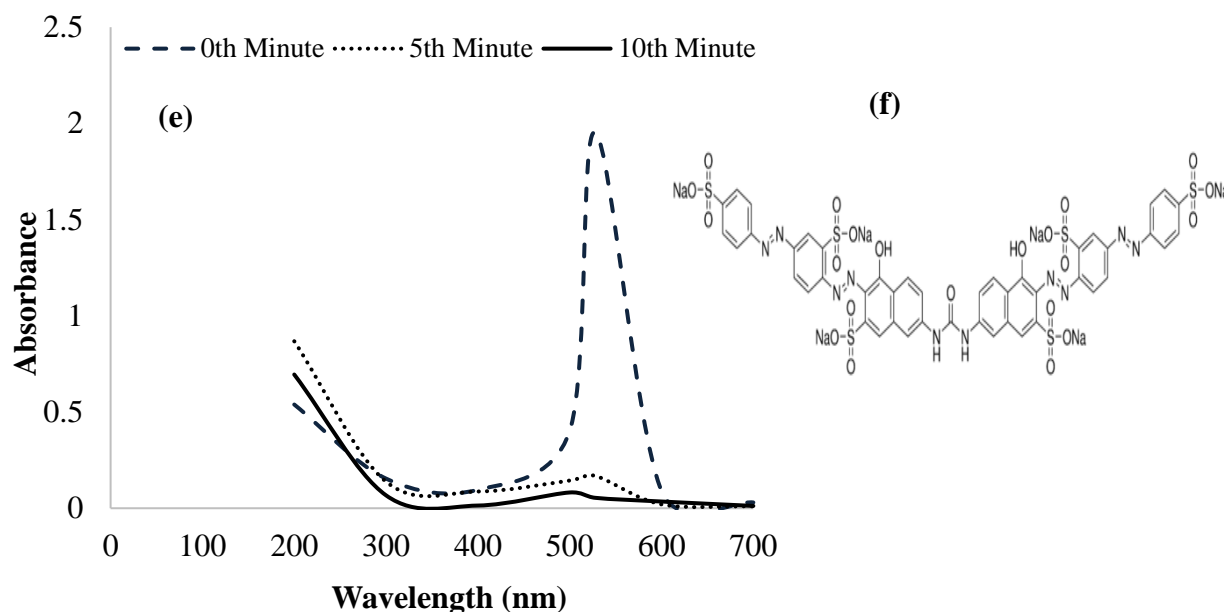224 intermediates containing aromatic ring.

Fig. 1:

Fig. 1: (a) Spectral graph of RO 16 dye (Untreated & Treated at 0th, 5th and 10th minute) **(b)** Structure of RO 16 **(c)** Spectral graph of RR 120 dye (untreated & Treated at 0th, 5th and 10th minute) **(d)** Structure of RR 120 **(e)** Spectral graph of DR 80 dye (Untreated & Treated at 0th, 5th and 10th minute) **(f)** Structure of DR 80

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226 **3.2 Optimisation of process parameters for the degradation of azo dyes by ozonolysis**

227 **3.2.1. Effect of exposure time**

228   Table 3 illustrates the influence of ozone exposure time on the degradation of RO 16, RR

229 120 and DR 80. From the results, at pH 11.0 and 10 minutes exposure time, 98.4% (492.11 mg/L),

230 94.93% (474.64 mg/L) and 85.58% (495.4 mg/L) degradation was observed in RO 16, RR 120

231 and DR 80 respectively. Interestingly, after 20 minutes of ozone exposure, more than 99% of

232 RO16, RR120 and DR80 dyes were degraded. It could be inferred that, at lower exposure time,

233 the difference of 15% was observed in the degradation of dyes as the complexity increases. The

234 prolonged exposure of ozone completely degrades all the classes of dyes. The minimum time

235 required to degrade maximum concentration of the mono azo dye (RO 16) is relatively less than

236   that for the degradation of di azo (RR 120) and poly azo (DR 80) dyes. The possible reason for the

237   difference in degradation could be the complexity in the structure of the dye molecules.

Table 3: Effect of exposure time on degradation of azo dyes

Time (mins)	Concentration of dye degraded (mg/L)		
	RO 16 (%removal)	**RR 120** (%removal)	**DR 80** (%removal)
10	492 (%98.4)	474 (%94.9)	427 (%85.6)
20	**500**	**498.93**	**495.4**
30	500	500	500

Constant initial dye concentration = 500 mg/L and pH=11 for the degradation RO

*16, RR 120 and DR 8*0

238   3.2.2. Effect of initial pH

239   The effect of pH on the ozonolysis of RO 16, RR 120 and DR 80 was studied and the results

240   are shown in Table 4. pH of the solution influences the degradation by altering the chemical nature

241   of ozone. At acidic pH, ozone tends to remain in the molecular state and oxidizes the dye molecules

242   through selective reactions such as electrophilic, nucleophilic or dipolar addition reaction (direct

243   oxidation pathway). Indirect radical oxidation pathway predominates at alkaline pH because at

244   alkaline pH, ozone is unstable and rapidly decomposes into hydroxyl radical, which is the chief

245   oxidant in indirect oxidation. From the results (Table 4) it is evident that, the degradation of azo

246   dyes is more efficient at alkaline pH. The oxidation potential of hydroxyl radical ($E_0 = 2.8$) is

247   greater than that of ozone ($E_0 = 2.1$), this might be the reason for the faster and efficient

248   mineralization of the azo dyes at alkaline pH than acidic pH [6, 8, 29].

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Table 4: Effect of initial pH on degradation of azo dyes

pH	Concentration of dye degraded (mg/L)		
	RO 16	**RR 120**	**DR 80**
3	238.07	209.67	146.8
5	423.1	391.46	363.64
7	458.4	438.84	388.96
9	482.03	462.65	443.14
11	500	498.11	496.87

Constant initial dye concentration= 500 mg/L and ozone exposure time = 20 mins (RO

16, RR 120 and DR 80)

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3.2.3. Effect of Initial dye concentration of azo dyes

The influence of initial dye concentration on the degradation of RO 16, RR 120 and DR 80

was studied and the results are shown in the Table 5. The concentration of dye degraded increases

with respect to increase in the initial concentration of dye irrespective of all types of azo dyes. In

all concentrations of RO 16, RR 120 and DR 80 more than 94%, 92% and 87% of dyes were degraded. Though a decreasing trend was observed in the percentage of dye degraded, the concentration of dye degraded increased with the increasing initial dye concentration over the experimental range f or all the azo dyes.

Table 5 : Effect of initial dye concentration on degradation of azo dyes

Dye Concentration (mg/L)	Concentration of dye degraded (mg/L)		
	RO 16	RR 120	DR 80
200	200	198.11	197.26
400	400	397.34	395.72
600	583.67	576.81	568.41
800	768.32	752.95	729.07
1000	940.48	926.14	875.22

Constant pH= 11.0 and ozone exposure time = 20 mins (RO 16, RR 120 and DR 80)

3.3. Degradation of dyes – Statistical Modelling

3.3.1. Optimization of degradation parameters using CCD method

An empirical relationship between the variables and responses are represented by the second order polynomial equations. The polynomial equations, which explain the degradation of RO 16 (Mono), RR 120 (Di) and DR 80 (Poly) azo dyes were transformed to $\log_{10}$ scale based on the Box-Cox plot (Figures 2e, 3e and 4e) and given in the equations 9, 10 and 11 respectively. These equations are used to relate the dependent variable (concentration of the degraded dye) and the independent variables involved in the process.

$$\mathbf{Log10\ (Conc\ of\ RO-16\ degraded)} = +1.07937 + 0.25923 * A + 0.0005612 * B + 0.019843 * C + 0.0000154724 * AB - 0.00211223AC + 0.00000577916 * BC - 0.012862 * A^2 - 0.0000002025 * B^2 \tag{9}$$

