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Decolorization of direct red and direct blue dyes used in handmade paper making by ozonation treatment

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ABSTRACT

Handmade paper utilizes direct dyes for imparting it bright colors to be used in wedding cards, fancy, decorative arts, etc. The effluent of handmade paper industry faces problem of highly colored effluent. The present study aims at decolorization of direct red and direct blue dyes, used abundantly in the industry, with the help of ozonation treatment. The batch studies have been conducted on decolourization of synthetic samples of these dyes at various initial concentrations, temperature, and pH. The effect of these parameters has been studied on decolorization efficiency. The maximum decolorization is achieved at pH of 10 and temperature of 313 K. The equilibrium time of decolorization with ozonation treatment for direct red and direct blue dye for 50 ppm initial concentration was 6 and 4 min, respectively. The kinetics of decolorization was found to be pseudo-first-order type.

Keywords: Ozonation; Decolorization; Handmade paper

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1. Introduction

Handmade paper making is a traditional art of India, which has emerged as one of the prominent export-oriented sectors of India. Handmade paper utilizes nonwoody raw material and minimum amount of chemicals, thus called as “Totally Eco-Friendly Paper.” Paper has traditionally been defined as a felted sheet formed on a fine screen from a water suspension of fibers [1]. The art of handmade paper making in India goes back to the third century BC [2]. The Indian handmade paper industry has been identified as one of the village industries, which has seen significant growth in last one decade because of increased demand not only on national level but also at the international arena [3]. Huge amount of direct dyes is used for dyeing of pulp to make bright-colored handmade paper, and therefore, the wastewater discharged from these industries is highly colored. Dyes usually have complex aromatic molecular structures, which make them more stable and difficult to biodegrade [4,5]. Ozone is a strong oxidant ($E_0 = 2.08$ V) [6] and is able to form powerful, nonselective oxidant of the hydroxyl radical ($E_0 = 3.06$ V) at high pH values [7]. Due to its high oxidation potential, ozone can effectively breakdown the complex aromatic rings of

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dyestuffs, resulting in the decolorization and transformation of the dye compounds [8]. Ozonation is one of the most effective means of decolorizing dye-laden wastewater [9–11]. It results in simultaneous interaction and breakdown of refractory organic matter or dissolved organic carbon by breaking complex compounds into simpler molecules [12]. The ozone can be applied directly in its gaseous state and does not increase the volume of wastewater and sludge [13–15]. Ozone is known to be effective for decomposing organic chemicals containing carbon–carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon–nitrogen double bonds, carbon–hydrogen bonds, silicon–hydrogen, and carbon–metal bonds [16]. Ozone react by either direct oxidation of compounds by molecular ozone or oxidation of compounds by hydroxyl free radicals produced during the decomposition of ozone [17,18].

2. Materials and methods

2.1. Preparation of dye solution

Commercial grade Indosol Direct Red and Indosol Blue GLL p of Clariant make, which is widely used in handmade paper industry, was taken for the study. Stock solutions of 1,000 ppm concentration of both direct red and direct blue dyes were prepared by dissolving dry dye powder in 1,000 ml of distilled water. The dye solutions of various concentrations were prepared by dilution of stock solution for further studies.

2.2. Experimental set up

The ozonation system consists of oxygen concentrator, ozone generator, and ozone–water reaction system. The oxygen concentrator, 5 LPM Faraday make, provides oxygen of 90% purity using air as feed gas. The concentrated oxygen at desired flow rate of 0 to 5 LPM was fed to ozone generator (Model 15 G, Faraday). Ozone generator has a capacity of 15 g/h using coronal discharge technology. PTFE tubing is used to connect the ozone outlet port from ozone generator to gas washing bottle of 500 ml capacity. A rotameter with regulating valve for flow adjustment was provided on oxygen concentrator and ozone generator. The applied ozone dose could be readily adjusted by varying ozone weight percentage and gas flow rate. The schematic of the experimental setup is shown in Fig. 1.

