

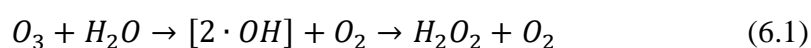
## **6 Optimization for Minimizing the Cost of Ozonation of Highly Concentrated Textile Dyeing Wastewater in a Bubble Column Reactor**

Textile manufacturing contributes significantly to the economies of several countries, including Bangladesh, India, China, Turkey, Vietnam, and Nigeria (Çelekli, Yavuzatmaca, and Bozkurt 2009). Although a significant contributor to the world economy, textile industries have substantial negative impacts on the environment, particularly aquatic ecosystems. The release of untreated or partially treated textile effluent into the environment and natural water bodies is a significant subject of concern since it impairs the photosynthetic activities of aquatic biota and causes bio-magnification. Synthetic dyes are estimated to be generated at a rate of  $7 \times 10^5$  metric tonnes per year, with the global consumption by the textile sector alone exceeding 10,000 tonnes per year (Yagub et al. 2014). The use of reactive dyes comprising azo-based chromophores with reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, and dichloro-fluoropyrimidine has increased in the last decade as they offer brilliant, vibrant colors to the fabrics (Körbahti 2007). Many of these compounds are recalcitrant and have carcinogenic, mutagenic, or teratogenic consequences in biological systems.

The dyeing wastewater has been treated using various physicochemical, biological, and advanced oxidation techniques. The conventional methods such as activated carbon adsorption, flocculation, coagulation, ultrafiltration, and reverse osmosis create vast amounts of sludge and necessitate post-treatment of the captured dyes (Paździór, Bilińska, and Ledakowicz 2019; Singh and Arora 2011). Biological methods such as activated sludge, sequential batch reactor, and membrane and packed bed bioreactors have been extensively investigated. Although the anaerobic degradation effectively degraded the azo dyes, the generation of poisonous aromatic amines and the slow rate of biological treatments are the major drawbacks (Chaturvedi et al. 2021c; Punzi, Nilsson, et al. 2015b).

The advanced oxidation processes (AOP) generally utilize hydroxyl radicals to oxidize a broad spectrum of organic dye molecules by radical oxidation pathways. The ozonation process is usually preferred to other advanced oxidation methods such as Fenton and photocatalytic treatments as it offers a high oxidation rate, no sludge formation, adaptability across an extensive pH range, and selective oxidation of complex hydrolyzed dye molecules (Buthiyappan, Abdul Aziz, and Wan Daud 2016). The ozonation process offers oxidation directly *via* ozone molecules and indirectly *via* the hydroxyl radicals. The indirect route yields a rapid oxidation rate due to the higher oxidation potential of hydroxyl radicals (2.8 Volts) over that of ozone (2.07 Volts) (Palit 2010). As air is the primary source for ozone generation, the ozone can be applied for on-site usage and is a well-suited technology for even small-scale cottage industries working in textile dyeing. However, the high processing cost associated with ozonation remains a concern.

Generally, the dyeing wastewater discharged from the textile industries has low dye loading (~0.5 g/l) [as per standards of Central Pollution Control Board, India]. As the rate constant ( $k = 10^4 \text{ M}^{-1}\text{s}^{-1}$ ) for hydroxyl radical generation in the ozonation process is exceptionally high (Schöne and Herrmann 2014), the wastewater with low dye concentrations do not utilize the generated hydroxyl radicals effectively. It leads to the recombination of the excess produced hydroxyl radicals according to the following chemical reaction (Cuerda-Correa, Alexandre-Franco, and Fernández-González 2020), and therefore raises the overall operating cost of the process.