Log10 (**Conc of RR 120 degraded**) $= +0.99521 + 0.27631 * A + 0.0005832 * B + 0.019742 * C + 0.00001448 * AB - 0.00208 AC + 0.00000570716 * BC - 0.01385 * A^2 - 0.000000209 \, B^2$ **(10)**

Log10 (**Conc of DR 80 degraded**) $= +0.39 + 0.336 * A + 0.00092 * B + 0.0306 * C - 0.00221 * AC - 0.0163 * A^2 - 0.000000255 * B^2$ **(11)**

274

275 The factors that a positive influence on the degradation of RO 16, RR 120 and DR 80 are A, B and

276 C. In addition, the interactive effect of AB and BC had positive influence on the degradation of

277 the RO 16 and RR 120 azo dyes. The factors which negatively influences the degradation of RO

278 16, RR 120 and DR 80 are A^2, B^2 and AC. Analysis of Variance (ANOVA) was used to determine

279 the importance and adequacy of the developed models [30]. Tables 6, 7 and 8 summarises the

280 results of ANOVA for the degradation of RO 16, RR 120 and DR 80 by Ozonolysis. The Fischer

281 variance ratio (F-value) is the ratio of mean square value due to model variation to mean square

282 value due to error variance [30]. It explains the variation in data about its mean [26, 31]. The

283 significance of each coefficient in the models can be interpreted from the P-value. It facilitates the

284 understanding of mutual interactions between the test variables. The variables whose coefficients

285 have larger F-value and lower P-value are considered to be more significant in comparison with

286 the other variables [23]. The significant model terms with P value < 0.05 are listed in Table 6, 7

287 and 8. From the results, it can be inferred that pH (A) is the most significant linear parameter which

288 had greater influence than initial dye concentration (B) and ozone exposure time (C) in the

289 degradation of RO 16, RR 120 and DR 80 dyes. Similarly, AC was found to be the highly

290 significant interactive term in the degradation of all the three classes of azo dyes used in the study.

291 R^2 values obtained in the present study for the degradation of RO 16, RR 120 and DR 80 are

292 0.9814, 0.9815 and 0.9685, respectively. These results implies that, the response values

293 (concentration of dye degraded mg/L) can be computed with 98.14%, 98.15% and 96.85% of

294 variations by the independent variables and their interactions in the degradation of RO 16, RR 120

295 and DR 80 dyes, respectively. The difference between the adjusted R^2 and predicted R^2 in the

296 models should be less than 0.20 to confirm the reliability of the model [26, 32]. In the present

297 study, adjusted R^2 and predicted R^2 are in good agreement (Table 4, 5 and 6) which proves that,

298 the models developed are reliable. The signal to noise ratio (Adequate precision) should have a

299 value greater than 4 [33]. 31.611, 31.327 and 29.68 are the adequate precision of RO 16, RR 120

300 and DR 80 respectively, this indicates the fitness of the model. The accuracy of the models are

301 apparent from the relatively less coefficient of variation (C.V %), 1.83 (RO 16), 1.88 (RR 120)

302 and (DR 80) 2.57 [25, 34]. This shows the applicability of all the developed models.

Table 6 Analysis of variance (ANOVA) for the degradation of RO 16 by ozonation

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1.6	8	0.2	72.53	< 0.0001
A-pH	0.51	1	0.51	183.5	< 0.0001
B-Initial dye concentration	0.44	1	0.44	158.51	< 0.0001
C-Ozone exposure time	0.15	1	0.15	54.65	< 0.0001
AB	0.017	1	0.017	6.25	0.0296
AC	0.057	1	0.057	20.69	0.0008
BC	0.015	1	0.015	5.45	0.0396
A^2	0.14	1	0.14	49.11	< 0.0001
B^2	0.042	1	0.042	15.04	0.0026
Residual	0.03	11	2.76E-03		
Lack of Fit	0.03	6	5.06E-03	7966	< 0.0001
Pure Error	3.18E-06	5	6.35E-07		
Cor Total	1.63	19			

R^2: 0.9814; Adj R^2:0.9679; Adeq Precision:31.611; C.V%: 1.83

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Table 7 Analysis of variance (ANOVA) for the degradation of RR 120 by Ozonation

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1.69	8	0.21	73.03	< 0.0001
A-pH	0.55	1	0.55	191.24	< 0.0001
B-Initial dye concentration	0.43	1	0.43	148.26	< 0.0001
C-Ozone exposure time	0.15	1	0.15	52.17	< 0.0001
AB	0.015	1	0.015	5.22	0.0431
AC	0.056	1	0.056	19.26	0.0011
BC	0.015	1	0.015	5.07	0.0457
A^2	0.16	1	0.16	54.38	< 0.0001
B^2	0.044	1	0.044	15.32	0.0024
Residual	0.032	11	2.89E-03		
Lack of Fit	0.032	6	5.30E-03	2578.31	< 0.0001
Pure Error	1.03E-05	5	2.06E-06		
Cor Total	1.72	19			

R^2: 0.9815; Adj R^2:0.9681; Adeq Precision:31.327; C.V%: 1.88

305

Table 8 Analysis of variance (ANOVA) for the degradation of DR 80 by Ozonation

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	2.08	6	0.35	66.65	< 0.0001
A-pH	0.67	1	0.67	127.98	< 0.0001
B-Initial dye concentration	0.46	1	0.46	88.28	< 0.0001
C-Ozone exposure time	0.23	1	0.23	44.02	< 0.0001
AC	0.063	1	0.063	12.06	0.0041
A^2	0.22	1	0.22	41.61	< 0.0001
B^2	0.066	1	0.066	12.58	0.0036
Residual	0.068	13	5.210E-003		
Lack of Fit	0.068	8	8.467E-003	33877.24	< 0.0001
Pure Error	1.250E-006	5	2.499E-007		
Cor Total	2.15	19			

R^2: 0.9685; Adj R^2:0.954; Adeq Precision:29.68; C.V%: 2.57

306   Figure 2a, 3a and 4a represents the graphical plot between the predicted and experimental values

307   for the degradation of RO 16, RR 120 and DR 80 respectively. From the figures, it is inferred that

308   the predicted and the experimental values are in good agreement signifying the fitness of the

309   models. Figure 2b, 3b and 4b shows the plots of normal probability of the response (concentration

310   of dye degraded) versus the internally studentized residuals for the degradation of RO 16, RR 120

311   and DR 80 respectively. The figures show that the residual points are in close proximity to the

312   straight trend line as there is no disperse effect. The residuals are plotted against the predicted

313   response values (Figure 2c, 3c and 4c) and the run number (Figure 2d, 3d and 4d). It can be

314   observed that the residuals are dispersed randomly within the constant range of $\pm$ 3.00 across the

315   graphs. This shows that the variance of the original observations are constant for all the responses