2.3. Ozonation studies

The ozonation studies were conducted by varying the parameters including pH ranging from 2 to 10, temperature from 313 to 333 K, and initial concentration of direct blue and direct red dye solution varying from 50 to 1,000 ppm. The ozone at 15% weight and 2 LPM was bubbled to 200 ml of dye solution through gas washing bottle. The samples were withdrawn after every 2 min to analyze residual color. The residual ozone from gas washing bottle was passed through the ozone destructor. The initial pH of the dye solution was varied from 2 to 10 with the help of 1 N HCl or 1 N NaOH. The decolorization efficiency was expressed as a percentage decrease in absorbance at maxima for samples of dye solutions as shown below.

$$\text{Decolorization,} \quad \% = \frac{\text{Absorbance}_{\text{initial}} - \text{Absorbance}_{\text{final}}}{\text{Absorbance}_{\text{initial}}} \times 100 \tag{1}$$

3. Results and discussions

3.1. Characterization of dye

The dye solution was scanned from 200 to 1,100 nm with the help of double beam UV–vis spectrophotometer. The maximum absorbance was obtained for direct blue and direct red dyes at 574 and 525 nm, respectively. It was also found that Beer's law was followed for dye concentration up to 50 ppm. The chemical structure of direct red and direct blue dye [19,20] is shown in Figs. 2 and 3, respectively. The characteristics are summarized in Table 1. The standard calibration charts of direct red and direct blue dyes of various concentrations were prepared for determining concentration by analyzing the absorbance at their respective maxima. The standard calibration charts of direct red and direct blue dye are shown in Figs. 4 and 5, respectively.

3.2. Effect of initial concentration and time on color removal

The decolorization study was conducted for various initial concentrations of dyes in the range of 50–1,000 ppm. The decolorization efficiency of direct red and direct blue dye solutions with ozonation time is shown in Figs. 6 and 7, respectively.

The results show that the decolorization efficiency of ozone treatment is dependent on initial concentration of dye solution. The time required for complete color removal increases in increasing the initial dye concentration. For initial dye concentration of 50, 500, and 1,000 ppm, the time required for complete color removal is 5, 15, and 30 min, respectively, for both

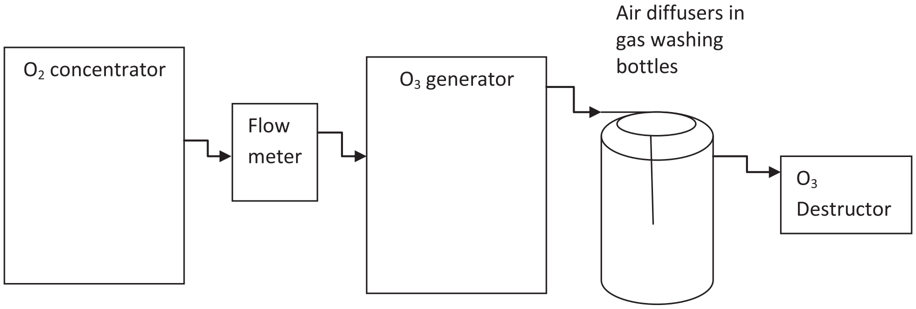

Fig. 1. Scheme of process for decolorization of dye solution with ozone.

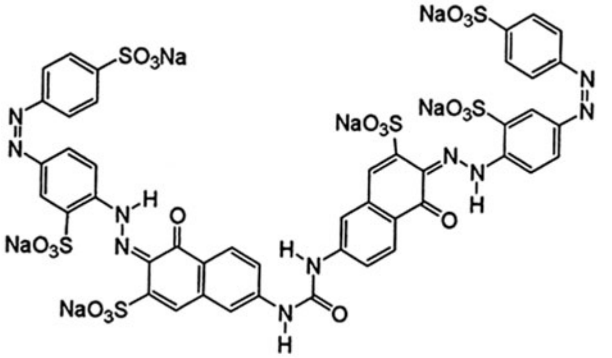

Fig. 2. Chemical structure of direct red dye.