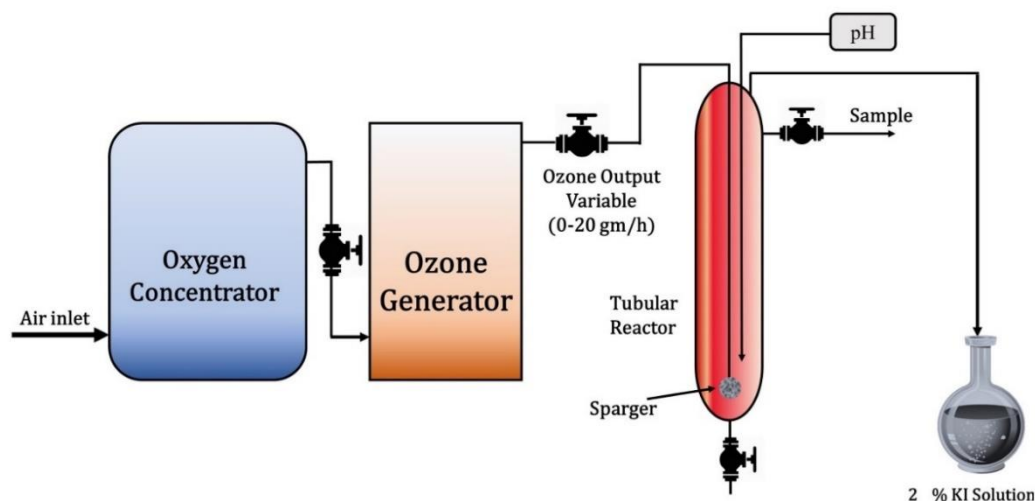
The present work aims to conduct the ozonation treatment of highly concentrated dyeing wastewater (with Reactive Blue dye) and optimize the process parameters (such as inlet ozone concentration, initial dye concentration, and initial pH level) to minimize the overall electricity consumption of the process. A central composite design (CCD) based *Response Surface Method* (RSM), a statistical tool, was used to study various process parameters'

interactions to optimize the process. An empirical correlation was developed for the average specific electricity consumption for the ozonation process. The optimization study also yielded the value of process parameters that can minimize ozonation's electricity consumption (main component in the operating cost). Material required

A Reactive Blue dye obtained from a local textile industry was used, without any purification, in double-distilled water for making the simulated dyeing wastewater. The ozonation experiments of dyeing wastewater were performed at a wide range of dye concentration (0.5 g/l to 10 g/l) and pH (4-12) to evaluate the effect of dye loading and pH. The variation in pH was done using 0.1 N sodium hydroxide (NaOH) and 50 % hydrochloric (HCl) acid solution. The ozonation was carried out in batch mode.

## **6.1 Experimental Setup**

A schematic of the experimental setup used in this study is shown in Figure 1. Ozone was generated from the atmospheric air using Faraday's Ozone Generator, which can operate with a production range of 0-25 g/h. It was introduced into dyeing solution in a cylindrical bubble column (of 1.2 L working volume) at a constant flow rate of 0.5 L/min. A thin porous diffuser made of ceramic was utilized at the reactor's bottom to create a homogenous distribution of ozone and diffusional transition inside the wastewater. The samples were collected at a definite time interval to analyze the amount of dye present in the wastewater. The unreacted ozone was sent to a gas scrubbing bottle filled with 2 % KI solution. The pH of the samples was measured at each time step using a benchtop pH meter. The amount of dye removed and the specific electricity consumption was calculated for the ozonation treatment.



**Figure 6.1 Schematic of the Ozonator setup for the degradation of Reactive Blue dye**

## 6.2 Design of experiment

The CCD tool of RSM was employed to investigate the effects of the three independent variables on the response functions (Shen et al. 2017). The chosen independent variables were inlet ozone concentration (A), initial dye concentration (B), and initial pH (C). The specific electricity consumption was the response function in the optimization study. The response function was minimized for the maximum dye removal. The selected experimental levels of all independent variables are summarized in Table 6.1.

