A Pilot-scale Investigation for Simultaneous Reuse and Decolourization of Textile Wastewater Using Ozone

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***Abstract*-The first patented textile dyeing machine having an Ozone injection system was developed to treat wastewater liquor coming from the reactive dyeing process. Controlled quantities of ozone gas were injected in the machine during the washing process to decolourize dyes present in wastewater as well as on fabric surface. Several different dyings were carried out in the machine using variety of reactive dyes. At the completion of dying process, washings were carried out using ozone in the jet dyeing machine, and the process was continued until the wastewater is decolorized around 90-100%. The decolourization effectiveness of liquor was considered as an indicative of colour removal from the dyed fabric because fabric was being rinsed simultaneously during oxidative decolourization treatment. Fabric samples rinsed with both conventional and ozone based methods were evaluated for fastness properties, change of shade, fabric appearance, and colour fading. On the whole, the results suggested that the application of O3 during textile washing process resulted into reduced water consumption and lowered processing time without deteriorating colour and fastness properties.**

Keywords- Ozone; Wash-off; Reactive dyes; Jet Dyeing Machine; Fastness

I. INTRODUCTION

One of the key environmental issues today refers to the effects associated with the dumping of industrial effluents, and other residues into the superficial and underground water bodies. Cotton dyeing using reactive dyes is one of the most widely used coloration methods because of colour brilliancy, simplicity of application, and adequate fastness properties [1]. The reactive groups of reactive dyes, such as Monochlorotriazine (MCT), Monofluorotriazine (MFT), and Vinyl sulphone (VS), help dye to form covalent bonds with –OH radicals of cotton. Unfortunately, the yield of this process is not 100% and 40 to 50% dyes do not transfer to the textile substrate. Consequently, at the end of dying process, extensive washing process becomes an absolute necessity to clear these unfixed dyes off the textile material.

Environment seems to be the dominant motivation for the growth of textile processes nowadays. Textile companies worldwide seek new processing methods which require less energy, lowered water consumption, and reduced wastewater loads in terms of effluent toxicity and magnitude. The latest research has been focussed to degrade water pollution in terms of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), temperature, pH colour, nutrients, and chlorides [2].

The application of ozone (O_3) in water, wastewater, and other industrial applications is widespread practice [3]. Since Ozone carries a very high oxidation potential of 2.07 volts, it has the capacity to break down majority of aromatic structures and bonds. For example, –N=N– and –C=C– structures are commonly found in the chemical structures of textile dyes and pigments, and Ozone can instantly degrade them [4]. The molecule of Ozone (O_3) gain very high oxidation potential due to the presence of extra oxygen atom (O_2) that can immediately destroy complex chemical compounds into simpler and biodegradable products [5]. The use of Ozone is advantageous to its counter parts owing to the fact that ozonation process does not create any residual sludge [6, 7]. Furthermore, ozonation is also capable of reducing chemical oxygen demand (COD) of wastewater, making it suitable for the direct release to the water streams [8]. Added benefit of using Ozone in wastewater treatments is that ozone is applied as gas, and thus it does not increase the volume of sludge and wastwate.

Ozone is sparingly soluble in water and the solubility of 100 percent ozone is only 570 ppm at 20^{o}C. Ozone reacts with organic pollutants via two different pathways, either by direct oxidation using molecular ozone, or by indirect oxidation using OH^- free radicals [9, 10]. The action between OH^- and O_3 can lead to the production of HOO^-radicals [11]. When the pH values of wastewater turn to acidic range, ozone is found in molecular form [12].

This investigation evaluated the efficacy of O_3 oxidation in a dyeing procedure for real-time colour removal from the dyeing effluent and its simultaneous reuse.

II. METHODS AND MATERIALS

Knitted fabric having 100% cotton composition (single jersey) having 200 weight (grams per squared meter) was used in this study. Selected dyes from the reactive colour range were kindly supplied by Dystar, Pakistan (Table 1). Auxiliary chemicals like sodium sulphate, sodium carbonate, sodium hydroxide, and acetic acid used were of commercial grade.

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TABLE 1 LIST OF DYES, CHEMICAL AUXILIARIES USED IN THE EXPERIMENTAL WORK

Dye name	**Shade Recipe (% owm)**			**Colour index (C.I.)**
Colours	Red	Yellow	Blue	
Remazol Red RR	2.50	0.50	0.50	Reactive Red 231
Remazol Yellow RR	0.25	2.50	0.50	Reactive Yellow 138
Remazol Blue RR	0.25	0.50	3.0	Reactive Blue 198
NaCl	70	80	90	
Na_2CO_3	18	20	20	

A. Application of Ozone

Fig. 1 shows an exhaust dyeing machine (jet) which was designed and built by Thies GmbH & Co., Germany. The jet machine was consisted of 10kg kier chamber, an injector pump, an O_3 generator (OZ-50, Kaufman), O_3 analyzer (UVP 200, Ozonova), O_3 catalyst, O_3 gas leakage device, O_3 monitor in air (Micro III, Gfg), and an ORP meter.