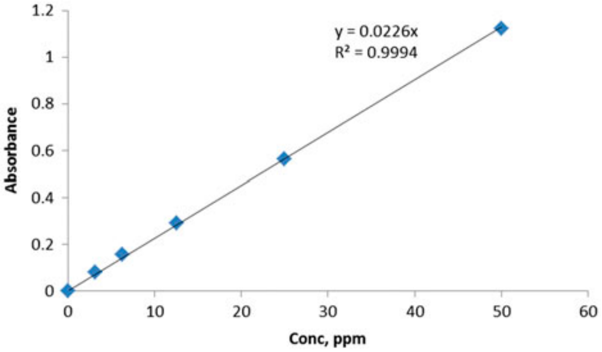

Fig. 4. Standard calibration chart of direct red dye.

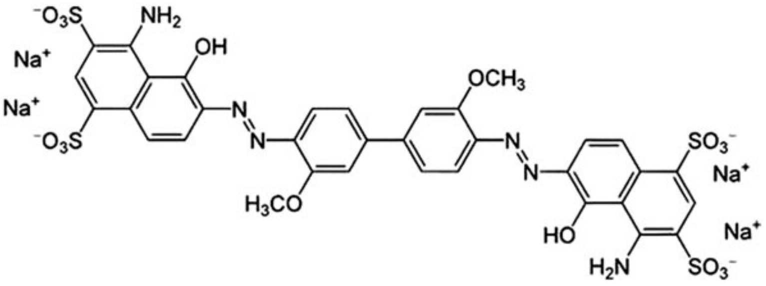

Fig. 3. Chemical structure of direct blue dye.

Table 1
Characteristics of dye

Chemical name	Direct red	Direct blue
λ_{max} (nm)	509	566
Molecular formula	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$	$C_{34}H_{22}N_4Na_4O_{16}S_4$
Molecular weight	1,373.08	962.78

direct red and direct blue dyes. The results are well in agreement with the studies conducted by other researchers [21–25].

3.3. Effect of temperature on color removal

The temperature has a notable effect on the decolorization efficiency of ozone. Some waste streams

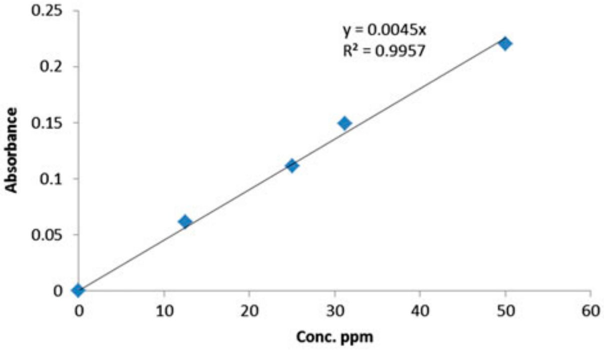

Fig. 5. Standard calibration chart of direct blue dye.

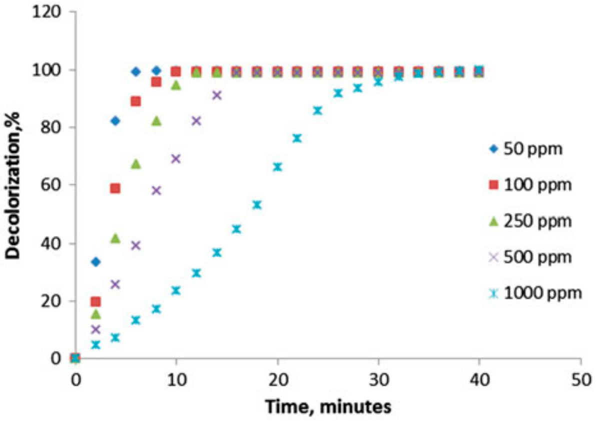

Fig. 6. Effect of initial concentration on decolorization of direct red dye.