**Table 6.1 Experimental ranges and levels of the independent variables**

Variables	Range and Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Initial % Ozone	20	40	60	80	100
Initial Dye Concentration (g/l)	2	4	6	8	10
Initial pH	4	6	8	10	12

The regression analysis of the experimental data and the plotting of response surfaces were performed using *Design Expert 11.0* software. Once the outcomes of the optimization studies

were obtained, a mathematical model was developed to represent the interaction between the response function and the independent variables. A second-order polynomial relation of the following form was obtained:

$$y = a_o + \sum a_i x_i + \sum a_{ij} x_i x_j + \sum a_{ii} x_i^2 \quad (6.2)$$

where  $y$  represents the response function,  $a_o$  is a constant,  $a_i$ ,  $a_{ij}$  and  $a_{ii}$  are the linear, interactive, and quadratic coefficients, respectively and  $x_i$  and  $x_j$  are the levels of the independent variables.

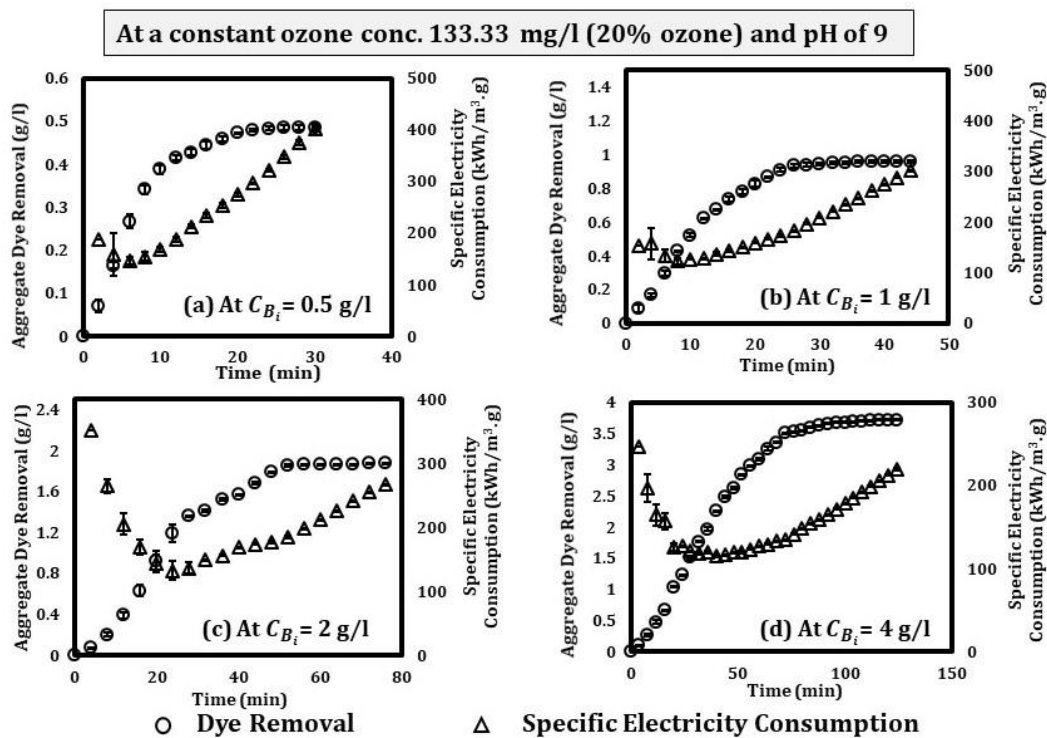
### 6.3 Dye removal and electricity consumption at various initial dye concentration

First, the ozonation experiments were performed at varying initial dye concentrations keeping ozone concentration and pH at constant values, and the corresponding dye removal and specific electricity consumption rates were determined. The specific electricity consumption ( $SEC$ ) was defined as the kWh of electricity consumed to remove one gram of dye from one m<sup>3</sup> of dyeing wastewater:

$$SEC = \frac{P(kW) \times t(min.) \times 1000}{V(l) \times 60 \times DR(g)} \quad (6.3)$$

