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In-situ Decolorization of Residual Dye Effluent in Textile Jet Dyeing Machine by Ozone

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Abstract

In this study, a new idea of decolourization was investigated in which residual dyeing effluent from textile dyeing process was treated using O_3 in the same machine where it was generated. The novelty comes from the idea of doing dyeing and treatment simultaneously. At the completion of dyeing process, O_3 gas was injected directly into the machine to remove colour and COD from the wastewater. To evaluate the effectiveness of new method, pilot-scale studies were performed, and decolourization of residual dyeing effluents containing C.I. Reactive Orange 7, C.I. Reactive Blue 19, and C.I. Reactive Black 5 was carried out in specially built textile jet dyeing machine. The results showed that almost 100% colour removal and 90% COD reduction were achieved when process conditions such as pH, dye concentration (mg/L), ozone production rate (g/hr), and temperature were optimized. The study concludes that new method has a great potential to eliminate the need of a separate end-of-the-pipe wastewater treatment system, thus offering an on-site and cost-effective solution.

Keywords: Ozonation; Advanced Oxidation Processes; Reactive dye; Decolourization

Introduction

As environmental laws are becoming more stringent, industries are forced to seek technologically advanced treatment methods. Considerable quantity of dye remains unfixed during textile dyeing processes. The presence of dyes in effluent is considered a problem of significant environmental concern in many countries. Since dyes are designed to resist chemicals, they become resistant to biodegradation in the environment [1].

Wastewater discharge from a textile mill is extremely variable in composition, exhibiting strong colour, fluctuating pH, and significant Chemical Oxygen Demand (COD) loads. Due to these characteristics, treatment of textile wastewater has become a difficult and expensive task. Traditional methods for dealing with textile effluents include biological treatments, activated carbon adsorption, coagulation, precipitation, ion exchange, and membrane filtration [2]. These methods are usually not well suited for oxidizing textile wastewater because BOD/COD ratio falls in the range of 0.10 to 0.25, which indicates the presence of large amount of non-biodegradable organic matters [3].

Although reactive dyes react with cellulosic chain to form covalent bonding (fixation) with the substrate, however, this fixation

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*Corresponding Author Email: textilemaster@gmail.com process is always accompanied by some degree of hydrolysis [4]. These hydrolyzed dyes are mainly responsible for the colour in textile effluent. The reactions of reactive dye can be illustrated in (Fig.1).

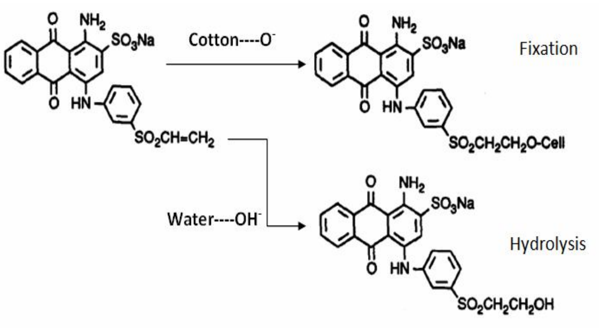


***Figure 1*. Reaction pathway for C.I. Reactive Blue 19 with cellulose fiber or water.**

In recent years, advanced oxidation processes (AOPs) have been extensively studied for the treatment of organic contaminants in textile wastewater [5,6]. A list of several possibilities offered by AOPs is shown in Table-1 [7].

***Table 1*. List of advanced oxidation processes**

Non-Photochemical
Ozonation at elevated pH (>8.5)
Ozone + hydrogen peroxide (O_3/H_2O_2)
Ozone + catalyst (O_3/CAT)
Fenton system (H_2O_2/Fe^{2+})
Photochemical
O_3/UV
H_2O_2/UV
O_3/H_2O_2/UV
Photo-Fenton/Fenton-like systems
Photocatalysis

Ozone in aqueous solution can react with variety of organic compounds using two different pathways: by direct oxidation as molecular O_3 or by indirect reaction through $OH^\bullet$ radicals. Ozonation process does not produce any sludge or toxic by products [7]. According to the literature [8, 9], O_3 decomposition in aqueous solution may undergo as follows.

$$O_3 + HO^- \rightarrow HO_2^{\bullet} + O_2^{-\bullet} \tag{I}$$
$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \tag{II}$$
$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \tag{III}$$
$$O_3^{-\bullet} + H^+ \rightarrow HO_3^{\bullet} \tag{IV}$$
$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{V}$$
$$HO^{\bullet} + O_3 \rightarrow HO_4^{\bullet} \tag{VI}$$
$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2^{\bullet} \tag{VII}$$
$$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3 \tag{VIII}$$
$$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_3 + O_2 \tag{IX}$$