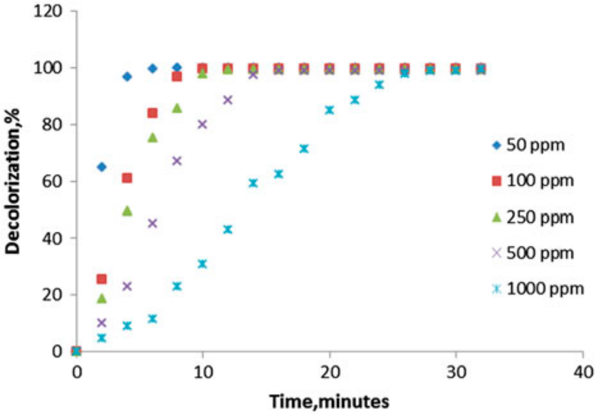

Fig. 7. Effect of initial concentration on decolorization of direct blue dye.

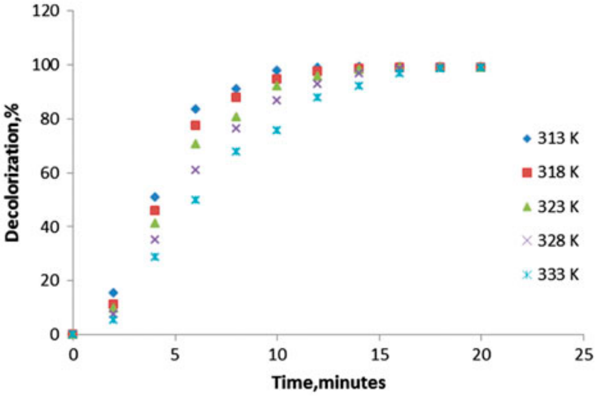

Fig. 8. Effect of temperature on decolorization of direct red dye.

coming out of the industry may have raised temperatures due to the processing of the product and hence, this study was designed to cover temperature range of 313–333 K, usually observed in such streams. The influence of temperature on ozonation is the net result of two simultaneous effects: increase in the rate constant of the reaction and the variation of ozone solubility with temperature. The decolorization of direct red and direct blue dyes with ozonation time is as shown in Figs. 8 and 9, respectively.

The results showed the best decolorization efficiency of ozone at lowest temperature studies i.e. 313 K for both direct red and direct blue dye solutions. The reason might be due to the fact that the solubility of ozone decreases with an increase in the temperature, thereby resulting in reduced amount of ozone available for the reaction lowering the overall degradation. The difference in solubility inhibits reactions between ozone and organics [26,27].

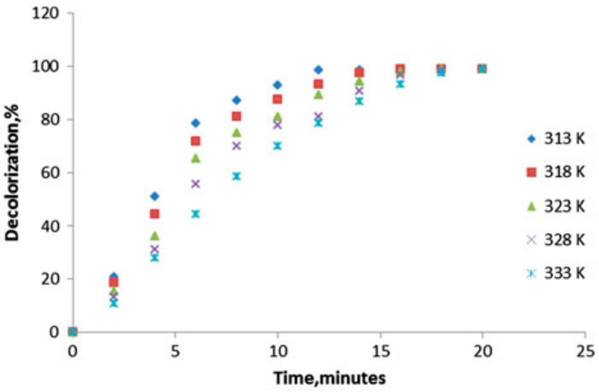

Fig. 9. Effect of temperature on decolorization of direct blue dye.

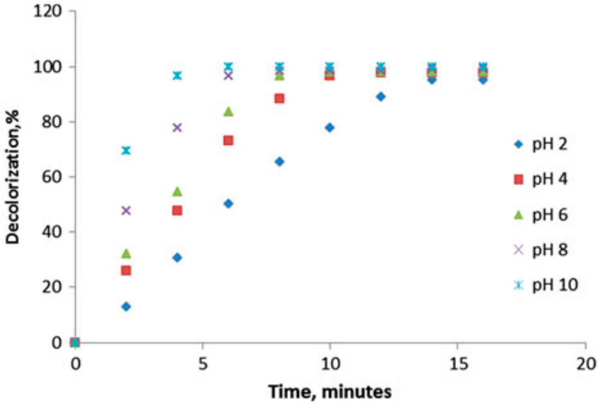

Fig. 10. Effect of pH on decolorization of direct red dye.