where  $P$  is the power consumed (kW),  $V$  is the volume of dyeing wastewater treated,  $t$  is the ozonation time, and  $DR$  is the amount of dye removed (g). The initial dye concentration was varied from 0.5 g/l to 4 g/l at a constant ozone concentration of 133.33 mg/l (20 % ozone) and pH of 9. The variations in the aggregate dye removal (g/l) and the specific electricity consumption (kWh/m<sup>3</sup> g) with the ozonation time (min) are shown in Fig. 6.2 (a-d). It was observed that the *dye removal rate* (i.e., the slope of the aggregate dye removal vs. ozonation time curve) decreased with time, and the total amount of removed dye got saturated after a specific time at all initial dye concentrations. This is attributed to a reduced pH in the acidic range due to the formation of the organic acids (e.g., maleic, formic, oxalic, and fumaric acids) as by-products in the ozonation of dyes (Chaturvedi et al. 2021b). The oxidation during

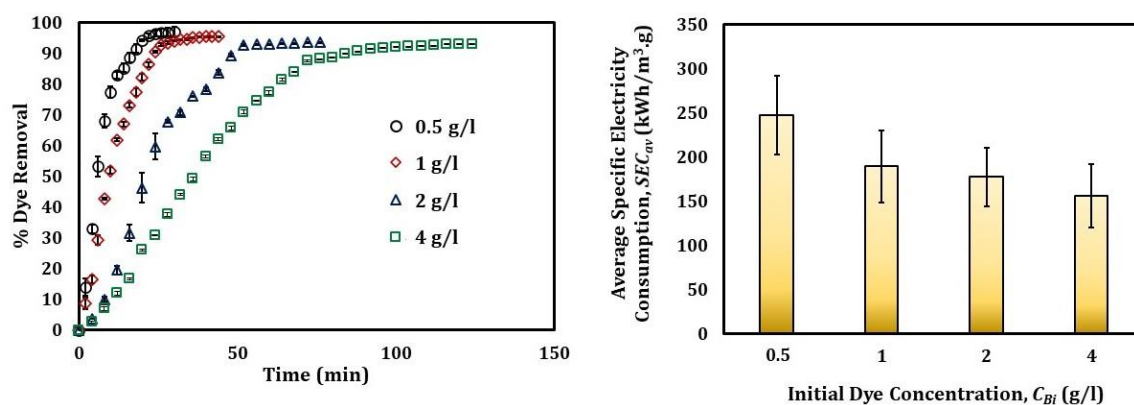
ozonation occurs by hydroxyl radicals (which renders fast oxidation) at alkaline pH and by molecular ozone (which is very slow) at acidic pH conditions. Further, the specific electricity consumption was also changing with the ozonation time in Fig. 6.2. The increase in the particular electricity consumption after a long ozonation time is attributed to the slow dye removal rate.



**Figure 6.2 Aggregate dye removal and specific electricity consumption at increasing concentration of dye: (a) 0.5 g/l (b) 1 g/l (c) 2 g/l (d) 4 g/l**

Fig. 6.3(a) depicts the percentage of removed dye with time at different cases of initial dye concentrations. It was observed that the dye removal became saturated in all cases after the removal of about 85% or more dye; however, it naturally took a longer time to achieve the saturation for the case with a higher initial dye concentration. Therefore, continuing the ozonation process after the occurrence saturation is not recommended as the dye removal rate is prolonged. As the specific electricity consumption (shown in Fig. 6.2) was not constant during the ozonation of a dye, it was averaged from the beginning till the saturation to determine ‘average’ specific electricity consumption ( $SEC_{av}$ ) for the overall ozonation

process. Fig. 6.3 (b) displays the  $SEC_{av}$  for different initial dye concentrations keeping the inlet ozone concentration and pH at 20% and 9, respectively. Notably, the  $SEC_{av}$  for the ozonation process decreased when the initial dye concentration was increased. It suggested that the operating cost of ozonation can be reduced by operating at a high initial dye concentration. Hence, it necessitates optimizing the ozonation process parameters to minimize electricity consumption.