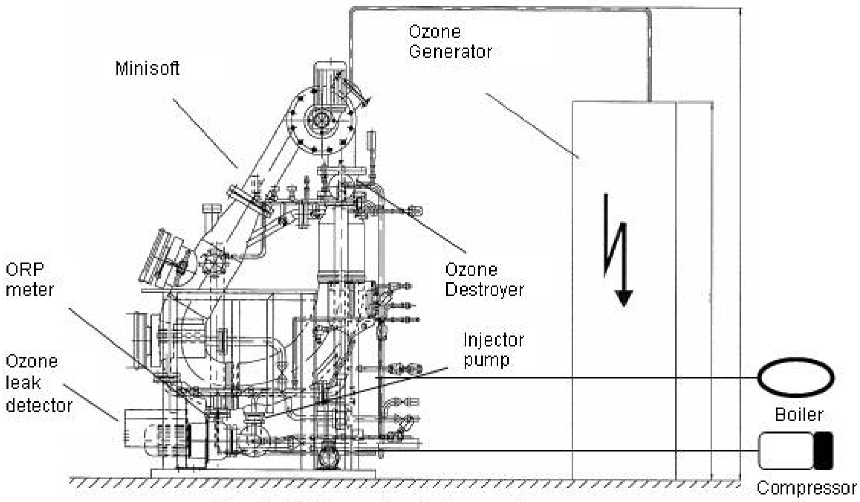

Fig. 1 Schematic of textile machine built for O_3 application

An O_3 generator having capacity of producing 1- 50 g/hr ozone was used to produce O_3 gas. O_3 was applied to the jet machine using the gas flow rate of 600 litres per minute to achieve highest transfer of O_3 into the wastewater. Ozone generator was kept cooled with the help of cold water which circulated continuously in the jacket of ozone generator. Especially designed pump (injector) was used to inject ozone gas to the jet machine. The ozone generator and main kier of the jet machine was connected using stainless pipe. To achieve optimum mixing of O_3 and wastewater, the gas was applied at the suction of the main pump of jet machine. The no reacted ozone gas from the machine was destructed using a catalyst destructor installed at the exhaust of the jet machine. In order to observe the concentration of dissolved O_3 in the jet machine liquor, an Oxidation-Reduction Potential (ORP) meter was mounted on the jet. To detect any leakages of ozone from the jet, a gas leakage detector was also placed on the jet.

B. Decolourization Efficiency

The coloured wastewater underwent ozone oxidation, and colour removal (%) efficiency was determined employing the following equation:

$$D = \frac{c_0 - c_t}{c_0} \qquad (1)$$

Whereas D = Colour removal (%), C_0 = concentration of dye before O_3 treatment, C_t = concentration of dye after O_3 treatment

C. Colour Difference and Colour Fastness Properties

Standard testing procedure adopted from AATCC 61-2001-2A was used to assess change of colour. Crocking (rub) fastness properties of samples were determined using AATCC Test Method 8-2001 [13, 14]. A Spectrophotometer (SF 600, Datacolor) was employed to evaluate the colour difference values of fabric swatches using the CIELAB colour settings.

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III. RESULTS AND DISCUSSIONS

A. Impact of Ozonation on Wastewater Characteristics

At a liquor ratio (L:R) of 1:10, 5 kg of fabric and 50 litres of water were loaded in the jet dyeing machine, and ozone application was given for a period of 1 hour. The characteristics of wastewater under investigation and experiment settings for different dyeing were reported in Table 2.

TABLE 2 EFFECTS OF O3 APPLICATION ON WASTEWATER

Shade	O_3 dosage (mg/min.)	O_3 Treatment Time (min)	Conductivity (μS/cm)	pH	Temp. (^0C)	Decolourization (%)
RED	167	0	9	10.6	57	-
		10	19	10.1	46	65
		20	35	8.9	41	77
		30	38	8.2	35	79
		40	47	7.1	30	89
		50	48	6.8	28	98
		60	54	6.7	26	99
Yellow	133	0	9	10.8	59	-
		10	11	9.7	46	67
		20	19	9.5	39	79
		30	24	9.4	35	81
		40	31	8.5	31	89
		50	37	8.2	29	91
		60	42	8.0	25	96
Blue	167	0	13	9.9	52	-
		10	23	9.7	47	70
		20	34	9.1	41	74
		30	38	8.8	38	79
		40	41	8.5	32	84
		50	43	8.1	30	91
		60	47	7.8	27	96

For dyeing using Remazol Red RR dye, ozone-air flow rate and ozone out were kept at 600 l/min and 10g/hr, respectively. In order to avoid the accumulation of O_3 gas in the dyeing machine, gas flow rate was maintained in such a way that the differential pressure (ΔP) of the machine remained on -ve side. At this flow rate (600 l/min), O_3 concentration in air was set at 0.22 ppm. During the ozone application, the pH of the liquor was not maintained, however, the pH values of the wastewater varied during O_3 application. A 98% colour removal efficiency was achieved at the completion of 60 minute of ozone exposure. For Remazol Yellow RR dyeing, 60 minutes of O_3 treatment yielded 96% decolourization when O_3 dose of 133 mg/min was maintained. Similar results were obtained in the case of Blue shade dyeing using Remazol Blue RR.