3.4. Effect of pH on color removal

The influence of pH was studied for direct red and direct blue dye at various pH ranging from 2 to 10 and the results of decolorization at various pH are shown in Figs. 10 and 11, respectively.

Figs. 10 and 11 showed the best decolorization efficiency at pH of 10 for both the dyes, which is in well agreement with the studies conducted by other researchers [28–30]. This can be explained by the fact that under acidic conditions, ozone mainly decomposes to hydroxyl (OH) radicals, which react with the target pollutant and are more effective in carrying out the oxidation reactions.

3.5. The UV–vis spectra

The samples were scanned from 200 to 1,100 nm to find the generation of some intermediate compounds during ozonation treatment.

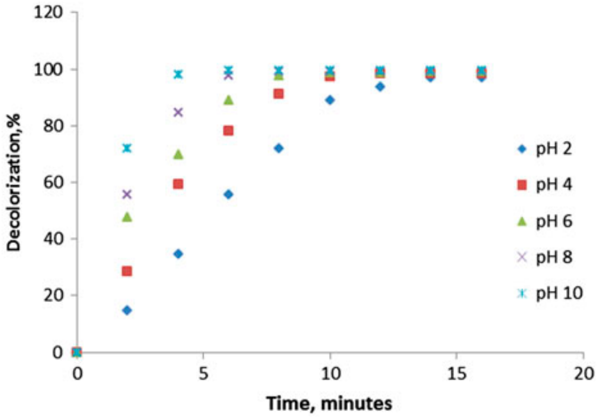

Fig. 11. Effect of pH on decolorization of direct blue dye.

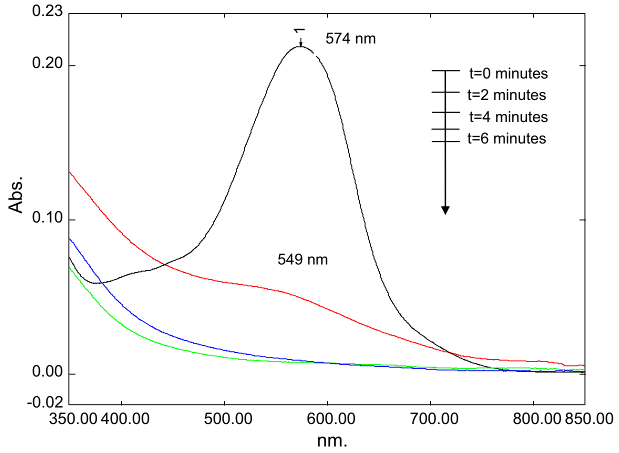

Fig. 12. UV–Vis spectral changes of direct blue dye at 50 ppm concentration after every 2 min of ozonation, Ozone dose—30% of 15 g/h, 2 LPM.

It has been observed from Fig. 12 that there is no shift in wavelength corresponding to the maximum absorbance showing that ozonation of direct blue dye solution finally yields a colorless solution. The indicators of another peak leading to the UV range may correspond to the intermediate organic products of ozonation reactions. The Fig. 13 shows a bimodal development in absorbance giving one peak corresponding to the original wavelength and another with a considerable shift of about 760 nm. The reason might be the rapid destruction of dye chromophore structure (–N=N–) by ozone. Another possibility is that this

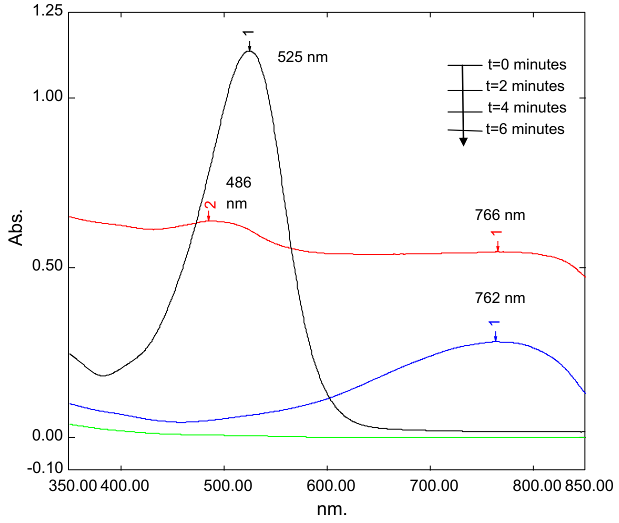

Fig. 13. UV–Vis spectral changes of direct red dye at 50 ppm concentration after every 2 min of ozonation, Ozone dose—30% of 15 g/h, 2 LPM.