**Figure 6.3 (a) Percentage dye removal vs. time at different initial dye concentrations, (b) Average specific electricity consumption ( $SEC_{av}$ ) for the ozonation process at different initial dye concentrations**

## 6.4 Development of an empirical correlation for the average specific electricity consumption during the ozonation of Reactive Blue dye

### 6.4.1 Measurement of the $SEC_{av}$ for the DOE

The ozonation rate of dyes depends on three key process variables: *inlet ozone concentration*, *initial dye concentration*, and *initial pH level*. The CCD design of the RSM statistical tool was used to generate a three-factor complete factorial design of the experiment (DOE) parameter matrix, as shown in Table 6.2. The  $SEC$  was measured for each set of independent variables at a uniform time interval during the experiment (until the dye removal rate saturated) and was then averaged to yield  $SEC_{av}$  (response function) for the given run. The same was performed

for all the 20 runs in random order, and the measured  $SEC_{av}$  have been summarized in Table 6.2.

**Table 6.2 Measured values of the response function (average specific electricity consumption) for the Central Composite Design (CCD) parameter matrix**

Run	A	B	C	R
	Initial Ozone Concentration (%)	Initial Dye Concentration (g/L)	pH	Average Specific Electricity Consumption ( $SEC_{av}$ ) (kWh/m <sup>3</sup> .g)
1	60	6	8	157.727
2	60	6	8	147.882
3	60	6	8	152.393
4	60	6	8	150.443
5	60	6	8	142.928
6	60	6	8	147.431
7	60	2	8	166.364
8	60	6	12	126.625
9	100	6	8	125.098
10	60	6	4	201.033
11	60	10	8	194.762
12	20	6	8	165.734
13	40	8	6	186.279
14	40	4	10	140.041
15	80	8	10	142.043
16	40	8	10	148.07
17	80	8	6	180.075
18	80	4	10	117.865
19	40	4	6	174.942
20	80	4	6	149.653

#### 6.4.2 Statistical modeling for the $SEC_{av}$ using RSM

The RSM-based statistical analysis was performed to find the empirical correlation for  $SEC_{av}$  incurred during the ozonation of Reactive Blue dye in a tubular reactor. The model



coefficients were calculated using multiple regression analysis and were validated using the *Analysis of Variance* (ANOVA) with a 95% confidence level. The following empirical correlation for  $SEC_{av}$  was obtained as the function of three chosen process variables:

$$SEC_{av} = 368.894 - 0.717A - 21.832B - 20.142C + 0.110AB + 1.808B^2 + 0.762C^2$$

(6.4)

where  $A$ ,  $B$ ,  $C$  indicate the inlet ozone concentration (in %), initial dye concentration (in g/L), and initial pH level (in number), respectively. The above correlation is the regression-based best numerically fit relation obtained to predict the  $SEC_{av}$  in the range of process variables (as mentioned in Table 6.1) used in this study. A sensitivity analysis was performed to determine the impact of various combinations of process variables on the  $SEC_{av}$ , and the results have been presented in Table 6.3. It is apparent from Table 6.3 that the other combinations of the process variables (such as  $A.C$ ,  $B.C$ ,  $A^2$ ) did not find any mention in Eq. 6.4 had high  $p$ -values (more than 0.05) or low  $F$ -values and therefore were not contributing significantly to the determination of  $SEC_{av}$ . Further, the process variables mentioned in Eq. 6.4 (such as  $A$ ,  $B$ ,  $C$ ,  $A.B$ ,  $B^2$ ,  $C^2$ ) do not contribute equally in the determination of  $SEC_{av}$ . The significance of their relative contributions can be assessed from their respective  $F$  values. The higher the value of  $F$ , the higher the impact of that particular variable group on the  $SEC_{av}$ . Therefore, the contributions of various process variable groups of Eq. 4 in the  $SEC_{av}$  were found in the following decreasing order:  $C$ ,  $B^2$ ,  $A$ ,  $B$ ,  $C^2$ , and  $A.B$ .