316   and the error in the experimental system is negligible [35].
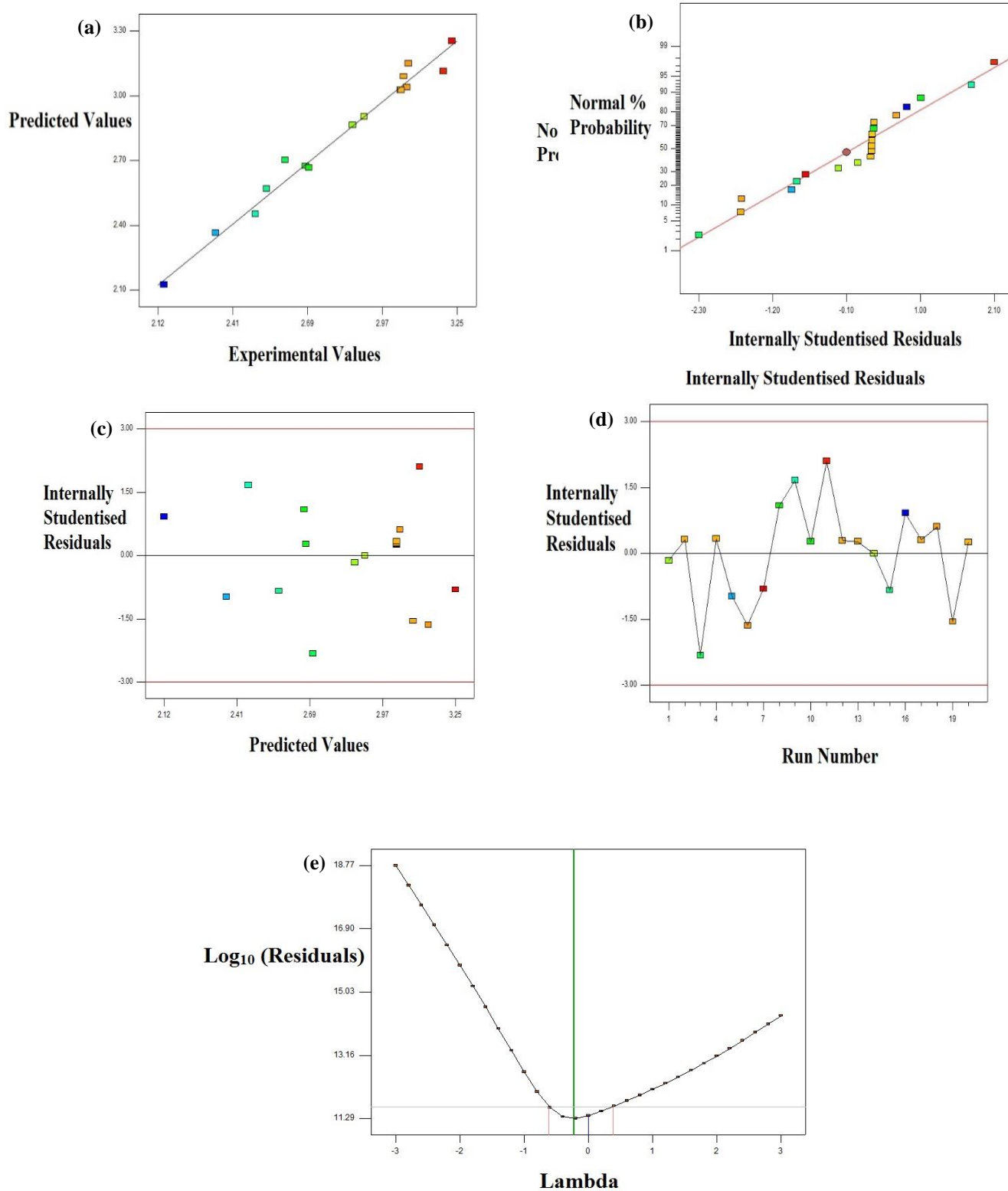
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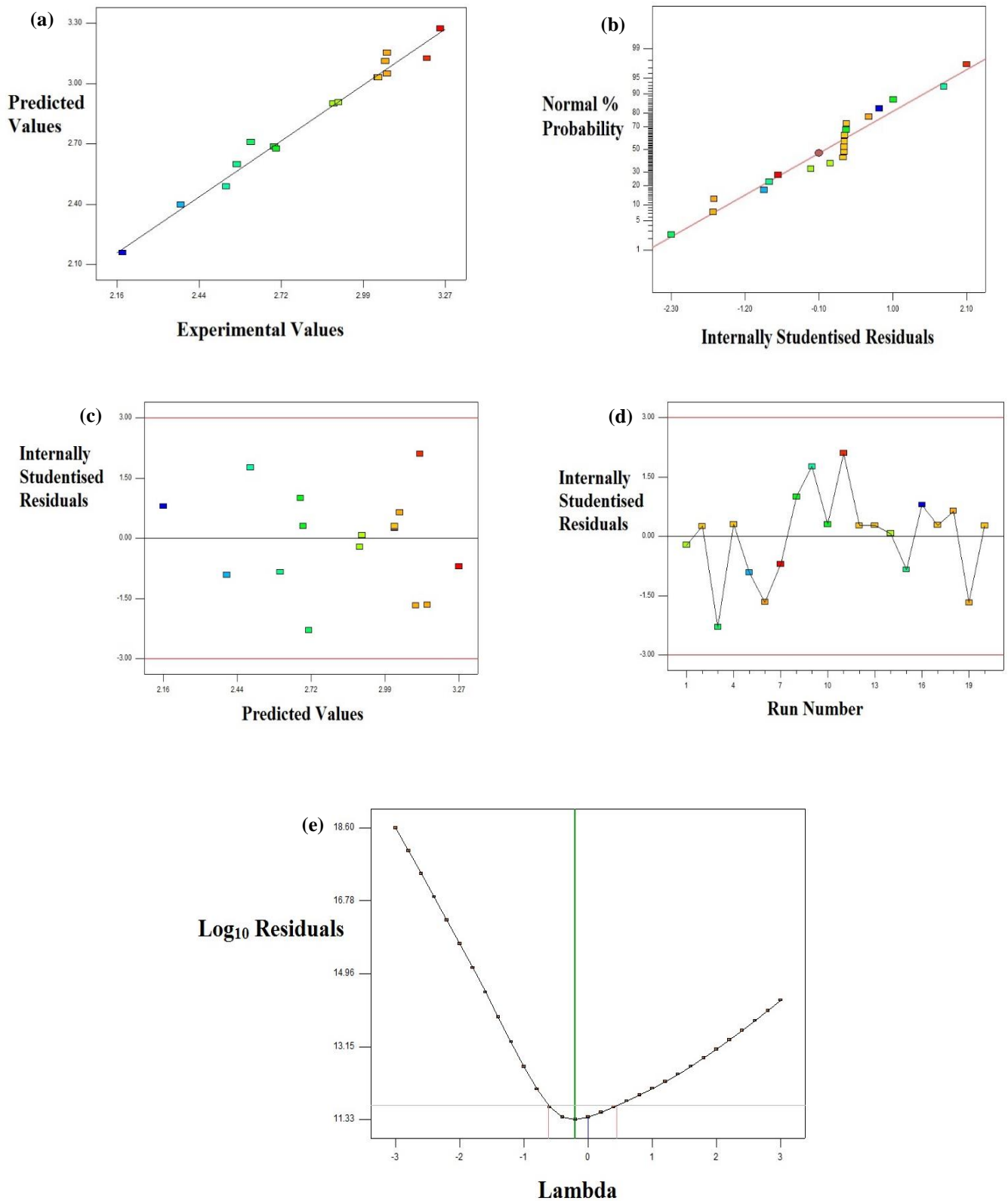
Figure 2 (a) A plot of the predicted versus the experimental degradation efficiency (Log_{10} Concentration of dye degraded) and (b, c and d) their corresponding residual plots and (e) Box-cox plot for the degradation of RO 16.
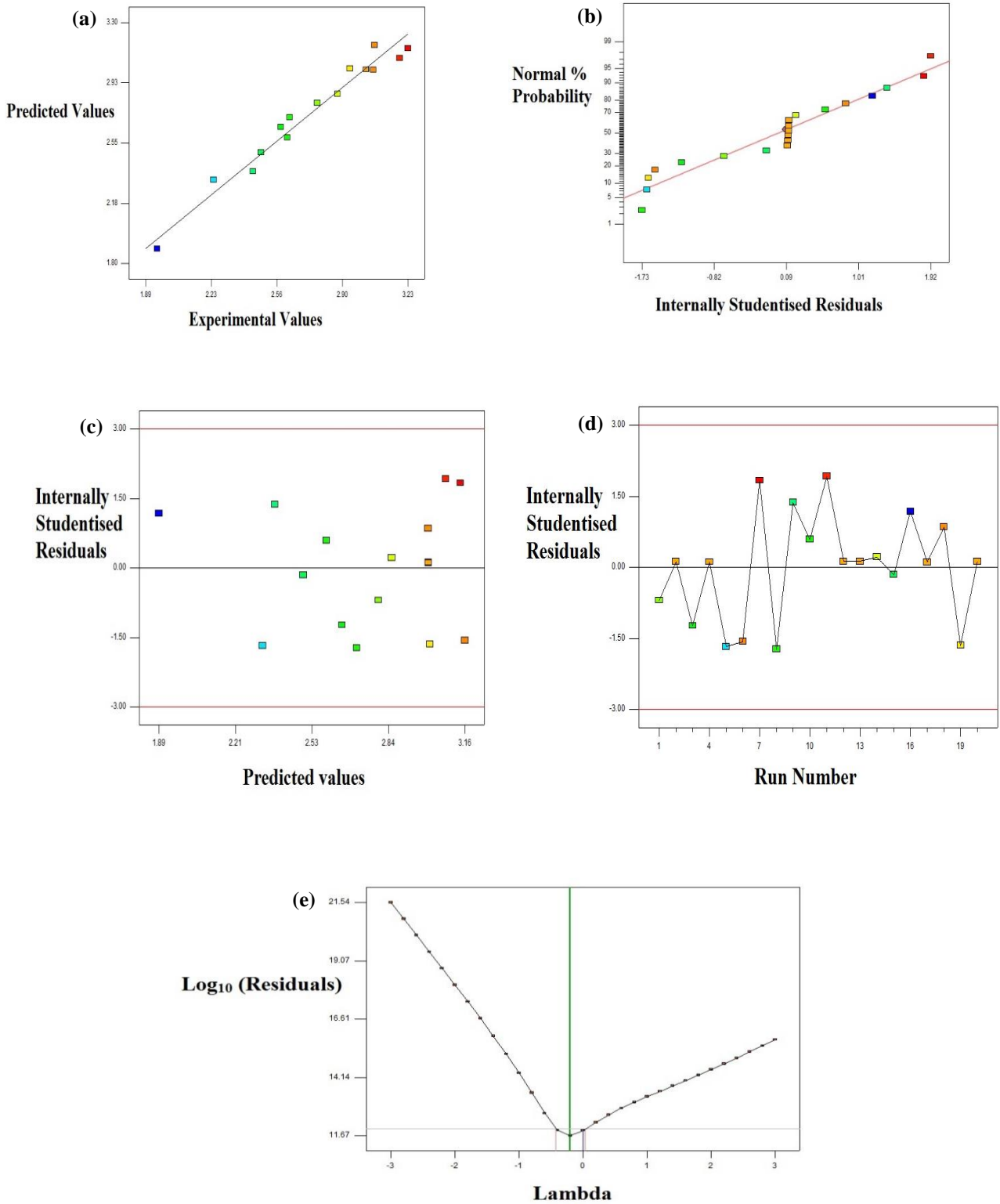
Figure 3 (a) A plot of the predicted versus the experimental degradation efficiency (Log_{10} Concentration of dye degraded) and (b, c and d) their corresponding residual plots and (e) Box-cox plot for the degradation of RR 120.