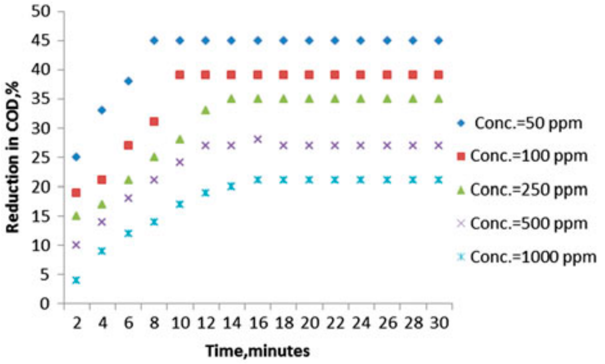

Fig. 14. COD variation of direct blue dye after ozonation treatment for various initial concentration.

commercially available dye has two hues with the one at 525 nm masking the other. Other researchers have also reported the peak absorbance for this dye in the vicinity of what we observed [31,32], where this wavelength should not correspond to red color. After initial ozone reactions, the red colored dye is perhaps first released showing the second peak at 760 nm, and then get oxidized further. The ozonation results well agree with those of their investigators [33–36], but the intermediate reaction products need to be analyzed to confirm our hypothesis.

3.6. Chemical oxygen demand reduction

The chemical oxygen demand (COD) variation of direct blue and direct red dye with time for various initial concentrations of dye is given in Figs. 14 and 15, respectively.

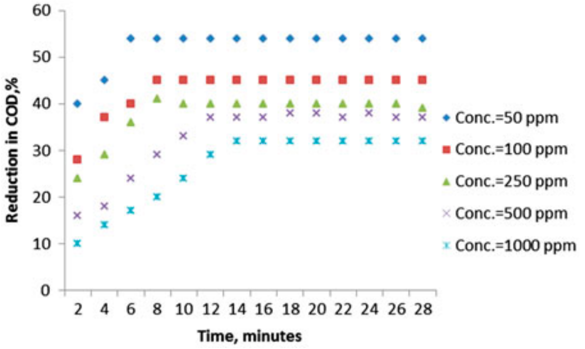

Fig. 15. COD variation of direct red dye after ozonation treatment for various initial concentration.

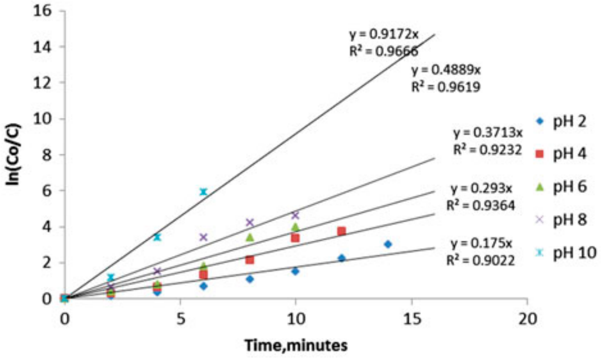

Fig. 16. Rate of degradation of direct red dye by ozone.

It has been observed that the ozonation efficiency for the reduction of COD is less for dye solution having higher initial concentration, while better results have been achieved for well-diluted dye solutions. The maximum COD reduction of direct blue dye is 45% and for direct red dye solution is 54%, respectively. The studies conducted by other researcher showed maximum 68% reduction of COD with Congo red dye [37,38]. The formation of nonreactive intermediates of the reaction not allowing COD to reduce sufficiently is a cause of concern which has to be further studied.