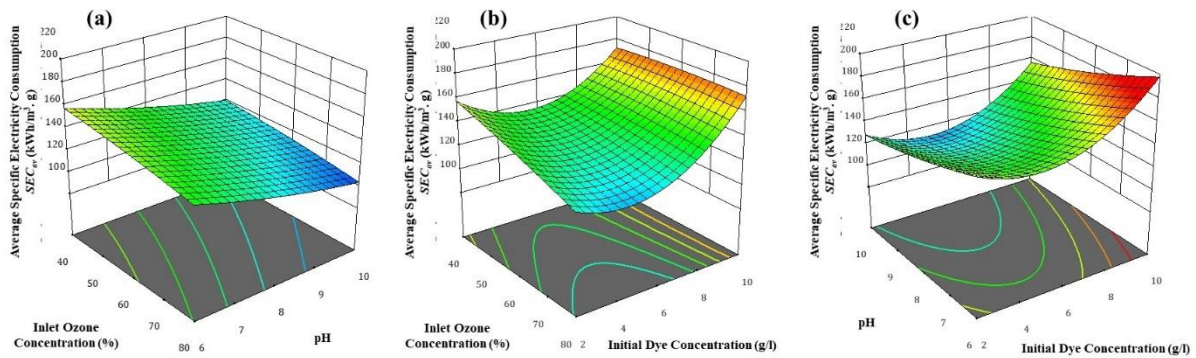
**Table 6.3 Analysis of variance (ANOVA) for ozonation process using response surface quadratic model**

Factors	Statistics				
Source	SS	df	MS	F-value	p-value
Model	9481.64	9	1053.52	36.62	< 0.0001
(A) $O_3$	1242.00	1	1242.00	43.17	<0.0001
(B) $C_{B_i}$	1068.67	1	1068.67	37.14	0.0001
(C) $pH$	5319.73	1	5319.73	184.90	< 0.0001
(A · B) $O_3 \cdot C_{B_i}$	155.18	1	155.18	5.39	0.0426
(A · C) $O_3 \cdot pH$	<b>1.35</b>	<b>1</b>	<b>1.35</b>	<b>0.0470</b>	<b>0.8327</b>
(B · C) $C_{B_i} \cdot pH$	<b>11.41</b>	<b>1</b>	<b>11.41</b>	<b>0.3964</b>	<b>0.5431</b>
A <sup>2</sup>	<b>60.68</b>	<b>1</b>	<b>60.68</b>	<b>2.11</b>	<b>0.1771</b>
B <sup>2</sup>	1315.46	1	1315.46	45.72	<0.0001
C <sup>2</sup>	233.85	1	233.85	8.13	0.0172
Residual	287.71	10	27.77		
Lack of Fit	161.22	5	32.24	1.27	0.3983
Pure Error	126.49	5	25.30		
<b>R<sup>2</sup></b>		<b>Adj. R<sup>2</sup></b>		<b>Pred. R<sup>2</sup></b>	
<b>0.9705</b>		<b>0.9440</b>		<b>0.8493</b>	

SS: sum of squares, df: degree of freedom, MS: mean square

### 6.5 Effect of process variables on the average specific electricity consumption in the ozonation of Reactive Blue dye

The developed empirical correlation (Eq. 6.4) was used to investigate the effect of independent variables, i.e., inlet ozone concentration, initial dye concentration, and initial pH level, on the  $SEC_{av}$  incurred in the ozonation of Reactive Blue dye in a tubular bubble reactor. In this study, two independent variables were altered, keeping the third variable at a constant value, and the predictions of  $SEC_{av}$  were made as shown in Fig. 6.4. Such response surfaces were used to examine the combined effect of two independent variables on the  $SEC_{av}$  in the ozonation.