318

Figure 4 (a) A plot of the predicted versus the experimental degradation efficiency (Log_{10} Concentration of dye degraded) and (b, c and d) their corresponding residual plots and (e) Box-cox plot for the degradation of DR 80.

319

3.3.2. Interactive effect of process parameters on the degradation of azo dyes

The interactive effect between two parameters was studied using contour (2D) plots and response surface plots (3D). In these plots two parameters are varied within the experimental range and the third parameter is kept constant [36]. From the results (Table 6, 7 and 8), it is clear that the interactive effect (AB) of pH with initial dye concentration and (BC) of initial dye concentration with the ozone exposure time do not have significant influence on the degradation of DR 80 (poly azo dye) and hence the model was reduced. On the other-hand all the interactions (AB, AC and BC) were found to be significant in the models developed for the degradation of RO 16 and RR 120.

Interactive effect of AB: The contour and response surface plots which show the interactive effect (AB) of pH (A) and initial dye concentration (B) on the degradation of RO 16 and RR 120 are represented by the figures 5a, 5b and 6a, 6b respectively. The interactive effect of AB on the degradation RO 16 and RR 120 substantiates that the concentration of dye degraded increases as the pH increases from 3.0 to 11.0 for the studied range of initial dye concentration (500 mg/L to 2000 mg/L). The rate of decomposition of ozone into hydroxyl radicals is greater at alkaline pH, this might be the reason for the accelerated degradation of the organic pollutants at high pH [6].

Interactive effect of BC: The influence of BC (initial dye concentration and Ozone exposure time) on the degradation of RO 16 (Figures 5c and 5d), and RR 120 (Figures 6c and 6d) reveals that the time required for degrading the dye increases with the increasing initial dye concentration [6]. Exposure time is directly proportional to the concentration of ozone and hydroxyl radicals, i.e. shorter exposure time is sufficient for degrading lower concentration of dye while longer time of ozone exposure is desirable for degrading higher dye concentration. At minimal exposure time of 10 mins (initial dye concentration = 500 mg/L, pH = 11.0), about 96.8% (484.17 mg/L) of RO 16 and 94.4% (472.06 mg/L) of RR 120 was degraded. Furthermore, the ozone exposure time required is relatively high for degrading dyes of higher concentration (initial dye concentration = 2000

345 mg/L, pH = 11.0) i.e. 30 mins for degrading 93.5% (1870.68 mg/L) of RO 16 and 89.7% (1794.73

346 mg/L) of RR 120.

347 **Interactive effect of AC:** The interactive effect (AC) of pH (A) and ozone exposure time (C) on

348 the degradation of RO 16, RR 120 and DR 80 are shown in the figures 5e, 5f; 6e, 6f and 7a, 7b

349 respectively. These plots reveal that as the pH of the dye solutions approaches higher range of pH

350 from 3.0 to 11.0, the concentration of degraded dye increases irrespective of the ozone exposure

351 time at a constant initial dye concentration of 1250 mg/L. In addition, it was also observed that as

352 the initial pH of the RO 16, RR 120 and DR 80 dye solutions (initial dye concentration= 1250

353 mg/L) increased from 3.0 to 11.0, the concentration of degraded dye increased by 4-5 folds at 10th

354 minute of ozone exposure and 2 fold increase was observed at 30th minute of ozone exposure. The

355 influence of pH was highly significant at lower exposure time than at higher time of exposure. As

356 such, this suggests that the processing time for dye degradation can be decreased when the