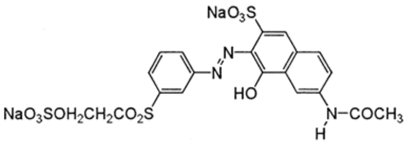
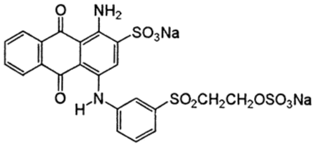
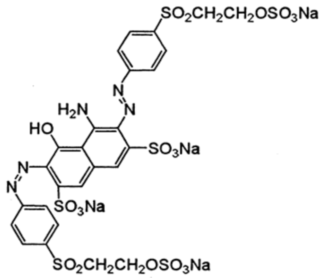
Because O_3 is an unstable molecule and rapidly decomposes to O_2, it is only generated at the point of application for use in wastewater treatments. The generation of O_3 is an endothermic reaction and requires a substantial input of energy. This pilot-scale study evaluated the possibility of using a textile jet dyeing machine as a reactor to carry out advanced oxidative colour removal from residual dyeing effluent. Using jet dyeing machine for oxidative decolourisation could be an economical treatment method because this would avoid building a separate end-of-the-pipe treatment facility, thus offering great savings. The efficacy of the new method was assessed in terms of colour removal efficiency and reduction of COD in various wastewaters under investigation. From this study, it is evident that oxidative colour removal in jet dyeing machine is a promising alternative to conventional wastewater treatments.

Materials and Method

Dyes, chemicals and dyeing procedure

Selected reactive dyes used in the study were kindly provided by Dystar. Chemical properties of these dyes are summarized in (Table-2). Dye exhaustion and fixation chemicals, Na_2SO_4 (sodium sulphate) and Na_2CO_3 (sodium carbonate) were of commercial grade and used without further purification. Based on the weight of fibres (owf), individual dyeing at varied depths of shade (1%, 3%, and 5% owf) was carried out on 100% cotton knitted fabric at 60 ^oC using liquor ratio (L:R) of 1:8. Concentrations of Na_2SO_4 and Na_2CO_3 were ranged between 50-100 g/L and 10-20 g/L, respectively. At the end of the dyeing process, the dyed fabric was unloaded without draining the dyebath. This residual effluent underwent ozone treatment.

Table 2. **Properties of reactive dyes used.**

Colour Index Name	Commercial Name	Molecular Formula & Weight	Chemical Structure	Chemical Class	λ_{max} (nm)
C.I. Reactive Orange 7	Remazol Brilliant Orange RR	$C_{20}H_{17}N_3Na_2O_{11}S_3$ 617.54		Azo	470
C.I. Reactive Blue 19	Remazol Brilliant Blue R (spec.)	$C_{22}H_{16}N_2Na_2O_{11}S_3$ 626.55		Anthra-quinone	595
C.I. Reactive Black 5	Remazol Black B	$C_{26}H_{21}N_5Na_4O_{19}S_6$ 991.82		Diazo	598

Ozone decolourisation in textile Jet dyeing machine

The residual dyeing effluent was treated in a specially designed (patented) jet dyeing machine (Fig. 2). The exact drawing of the machine is not disclosed here owing to the commercial confidentiality. Ozonation was carried out by injecting the ozone/air mixture into the machine using varied flow (500-1000 L/min). Ozone was introduced at the bottom of the dyeing machine using especially designed injector pump and nozzle. This nozzle was installed near the suction of main pump which ensured maximum mass transfer of ozone gas into the receiving liquor. Samples of effluent were taken at regular intervals to determine the extent of colour reduction. Ozone treatment was continued until 95 to 100% decolourization was attained. Ozone gas was produced using a corona charge generator (OZ-50 Kaufman, Germany). Concentration of ozone was monitored using ozone analyzer (UVP 200 Ozonova, Germany). The ozone production rate was set between 20-50 g/hr. All trials were conducted at ambient temperature. Unused ozone gas was destroyed using a catalyst ozone destructor installed on the exhaust of the machine.

Figure 2. **Picture of newly developed textile dyeing machine.**

Colour measurements

The colour removal efficiency (%) was determined by Lambda 25 UV/VIS Spectrometer (Perkin Elmer, USA) using the following relationship:

$$D = \frac{C_0 - C_t}{C_0} \times 100$$

Where D = decolorization (%), C_0 = initial concentration of dye, C_t = concentration of dye at time t.