**Figure 6.4** Predicted surface plots of average specific electricity consumption ( $SEC_{av}$ ) as a function of two independent variables (while the third variable was held constant at its respective center level shown in Table 6.1): (a) inlet ozone concentration and the initial pH were varied keeping initial dye concentration at 6 g/l, (b) inlet ozone concentration, and initial dye concentration were varied keeping pH constant at 8, (c) initial dye concentration and initial pH were varied keeping ozone concentration at 60%

#### 6.5.1 Effect of inlet ozone concentration

The surface plots of predicted  $SEC_{av}$  vs. inlet ozone concentration are shown at various initial dye loading keeping a constant pH of 8 in Fig. 6.4(a), and at different initial pH levels keeping a constant initial dye concentration of 6 g/l in Fig. 6.4(b). The  $SEC_{av}$  was found to be decreasing monotonically as the inlet ozone concentration was increased from 20 % to 100 %. It was naturally expected as the exposure of high ozone concentration would generate high loading of hydroxyl radicals and, therefore, cause rapid dye degradation, leading to a lower value of  $SEC_{av}$ .

#### 6.5.2 Effect of initial pH level

The surface plots of predicted  $SEC_{av}$  vs. pH are shown at various inlet ozone concentrations keeping a constant initial dye concentration of 6 g/l in Fig. 6.4(b), and at different initial dye concentrations keeping constant inlet ozone at 60 % in Fig. 6.4(c). The  $SEC_{av}$  was found to be decreasing monotonically as the pH was increased from 6 to 10. It was attributed to a high

concentration of hydroxyl radicals formed in a highly alkaline environment. It led to fast degradation of organic dye, yielding a lower value of  $SEC_{av}$  at a higher pH level.

### 6.5.3 Effect of initial dye concentration

The surface plots of predicted  $SEC_{av}$  vs. initial dye concentration are shown at various inlet ozone concentrations keeping initial pH constant at 8 in Fig. 6.4(a), and at different initial pH keeping constant inlet ozone at 60 % in Fig. 6.4(c). At a constant inlet ozone concentration and pH, it was noticed that the value of  $SEC_{av}$  first decreased with increasing the initial dye concentration between 4–6 g/l and then started increasing beyond a critical value of initial dye concentration. It suggested that the optimization of initial dye concentration could minimize the  $SEC_{av}$  to improve the economy of the ozonation process.

## 6.6 Optimization of process variables to minimize $SEC_{av}$

Numerical optimization was performed using the *Design Expert* software to optimize the process variables (inlet ozone concentration, pH, and initial dye concentration) to minimize the operating cost by lowering electricity consumption ( $SEC_{av}$ ) in the ozonation process. The process variables were varied in the defined range, and a tolerance limit of 5% was set on the objective function,  $SEC_{av}$ . Ten distinct solutions satisfying the set constraints were obtained. Out of these solutions, the combination of independent variables which yielded the minimum  $SEC_{av}$  value was chosen as the optimum condition. The optimum values of the process variables were found to be as follows: inlet ozone concentration of 80 %, pH at 10, and initial dye concentration of 4.427 g/l. This optimum condition yielded the minimum  $SEC_{av}$  of 119.27 kWh/g.m<sup>3</sup>. It indicated that 119.27 kWh of electricity would be consumed to remove one gram of dye from one m<sup>3</sup> of dyeing wastewater in conducting the ozonation process at optimum process variables. The optimization study suggests that the ozonation should be carried out at the initial dye loading of ~4.4 g/l, which is much higher than the regular dye concentration (of ~0.2-0.5 g/l) in the textile effluent. It requires a dye-enrichment step (such

as adsorption, coagulation, etc.) before ozonation to realize the cost-benefit of process optimization.

## 6.7 Model verification and cost analysis

The ozonation experiments were carried out at the optimum condition of process variables obtained in Section 6.7 and at the initial dye loading of 0.5 g/l (a regular dye concentration in the textile effluent). The experimentally measured  $SEC_{av}$  were compared with the theoretically predicted values (using the empirical correlation Eq. 6.4) and summarized in Table 6.4. The measured  $SEC_{av}$  obtained as 123.77 and 177.79 kWh/g.m<sup>3</sup> for the initial dye loading of 4.427 and 0.50 g/l, respectively, which were very close to the predicted values of 119.27 and 161.85 g/l. It validated the model's predictions for  $SEC_{av}$  with a 10% error.