357 treatment is performed at pH 11.
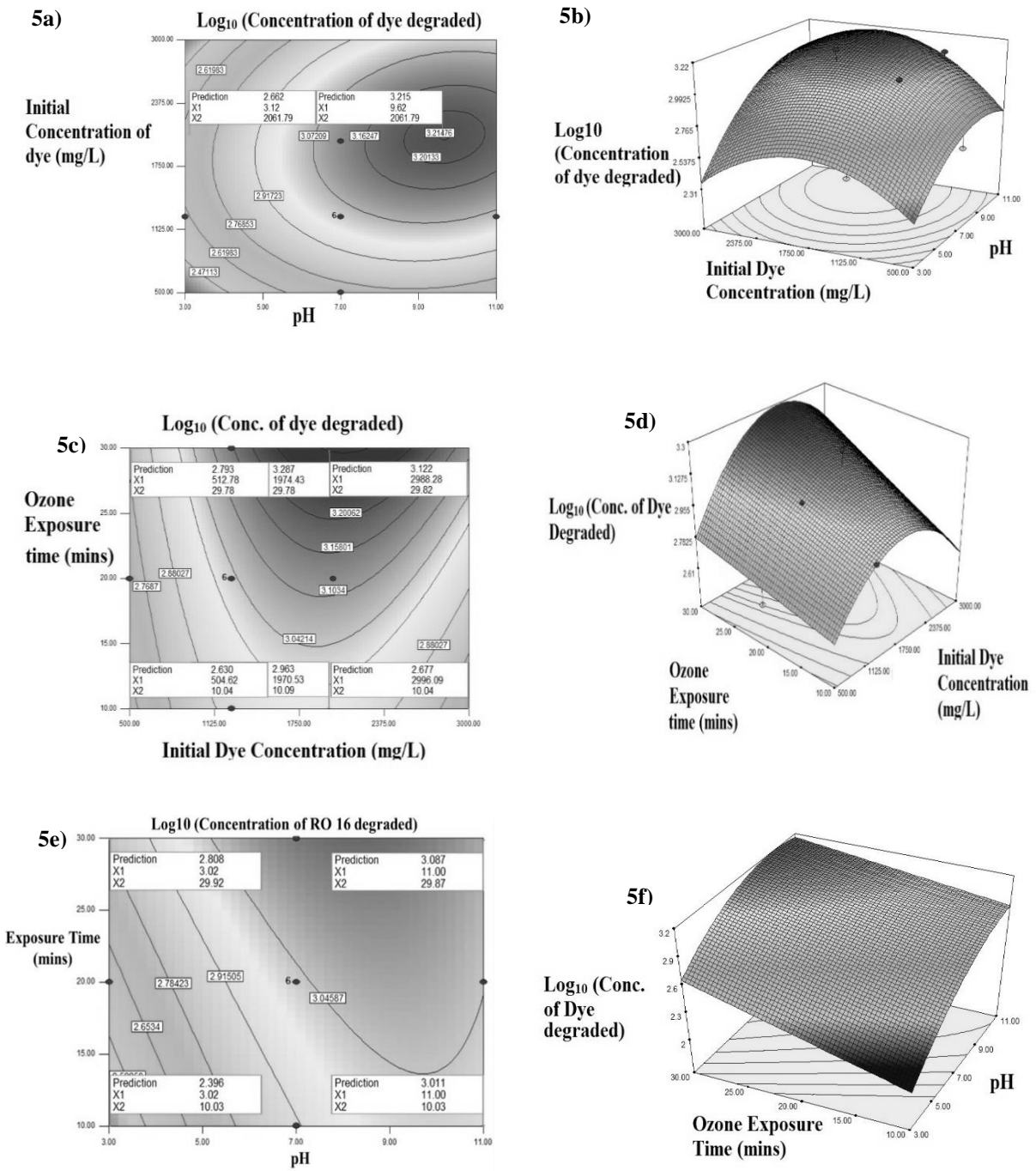
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5a)

5b)

5c)

5d)

5e)

5f)

Figure 5 Contour plots and 3D Response Surface plot of RO 16, **(5a, 5b)** as a function of pH and initial dye concentration at constant exposure time = 20 mins ; **(5c, 5d)** as a function of

initial dye concentration and exposure time at pH= 7.0 ; **(5e, 5f)** as a function of pH and exposure time at constant initial dye concentration = 1250 mg/L
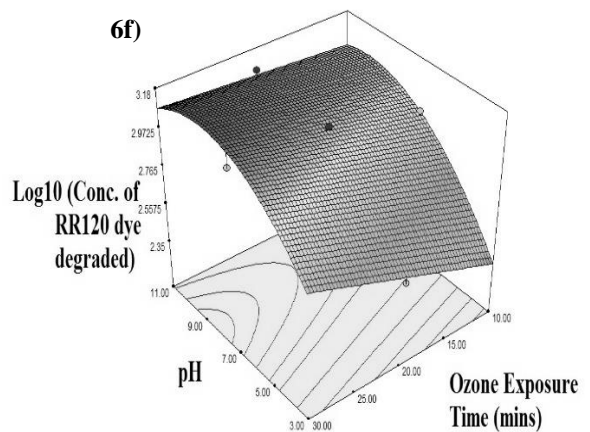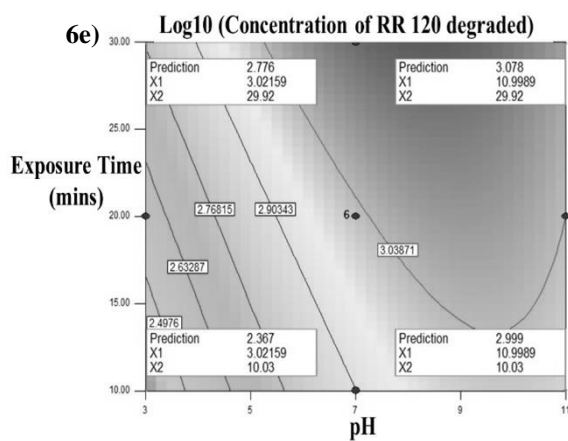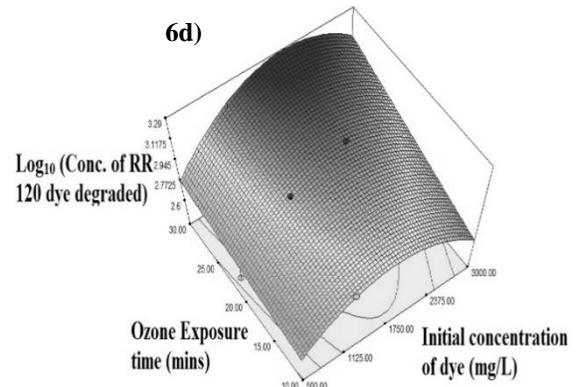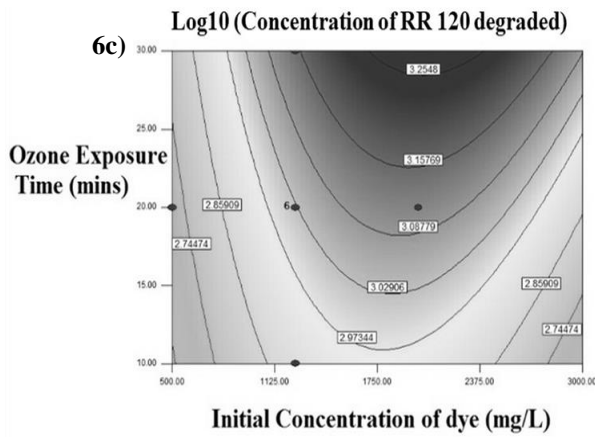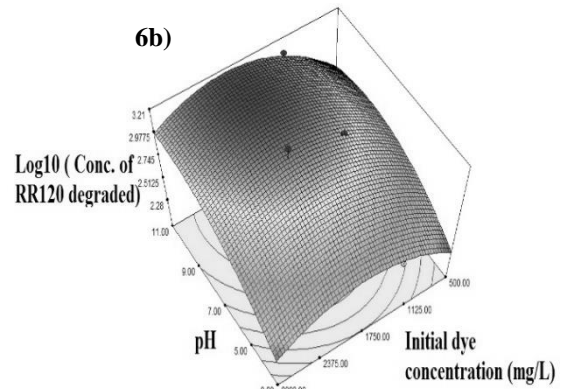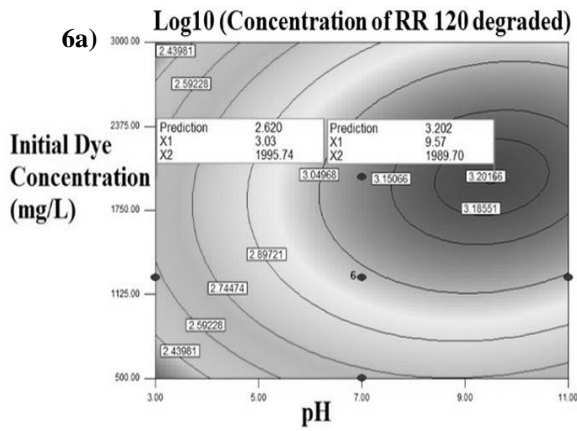
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Figure 6 Contour plots and 3D Response Surface plot of RR 120, **(6a, 6b)** as a function of pH and initial dye concentration at constant exposure time = 20 mins ; **(6c, 6d)** as a function of initial dye concentration and exposure time at pH= 7.0 ; **(6e, 6f)** as a function of pH and exposure time at constant initial dye concentration = 1250 mg/L.
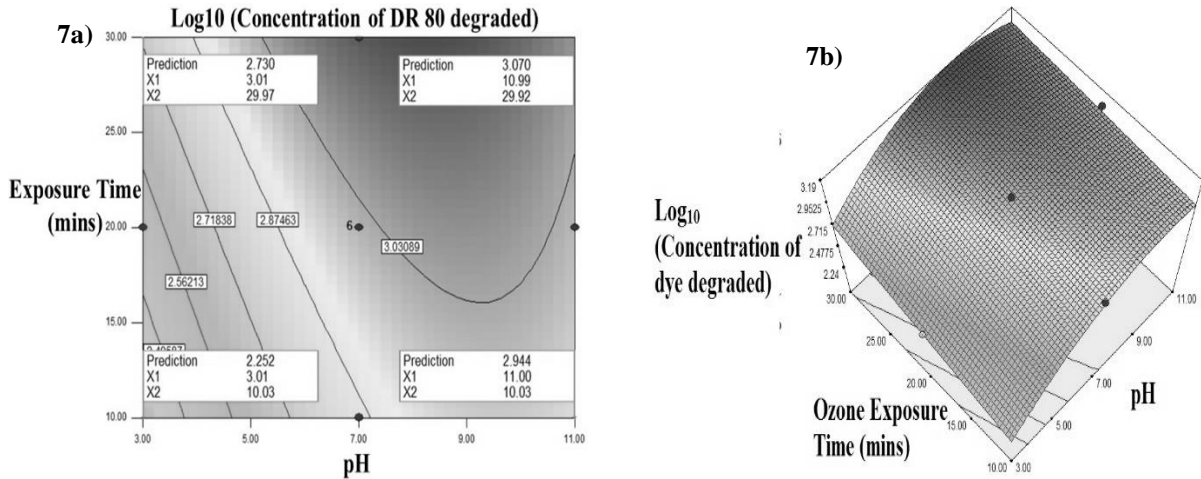
370