B. Effect of Ozonation on PH Values

Fig. 2 displays the pH values of wastewater during O_3 application. At the start of O_3 application, pH values of all dyeing were found between 9.9 and 10.8 due to residues of Na_2CO_3 in wastewater. The pH values were also found to be decreasing with increasing ozonation time. For all dyeings, the final pH values reached around 7.50 after 60 minutes of O_3 application. This drop in pH during O_3 application is in line with similar studies [15-17].

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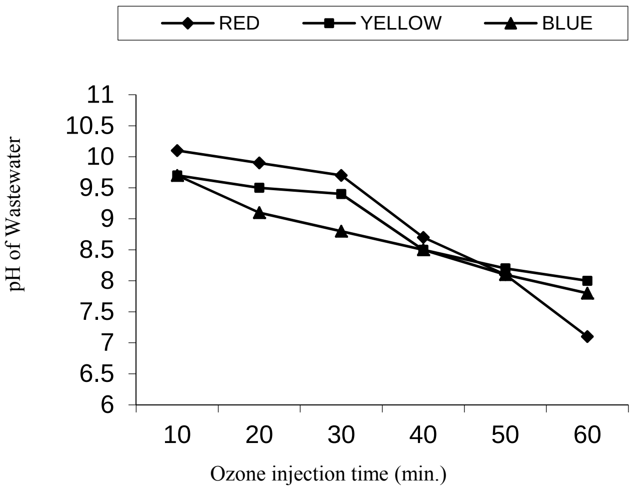

Fig. 2 Effect of ozonation on wastewater pH

C. *Colour Difference Values*

Reference samples (untreated) and dyed samples (O_3 treated) were compared with respect to redness/greenness (Δa*), yellowness/blueness (Δb*), brighter/duller (ΔC*), lighter/darker (ΔL*), and hue difference (Δh*). The results were summarized in Table 3. The results of red samples dyed using Remazol Red RR dye, acceptable colour differences in lightness (ΔL*= 0.48), colour saturation (ΔC*= -0.21), hue (ΔH*=0.23), and total colour difference (ΔE*=0.66) were noticed. For Remazol Yellow RR dyeing, the colour properties of fabric treated with O_3 was bit lighter (ΔL*= 0.25), saturated /brighter (ΔC* = 0.39), and was commercially acceptable (ΔE*=0.51). Similar trend was observed in case of Remazol Blue RR dyeing.

TABLE 3 COLOUR PROPERTIES

Colour	**ΔL***	**Δa***	**Δb***	**ΔC***	**Δh***	**ΔE^*_{cmc}**
Red	-0.48	-0.21	0.20	-0.213	0.23	0.66
Yellow	0.25	0.19	0.21	-0.39	0.58	0.51
Blue	-0.31	0.42	0.26	0.32	-0.51	0.48

D. *Assessment of Colour Fastness Properties*

Both conventional dyed and ozone treated samples were assessed with respect to colour fastness and results were shown in Table 4. The data showed that fabric samples underwent both conventional and O_3 treatments displayed identical fastness properties, mainly between 4/5 to 5. These results suggested commercially-acceptable fastness results. Moreover, results related to shade change showed similar results when shade of conventionally treated samples were compared with those of ozone treated samples.

TABLE 4 COMPARISON OF COLOUR FASTNESS VALUES

Colour	**Fabric samples**	**Rubbing**		**Staining to multifibre**			**change of shade**
		Dry	**Wet**	**Cotton**	**Nylon**	**PES**	
Red	Control	5.0	4.50	4.50	5.0	5.0	-
	Ozone treated	4.50	4.50	4.50	5.0	5.0	4.5
Yellow	Control	5.0	4.50	4.50	4.50	4.50	-
	Ozone treated	5.0	5.0	5.0	5.0	5.0	4.0
Blue	Control	5.0	4.5	5.0	5.0	5.0	-

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	Ozone treated	5.0	5.0	4.50	5.0	5.0	5.0

IV. CONCLUSION

The current investigation showed that O_3 application in textile jet machine is a promising technique to reduce significant level of water consumption compared to the conventional textile dyeing method. It also proved to be an effective in-process colour removal technique in contrast to conventional wastewater treatments which are usually employed as an end-of-the-pipe treatment for the elimination of colour in the highly concentrated and complex wastewater. The results from the experimental work confirmed 57% saving of fresh water because rinsing and washing regime based on ozone application was finished with 3 filling of water as compared to 7 fillings used in conventional dyeing process. The ozone based decolourization did not utilize any steam or external heating, and consequently proved to be a cost-effective and environmental friendly method compared to the traditional dyeing process. Both conventional and ozone based dyeing processes exhibited comparable fastness and colour properties.

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