Next, the cost of ozonation (\$/ g of dye removed/ m<sup>3</sup> of wastewater) was calculated based on the electricity consumed during the ozonation process and shown in Table 6.4. The operating costs were calculated at the optimum and regular dye loadings of 4.427 and 0.50 g/l, respectively, in the simulated textile wastewater, keeping pH and inlet ozone concentration at the optimum values of 10 and 80%, respectively. It was found that the operating cost of ozonation of dyeing wastewater can be reduced by nearly 26-30 % when the ozonation was performed at the elevated initial dye concentration. As the reduction in the ozonation cost is significant, it is recommended to enrich dye concentration in the regular textile wastewater by physical means, which are very economical, before performing the ozonation process.

**Table 6.4 Model verification and cost comparison of the ozonation at the optimum initial dye concentration with respect to the regular dye concentration present in the textile effluent [The optimum values of inlet ozone concentration, 80%, and pH, 10, were used in all cases]**

Parameters		Initial dye concentration (g/l)		% Reduction
		0.50 [Regular level]	4.427 [Optimum level]	
Average specific electricity consumption, $SEC_{av}$ , (kWh/g.m <sup>3</sup> )	Model prediction	161.85	119.27	26.31
	Experimental measurement	177.79	123.77	30.38
Electricity cost in ozonation (\$/g.m <sup>3</sup> )	Model prediction	13.27	9.78	26.31
	Experimental measurement	14.58	10.15	30.38

## 6.8 Conclusion

This study showed that the ozonation could rapidly oxidize the Reactive Blue dye with loading in the range of 0.5 to 4 g/l in 30 to 90 min, respectively. However, the rate of dye removal became negligible, in all cases, after removing about 85-95 % dye due to a reduction in pH of the reactor medium from alkaline to the acidic range. A parameter named *average specific electricity consumption* ( $SEC_{av}$ ) was defined to compare the ozonation cost at various process conditions. An empirical correlation to predict  $SEC_{av}$  was developed as the function of three process variables, inlet ozone concentration, initial pH level, and initial dye concentration; and the correlation was also experimentally validated and found to be predicting the  $SEC_{av}$  within 10% of error. It was found that the  $SEC_{av}$  decreased monotonically with the increase in the inlet ozone concentration and initial pH level. However, at given inlet ozone concentration and pH, the  $SEC_{av}$  initially reduced with an increase in the initial dye concentration, although an upward trend in the  $SEC_{av}$  was witnessed beyond a critical initial dye concentration. The optimization study to minimize the cost of ozonation yielded the optimum values of process variables (inlet ozone concentration of 80

%, pH at 10, and initial dye concentration of 4.427 g/l) which ensured the minimum  $SEC_{av}$  of 119.27 kWh/g.m<sup>3</sup>. As the dye concentration in the regular textile wastewater is very low, it was recommended to have a dye enriching pre-treatment step for the regular textile effluent to achieve the desired high inlet dye concentration for ozonation. Under the optimized condition, the cost of electricity consumption in ozonation was found to be reduced significantly (by ~ 25-30 %). However, the nature, design and cost of the pre-treatment step (using adsorption, coagulation etc.) would determine the net gain in the overall treatment cost which may be focus of the future work.

## **7 Phyto-/Geno-Toxicity Assessments of the Dyeing Wastewater treated with Anaerobic-Aerobic Biodegradation (AnAB) vs. Ozonation-Aerobic Biodegradation (OAB) Processes**

The effluents of textile and dyeing industries are some of the vast sources of wastewaters containing high loads of dyes, pigments, and various associated contaminants such as oil, detergents, dissolved and suspended solids, and other non-biodegradable toxic