Figure 7 (a) Contour plots and **(7 b)** 3D Response Surface plot of DR 80 as a function of pH and exposure time at constant initial dye concentration = 1250 mg/L.

371 **3.3.3. <mark>Partial differential derivative based analysis of equation:</mark>**

372   The individual mathematical expression in logarithmic scale was differentiated partially

373 with respect to the influencing parameters A, B and C for the textile dyes (mono-, di-, and poly-).

374 The expressions were shown in the equation 9, 10 and 11. The response obtained by solving these

375 differential forms at specific constraints *(A: in the range of 10.0 – 11.0, B: maximum value in the*

376 *studied range and C: at 10 mins)* was compared with the predicted model response and equation-

377 based response.

378 *The partial derivative of equation 9,*

379 *With respect to A,*

380 $+\ 0.25923\ +\ 0.0000154724*B - 0.00211223*C - 0.025724*A\ =\ 0$ (12)

381 *With respect to B,*

382 $+\ 0.0005612\ +\ 0.0000154724*A\ +\ 0.00000577916*C - 0.000000405*B\ =\ 0$ (13)

383 *With respect to C,*

384 $+ 0.019843 - 0.00211223 * A + 0.00000577916 * B = 0$ (14)

385 On solving equation 12, 13 and 14 with above said constraints, the obtained response is 1291.22

386 mg/L and Log_{10} (3.111)

387

388 *The partial derivative of equation 10,*

389 *With respect to A,*

390 $+ 0.27631 + 0.00001448 * B - 0.00208 * C - 0.0277 * A = 0$ (15)

391 *With respect to B,*

392 $+ 0.0005832 + 0.00001448 * A + 0.00000570716 * C - 0.000000418 * B = 0$ (16)

393 *With respect to C,*

394 $+ 0.019742 - 0.00208 * A + 0.00000570716 * C = 0$ (17)

395 On solving equation 15, 16 and 17 with above said constraints, the obtained response is 1250.25

396 mg/L and Log_{10} (3.097)

397

398 *The partial derivative of equation 11,*

399 *With respect to A,*

400 $+0.336 - 0.00221 * C - 0.0326 * A = 0$ (18)

401 *With respect to B,*

402 $+ 0.00092 - 0.000000410 * B = 0$ (19)

403 *With respect to C,*

404 $+ 0.0306 - 0.00221 * A = 0$ (20)

405 On solving equation 18, 19 and 20 with above said constraints, the obtained response is 1096.5

406 mg/L and Log_{10} (3.040)

407

3.3.4 Process optimisation and confirmation

The parameters influencing the degradation of RO 16, RR 120 and DR 80 azo dyes by Ozonolysis were optimised for maximum degradation of dye within minimal time of ozone exposure. The optimal condition obtained for the degradation of all the three classes of azo dyes are as follows: Initial dye concentration = 2000 mg/L, pH = 11 and ozone exposure time = 10 mins. Under the condition mentioned above, the response (i.e. concentration of degraded dye) predicted by the models for the degradation of RO 16, RR 120 and DR 80 are 1285.28 mg/L, 1227.43 mg/L and 1035.14 mg/L respectively. In addition, the response predicted by the models were experimentally verified under the optimal condition and the concentration of dye degraded obtained for the degradation of RO 16, RR 120 and DR 80 are as follows: 1289.35 mg/L, 1224.98 mg/L and 1039.87 mg/L. The difference between the experimental and predicted response of RO 16, RR 120 and DR 80 are 4 mg/L, 3 mg/L and 4 mg/L respectively. This confirms the accuracy and applicability of the developed models.

Table 9: Comparison of response obtained by CCD at original and transformed scale with equation derived response

Response	RO 16		RR 120		DR 80	
	Original scale	**Transformed Scale**	**Original scale**	**Transformed Scale**	**Original scale**	**Transformed Scale**
Predicted Response	1285.28 mg/L	Log_{10} (3.109)	1227.43 mg/L	Log_{10} (3.089)	1035.14 mg/L	Log_{10} (3.015)
Experimental Response	1289.35 mg/L	Log_{10} (3.110)	1224.98 mg/L	Log_{10} (3.088)	1039.87 mg/L	Log_{10} (3.017)
Equation derived Response	1291.22 mg/L	Log_{10} (3.111)	1250.25 mg/L	Log_{10} (3.097)	1096.5 mg/L	Log_{10} (3.040)

Conditions: pH:11.0; Initial Dye Concentration: 2000mg/L;Time:10mins

3.4. Kinetics of Ozonolytic degradation

Based on the optimal condition from RSM-CCD, rate of degradation of RO 16, RR 120 and DR 80 was determined. The results are shown in Table 10. It was observed that, all the experimental runs followed a pseudo-first order kinetic model, which is in accordance with the earlier reported studies [19, 37-40]. Despite the complexity in the structure, the rate of degradation of the poly (DR 80) and di azo (RR 120) dyes were found to be greater than the rate of degradation of the mono (RO 16) azo dye. It is speculated that intermediate products formed during the ozonation of DR 80 and RR 120 might have catalysed the formation of hydroxyl radicals thus increasing the ozonation reaction [16].