3.7. Kinetic studies

The reaction of ozone with solute A (dye) may be described as:

$$A + O_3 \rightarrow A_{\mathrm{oxid}} \tag{2}$$

Assuming the reaction to be first order with respect to ozone and solute A, the rate of reaction can be formulated as:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{A}}[\mathrm{O}_3][\mathrm{A}] \tag{3}$$

where k_A is the rate constant for decolorization of dye solution by ozone.

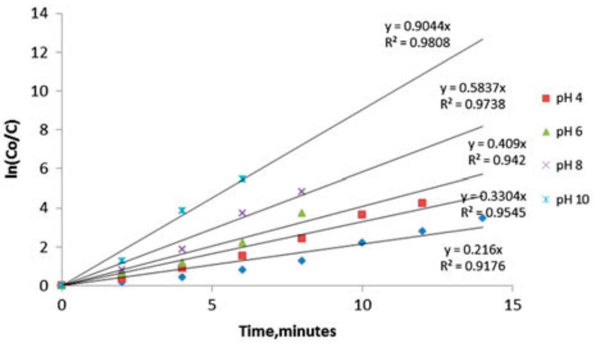

Fig. 17. Rate of degradation of direct blue dye by ozone.

Table 2
Pseudo-first-order constant for decolorization of direct red dye with ozone

Ozone dosage (g/h)	Initial concentration of dye (ppm)	pH	Pseudo first order constant k (min^{-1})	R^2
2.25	50	2	0.175	0.902
		4	0.293	0.936
		6	0.371	0.923
		8	0.488	0.961
		10	0.917	0.966

Table 3
Pseudo-first-order constant for decolorization of direct blue dye with ozone

Ozone dosage (g/h)	Initial concentration of dye (ppm)	pH	Pseudo first order constant k (min^{-1})	R^2
2.25	50	2	0.216	0.917
		4	0.330	0.954
		6	0.365	0.955
		8	0.583	0.973
		10	0.904	0.980

The oxidation with ozone comes from either molecular ozone or hydroxyl free radicals. Eq. (3) can be rewritten,

$$\frac{d[A]}{dt} = -k_o\,[A][O_3] - k_{OH}[A][OH^o] \tag{4}$$

where [A] is the concentration of dye in the solution. $[O_3]$ and $[OH^\circ]$ are the concentrations of ozone and hydroxyl radicals, k_O and k_{OH} are the corresponding rate constants. Assuming concentration of ozone and hydroxyl free radicals to be constant, Eq. (4) can be rewritten as,

$$\frac{d[A]}{dt} = -k[A] \tag{5}$$

The results from Figs. 16 and 17, Tables 2 and 3 indicate that the rate of degradation of both the dyes by ozonation follows the first-order reaction. The high values of R^2 confirm the applicability of pseudo-first-order model to the decolorization of direct red and direct blue dye by ozone. The similar studies were conducted by other researchers who also found these reactions to be of first order [39–42].

4. Conclusions

Ozonation treatment for color removal of direct red and direct blue dye synthetic solutions indicated great potential for the treatment of handmade paper industry effluent. The best results for color removal were obtained at a pH of 10 and effluent temperature of 313 K. The equilibrium time of decolorization with ozonation treatment for direct red and direct blue dye for 50 ppm initial concentration was 6 and 4 min, respectively. On increasing the initial concentration from 50 to 1,000 ppm, the color removal time increased from 6 to 32 min for direct red and 4 to 28 min for direct blue dye. The maximum COD removal of 45 and 54% was achieved for direct blue dye and direct red dye solution, respectively, indicating the formation of reaction intermediates that do not respond to further ozonation. The reaction of ozone with direct blue dye did not yield any new absorbance peak, while that with the direct red dye resulted in a bimodal peak development, which needs to be further studied. The decolorization of dye solutions with ozone followed pseudo-first-order reaction with the maximum rate constant for direct red and direct blue dyes as 0.917 and 0.904 min^{-1}, respectively, at pH of 10 and temperature of 313 K.

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