Results and Discussion

Effect of pH on Ozonation process

Fig. 3 shows the influence of initial pH of residual dyeing effluents on colour removal efficiency of O_3 in the machine. Overall results indicated that there was an increase in decolourization with an increase in the pH of the effluent. At a constant ozone dose of 20g/hr and 3% owf dyeing, the colour removal efficiency of O_3 was found to be the function of pH. In case of C.I. Reactive Orange 7, at 10 minutes ozonation, the colour removal efficiencies were 19, 50, 60, and 75% at pH 4, 7, 9, and 11, respectively. When ozonation time was increased to 30 minutes, these removal efficiencies approached to 50, 85, 99, and 100% at their corresponding pH values.

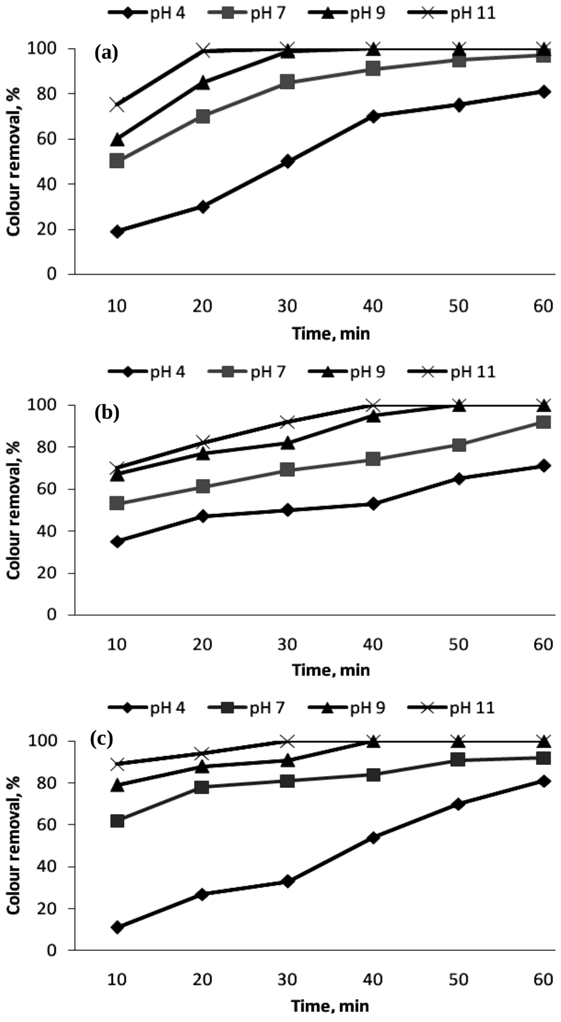


Figure 3. **Effect of initial pH on Ozonation process for colour removal of: (a) C.I. Reactive Orange 7, (b) C.I. Reactive Blue 19, (c) C.I. Reactive Black 5.**

For C.I. Reactive Blue 19, the complete decolouration (100%) was achieved at pH 11 and 40 minutes ozonation. C.I. Reactive Black 5 followed the similar trend and maximum dye removal rate was reached for a pH of 11.0. The results are in line with the findings of other investigators who demonstrated that O_3 decomposition was directly affected by the solution pH and OH radicals were formed from O_3 decomposition at higher pH values [11, 12, 13]. Table-3 displays the effect of pH on ozonation process for the reduction of COD in residual dyeing effluents. The results showed that COD removal efficiency increases with an increase in pH of the wastewater.

Table 3. **Effect of initial pH on ozonation process for COD removal (%).**

pH	C.I. Reactive Orange 7			C.I. Reactive Blue 19			C.I. Reactive Black 5		
	10 min	*30 min*	*60 min*	*10 min*	*30 min*	*60 min*	*10 min*	*30 min*	*60 min*
4	15	48	58	9	55	66	20	48	71
7	17	49	36	20	61	71	27	62	79
9	46	57	77	38	69	89	49	72	84
11	51	62	89	67	81	91	77	84	86

Effect of ozone generator output on colour removal

Fig. 4 shows the effects of varied O_3 production rate on decolourization efficiency. The results clearly indicated that increasing ozone dose was accompanied by increase in colour removal because applied ozone concentration per volume of dye solution increases. At 10 g/hr ozone generator output, the colour removal efficiencies for C.I. Reactive Orange 7, C.I. Reactive Blue 19, and C.I. Reactive Black 5 were found to be 45, 35, and 52%, respectively. When ozone output was increased to 30 g/hr, colour removal efficiencies were also increased to 98, 82, and 99% for C.I. Reactive Orange 7, C.I. Reactive Blue 19, and C.I. Reactive Black 5 dyes, respectively.