Table 10. Analysis of degradation kinetics at the optimal condition obtained by RSM for the degradation of RO 16, RR 120 and DR 80

Dye used	R^2	Rate constant k'_d (min^{-1})	Rate of the reaction (mg/L.min)	Residence time (sec)
RO 16	0.9071	0.0705	141	0.425
RR 120	0.9761	0.0986	197.2	0.304
DR 80	0.9839	0.1083	216.6	0.277

3.5. Ozonolytic degradation in simulated industrial dye effluent

The efficiency of the developed process is evaluated in simulated industrial dyes, which mimics the industrial effluent discharged from textile industries. The simulated effluent contains a mixture of dyes and was ozonated at the optimal condition obtained from RSM to determine the applicability and efficiency of the models. The spectral graph for the degradation of synthetic mixed dye effluent is shown in Figure 8. At 0th minute, a prominent and intense peak was observed in the visible region at 500 nm, this peak attributes to azo linkage. After 5th min and 10th min of

440 ozone exposure, intensity of the peak in the visible region decreased. This indicates the breakage

441 of chromophoric (-N=N-) azo group by the hydroxyl radicals, which is the first step in the

442 degradation of organic dye molecules. With the increase in ozone exposure time, new peaks

443 appeared in the ultraviolet region around 200-300 nm along with the simultaneous decrease of

444 peaks in the visible region. This might be due to the formation of multi-substituted benzene rings

445 resulting from the degradation of naphthalene rings present in the parent dye molecule. This result

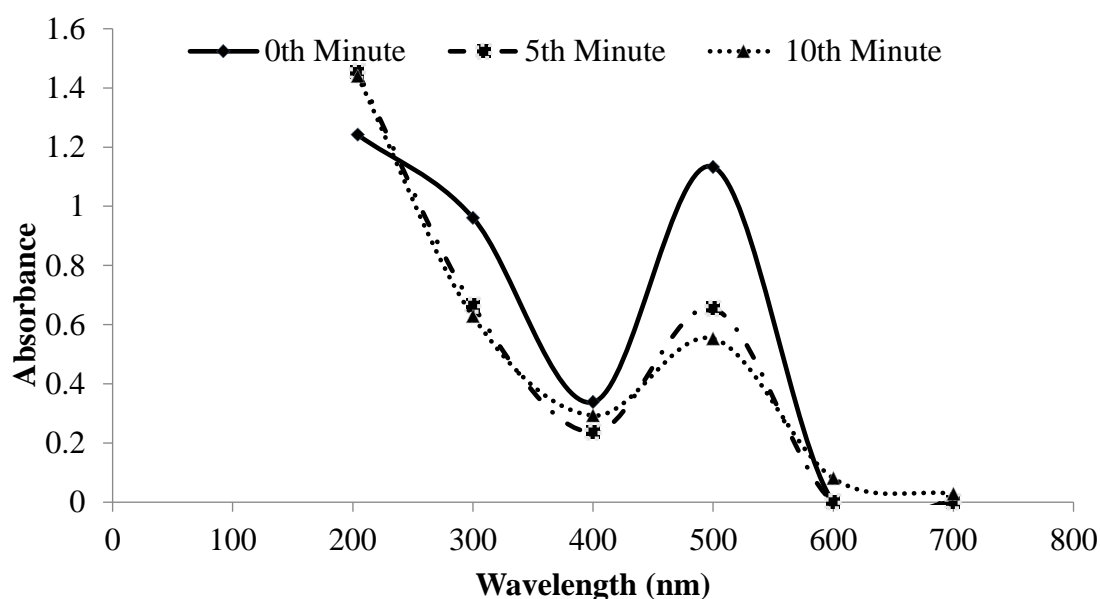446 proves the effectiveness of the process developed by RSM in degrading the textile dye effluent.

Figure 8: Spectrum of synthetic mixed dye effluent (RO 16 (666.3 mg/L), RR 120 (666.3

mg/L) and DR 80 (666.3 mg/L)) exposed to ozone for 10 mins at pH = 11.

447 **4.   Conclusion**

448   The degradation of mono, di and poly azo dyes such as RO 16, RR 120 and DR 80 was

449 studied by Advanced Oxidation Process - Ozonation. Response Surface Methodology using Box-

450 Wilson Face Centred Central Composite Design (CCF) was found to be effective in studying the

451 interactive effect of the process parameters (pH, initial dye concentration and ozone exposure time)

452 and in optimizing the process of degradation of RO 16, RR 120 and DR 80 by Ozonolysis. The

453 highest desirable response (i.e. concentration of dye degraded) predicted by the models for the

454 degradation of RO 16, RR 120 and DR 80 are 1289.35 mg/L, 1224.98 mg/L and 1039.87 mg/L

455 respectively. In addition the model predicted by CCD was validated by partial derivative based

456 equation modelling. The response obtained from partial derivative based modelling were

457 experimentally verified and found to be in agreement with the predicted response. The degradation

458 of dyes followed a pseudo-first order kinetic trend. The applicability of the process was evaluated

459 using synthetic mixed dye effluent. Thus the study was successful in developing a potent zero

460 discharge technology such as ozonation for textile dye degradation at laboratory scale. Upon

461 establishing the scale-up criteria and studying the effect of other salts present in the real-time

462 effluent, Ozone oxidation technology can be applied in the textile industries for effluent treatment.

463 **5.   References**

464 [1] Dadi, D., Stellmacher, T., Senbeta, F., Van Passel, S. And Azadi, H., Environmental And
465   Health Impacts Of Effluents From Textile Industries In Ethiopia: The Case Of Gelan And
466   Dukem, Oromia Regional State, Environ Monit Assess. 189 (2017) 11.

467 [2] Celekli, A., Yavuzatmaca, M. And Bozkurt, H., Kinetic And Equilibrium Studies On The
468   Adsorption Of Reactive Red 120 From Aqueous Solution On Spirogyra Majuscula, Chem Eng
469   J. 152 (2009) 139-145.

470 [3] Tizaoui, C. And Grima, N., Kinetics Of The Ozone Oxidation Of Reactive Orange 16 Azo-
471   Dye In Aqueous Solution, Chem Eng J. 173 (2011) 463-473.

472 [4] Buthiyappan, A., Aziz, A., Raman, A., Daud, W. And Ashri, W.M., Recent Advances And
473   Prospects Of Catalytic Advanced Oxidation Process In Treating Textile Effluents, Rev Chem
474   Eng. 32 (2016) 1-47.

475 [5] Yagub, M.T., Sen, T.K., Afroze, S. And Ang, H.M., Dye And Its Removal From Aqueous
476   Solution By Adsorption: A Review, Adv Colloid Interfac. 209 (2014) 172-184.

477 [6] Ulson, S.M.D.A.G., Bonilla, K.A.S. And De Souza, A.A.U., Removal Of Cod And Color
478   From Hydrolyzed Textile Azo Dye By Combined Ozonation And Biological Treatment, J
479   Hazard Mater. 179 (2010) 35-42.

480 [7] Sudarjanto, G., Keller-Lehmann, B. And Keller, J., Optimization Of Integrated Chemical–
481   Biological Degradation Of A Reactive Azo Dye Using Response Surface Methodology, J
482   Hazard Mater. 138 (2006) 160-168.

483   [8] Tehrani-Bagha, A. And Amini, F., Decolorization Of A Reactive Dye By Uv-Enhanced
484   Ozonation, Progress In Color, Colorants And Coatings. 3 (2010) 1-8.

485   [9] Körbahti, B.K., Response Surface Optimization Of Electrochemical Treatment Of Textile Dye
486   Wastewater, J Hazard Mater. 145 (2007) 277-286.

487   [10] Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N. And Pattabhi, S.,
488   Utilization Of Various Agricultural Wastes For Activated Carbon Preparation And
489   Application For The Removal Of Dyes And Metal Ions From Aqueous Solutions, Bioresource
490   Technol. 87 (2003) 129-132.

491   [11] Gunukula, R.V.B. And Tittlebaum, M.E., Industrial Wastewater Treatment By An Advanced
492   Oxidation Process, J Environ Sci Heal A. 36 (2001) 307-320.

493   [12] Ali, N., Hameed, A. And Ahmed, S., Physicochemical Characterization And Bioremediation
494   Perspective Of Textile Effluent, Dyes And Metals By Indigenous Bacteria, J Hazard Mater.
495   164 (2009) 322-328.