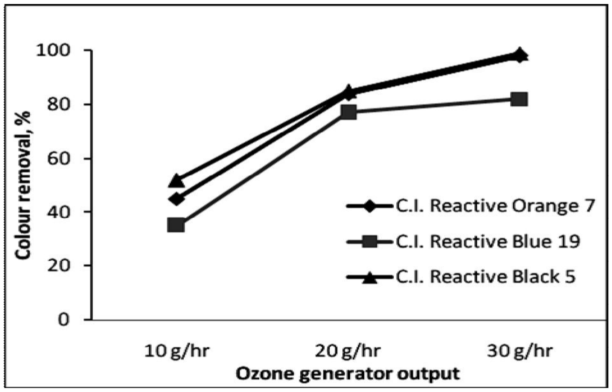


***Figure 4.* Colour removal efficiency of ozone in dyeing machine at varied ozone doses.**

Effect of depth of shade (owf%) on colour removal

Fig. 5 shows the effect of dye concentration (owf%) on the colour removal efficiency of ozonation process. At 30 minutes of ozonation and pH 11.0, high rate of decolourization (91-99%) for all dyes was achieved in lighter (1.0 owf%) depth of shades whereas low colour removal rate (74-90%) was attained in darker (3.0-5.0 owf%) depth of shades. These results are in agreement with the findings of others who found that inlet concentration of dyestuff played an essential role in determining the economical use of O_3 for decolourisation and the time required for decolourisation was dependent on inlet dye concentration as well as ozone consumption [14, 15].

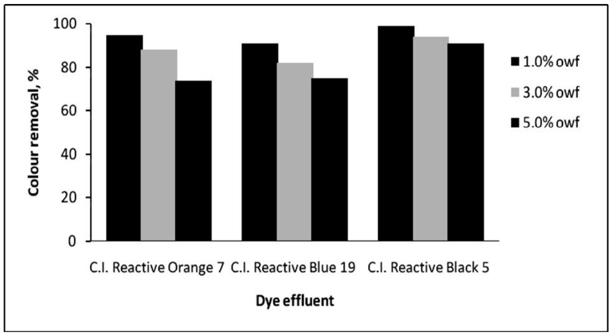


***Figure 5.* Colour removal efficiency of ozone in dyeing machine for varied depths of shade.**

Effect of machine temperature on colour removal

The effect of machine temperature on the reaction rate of O_3 for colour removal was investigated and results are exhibited in (Fig. 6). It can be observed from the results that colour removal rate was significantly decreased when temperature was increased from 30 to 70^{o}C. This lower colour removal efficiency could be attributed to the fact that when temperature of wastewater increases, O_3 stability in water decreases, resulting an overall reduction in the amount of O_3 available for reaction [16, 17].

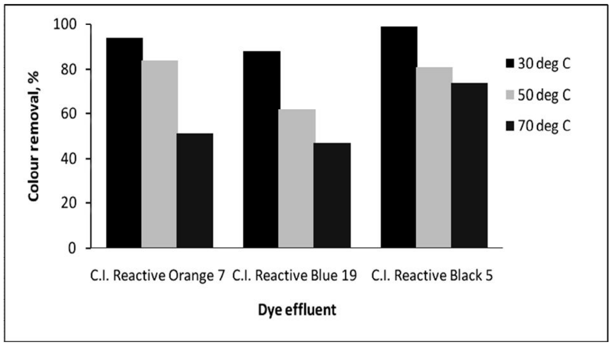


***Figure 6.* Colour removal efficiency of ozone in dyeing machine at varied temperatures.**

Conclusion

This paper investigated a new method wherein decolourization of dyes was carried out in a textile dyeing machine just after the completion of dyeing process. For this purpose, a special jet dyeing machine was developed in which ozone gas was injected to remove colour and COD from residual dyeing effluents. The new method was evaluated for number of dyeings using C.I. Reactive Orange 7, C.I. Reactive Blue 19, and C.I. Reactive Black 5. This study concludes that ozone decolourization of dyes in jet dyeing machine is an effective method which could possibly eliminate the need of a separate end-of-the-pipe wastewater treatment, thus offering a cost effective alternative to the conventional approach.

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