496   [13] Bes-Piá, A., Mendoza-Roca, J., Alcaina-Miranda, M., Iborra-Clar, A. And Iborra-Clar, M.,
497   Reuse Of Wastewater Of The Textile Industry After Its Treatment With A Combination Of
498   Physico-Chemical Treatment And Membrane Technologies, Desalination. 149 (2002) 169-
499   174.

500   [14] Domínguez, J.R., Beltrán, J. And Rodríguez, O., Vis And Uv Photocatalytic Detoxification
501   Methods (Using TiO_2, TiO_2/H_2O_2, TiO_2/O_3, $TiO_2/S_2O_8^{2-}$, O_3, H_2O_2, $S_2O_8^{2-}$,
502   Fe^{3+}/H_2O_2 And $Fe^{3+}/H_2O_2/C_2O_4^{2-}$) For Dyes Treatment, Catal Today. 101 (2005)
503   389-395.

504   [15] Al-Kdasi, A., Idris, A., Saed, K. And Guan, C.T., Treatment Of Textile Wastewater By
505   Advanced Oxidation Processes—A Review, Global Nest: The Int. J. 6 (2004) 222-230.

506   [16] Chu, W. And Ma, C.-W., Quantitative Prediction Of Direct And Indirect Dye Ozonation
507   Kinetics, Water Res. 34 (2000) 3153-3160.

508   [17] Gül, Ş. And Özcan-Yıldırım, Ö., Degradation Of Reactive Red 194 And Reactive Yellow 145
509   Azo Dyes By O_3 And H_2O_2/Uv-C Processes, Chem Eng J. 155 (2009) 684-690.

510   [18] Oguz, E., Keskinler, B. And Çelik, Z., Ozonation Of Aqueous Bomaplex Red Cr-L Dye In A
511   Semi-Batch Reactor, Dyes Pigments. 64 (2005) 101-108.

512   [19] Shu, H.-Y., Degradation Of Dyehouse Effluent Containing Ci Direct Blue 199 By Processes
513   Of Ozonation, Uv/H_2O_2 And In Sequence Of Ozonation With Uv/H_2O_2, J Hazard Mater.
514   133 (2006) 92-98.

515   [20] Tehrani-Bagha, A., Mahmoodi, N. And Menger, F., Degradation Of A Persistent Organic Dye
516   From Colored Textile Wastewater By Ozonation, Desalination. 260 (2010) 34-38.

[21] Kordkandi, S.A. And Ashiri, R., Modeling And Kinetics Study Of Acid Anthraquinone Oxidation Using Ozone: Energy Consumption Analysis, Clean Technol Envir. 17 (2015) 2431-2439.

[22] Venkatesh Prabhu, M., Karthikeyan, R. And Shanmugaprakash, M., Modeling And Optimization By Response Surface Methodology And Neural Network–Genetic Algorithm For Decolorization Of Real Textile Dye Effluent Using Pleurotus Ostreatus: A Comparison Study, Desalin Water Treat. 57 (2016) 13005-13019.

[23] Khataee, A.R., Zarei, M. And Moradkhannejhad, L., Application Of Response Surface Methodology For Optimization Of Azo Dye Removal By Oxalate Catalyzed Photoelectro-Fenton Process Using Carbon Nanotube-Ptfe Cathode, Desalination. 258 (2010) 112-119.

[24] Mohana, S., Shrivastava, S., Divecha, J. And Madamwar, D., Response Surface Methodology For Optimization Of Medium For Decolorization Of Textile Dye Direct Black 22 By A Novel Bacterial Consortium, Bioresource Technol. 99 (2008) 562-569.

[25] Soltani, R.D.C., Rezaee, A., Khataee, A. And Safari, M., Photocatalytic Process By Immobilized Carbon Black/Zno Nanocomposite For Dye Removal From Aqueous Medium: Optimization By Response Surface Methodology, J Ind Eng Chem. 20 (2014) 1861-1868.

[26] Mook, W., Aroua, M., Szlachta, M. And Lee, C., Optimisation Of Reactive Black 5 Dye Removal By Electrocoagulation Process Using Response Surface Methodology, Water Sci Technol. 75 (2017) 952-962.

[27] Kabdaşlı, I., Ölmez, T. And Tünay, O., Factors Affecting Colour Removal From Reactive Dye Bath By Ozonation, Water Sci Technol. 45 (2002) 261-270.

[28] Pachhade, K., Sandhya, S. And Swaminathan, K., Ozonation Of Reactive Dye, Procion Red Mx-5b Catalyzed By Metal Ions, J Hazard Mater. 167 (2009) 313-318.

[29] Sevimli, M.F. And Sarikaya, H.Z., Ozone Treatment Of Textile Effluents And Dyes: Effect Of Applied Ozone Dose, Ph And Dye Concentration, J Chem Technol Biot. 77 (2002) 842-850.

[30] Khataee, A., Gohari, S. And Fathinia, M., Modification Of Magnetite Ore As Heterogeneous Nanocatalyst For Degradation Of Three Textile Dyes: Simultaneous Determination Using Mcr-Als, Process Optimization And Intermediate Identification, J Taiwan Inst Chem E. 65 (2016) 172-184.

[31] Tak, B.-Y., Tak, B.-S., Kim, Y.-J., Park, Y.-J., Yoon, Y.-H. And Min, G.-H., Optimization Of Color And Cod Removal From Livestock Wastewater By Electrocoagulation Process: Application Of Box–Behnken Design (Bbd), J Ind Eng Chem. 28 (2015) 307-315.

550 [32] Mook, W.T., Ajeel, M.A., Aroua, M.K. And Szlachta, M., The Application Of Iron Mesh
551   Double Layer As Anode For The Electrochemical Treatment Of Reactive Black 5 Dye, J
552   Environ Sci. 54 (2017) 184-195.

553 [33] Soltani, R.D.C., Rezaee, A., Godini, H., Khataee, A. And Hasanbeiki, A.,
554   Photoelectrochemical Treatment Of Ammonium Using Seawater As A Natural Supporting
555   Electrolyte, Chem Ecol. 29 (2013) 72-85.

556 [34] Esfandiyari, T., Nasirizadeh, N., Ehrampoosh, M.H. And Tabatabaee, M., Characterization
557   And Absorption Studies Of Cationic Dye On Multi Walled Carbon Nanotube–Carbon
558   Ceramic Composite, J Ind Eng Chem. 46 (2017) 35-43.

559 [35] Tiwari, B., Muthukumarappan, K., O'donnell, C. And Cullen, P., Modelling Colour
560   Degradation Of Orange Juice By Ozone Treatment Using Response Surface Methodology, J
561   Food Eng. 88 (2008) 553-560.

562 [36] Olmez-Hanci, T., Arslan-Alaton, I. And Basar, G., Multivariate Analysis Of Anionic, Cationic
563   And Nonionic Textile Surfactant Degradation With The H_2O_2/Uv-C Process By Using The
564   Capabilities Of Response Surface Methodology, J Hazard Mater. 185 (2011) 193-203.

565 [37] Turhan, K., Durukan, I., Ozturkcan, S.A. And Turgut, Z., Decolorization Of Textile Basic
566   Dye In Aqueous Solution By Ozone, Dyes Pigments. 92 (2012) 897-901.

567 [38] Moussavi, G. And Mahmoudi, M., Degradation And Biodegradability Improvement Of The
568   Reactive Red 198 Azo Dye Using Catalytic Ozonation With Mgo Nanocrystals, Chem Eng J.
569   152 (2009) 1-7.

570 [39] Wu, J. And Wang, T., Ozonation Of Aqueous Azo Dye In A Semi-Batch Reactor, Water Res.
571   35 (2001) 1093-1099.

572 [40] Zhang, R., Yuan, D.-X. And Liu, B.-M., Kinetics And Products Of Ozonation Of Ci Reactive
573   Red 195 In A Semi-Batch Reactor, Chinese Chem Lett. 26 (2015) 93-99.

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