An Investigation to Adopt Zero Liquid Discharge in Textile Dyeing Using Advanced Oxidation Processes

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ABSTRACT

In this study, a novel idea of using ozone oxidation at the end of reactive dyeing process was explored in order to achieve zero discharge dyeing. An advanced oxidative treatment was given during the dyeing process to remove unfixed and hydrolyzed reactive dyes from cotton substrate. Three different shades were dyed using vinylsulphone reactive class of dyes. At the end of fixation step, washing of fabrics was carried out using appropriate quantities of ozone in the process. Ozone oxidation continued until the liquor was decolorized around 95-100% and COD (Chemical Oxygen Demand) was reduced about 80-90%, thus achieving ZLD (Zero Liquid Discharge) dyeing process. The decolouration efficiency of wastewater was regarded as an indicative of removal of dyes from the textile materials because fabric was being washed continuously in the same liquor. Fabric samples dyed with conventional and new methods were compared in terms of change in shade, colourfastness properties, colour stripping, and fabric appearance. Overall results showed that the use of ozone during reactive dyeing can result in less water consumption, reduced process time, and zero discharge of coloured effluents from textile dyeing factories.

Key Words: **Zero Discharge, Reactive Dyeing, Advanced Oxidation Processes, Ozone, Wastewater.**

1. INTRODUCTION

ZLD refers to a treatment method in which industries do not discharges any liquid wastewater into surface water streams, thus reducing environmental pollution associated with the process. Apart from this advantage, a ZLD process also makes efficient use of effluent treatment, recycling, and reuse, thereby contributing to water conservation through reduced intake of fresh water [1-2].

The textile dyeing and printing industries have now shifted from the developed to the developing countries, and started to create huge wastewater and pollution related issues. As one of the main pollution sources in Pakistan, the textile dyeing and finishing industries create a considerable proportion of water pollution in all major cities of the country [3]. Generally, conventional biological treatment processes have difficulties in degrading the majority of dyes and

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chemicals that cause high values of BOD (Biological Oxygen Demand), COD, TSS (Total Suspended Solids), and colour in textile dyeing effluents. Several studies using physical and chemical treatment method to reduce COD and colour from dyeing wastewater have been intensively reported [4-10]

In last twenty years, use of ozone as an advanced oxidative treatment has been widely researched for the removal of chemical pollutants such colour, chemical oxygen demand, biological oxygen demand, and total organic compounds from textile effluents as well as in other industrial wastewater processes [11-13]. Ozone possesses very high oxidation potential of about 2.07 volts which is able to degrade majority of organic compounds including textile colorants. The oxidizing capacity of ozone is the result of third oxygen atom that can easily destroy dye chromophores containing conjugated double bonds directly or indirectly by forming hydroxyl (OH) radicals [14]. Ozone can also convert refractory dyes and pigments in wastewater discharge into biodegradable species so that effective biological treatment can be performed [15].

In this experimental work, effluents from reactive dyeing were treated with ozone gas during the dyeing process, in the presence of textile material, so that the final wastewater discharge remains within NEQS (National Environmental Quality Standards) and true ZLD solution is achieved. The results obtained in this study suggested that use of ozone oxidation in reactive dyeing is a potential candidate treatment method where ZLD is obligatory to follow.

2. MATERIALS AND METHOD

2.1 Fabric, Dyes, and Chemicals

Bleached, single jersey knitted fabric (Ne 20/1, 220 gm^{-2}) was used in this study. Commercial samples of reactive dyes were kindly supplied by DyStar (Table 1). All the other chemicals like common salt (NaCl), soda ash (Na_2CO_3), and caustic soda (NaOH) used were of laboratory scale, and used without any further purification.

2.2 Dyeing Procedure

All dyeings were performed in a 10 kg jet dyeing machine (Minisoft, Thies GmbH & Co.) using an isothermal dyeing method displayed in Fig. 1. The fabric weight in each batch run was maintained at 10kg. Electrolyte (sodium chloride) and alkali (sodium carbonate) were used as per the recommendation of the dye supplier[16].

At the end of dyeing process, the machine was drained and half of the fabric (5kg) was unloaded from jet machine. The fabric remained in the machine was subjected to conventional washing treatment (Table 2) and regarded as control sample. The remaining 5 kg of fabric was subjected to ozone based washing regime.

2.3 Application of O_3

Ozonation was carried out in a specially designed jet dyeing machine by introducing the ozone/air mixture into the washing wastewater, at a flow of 600 L/h using a special technique that ensured fabric protection from ozone gas. This is a patented technique[17] and owing to the commercial confidentiality, the exact design is

TABLE 1. TEXTILE DYES AND RECIPES USED IN THE STUDY

CI Names of Dyes	Depth of Shade (%)				Commercial Name
	Grey	Red	Navy	Black	
CI Reactive Orange 107	0.50	0.25	0.50	1.0	Remazol Golden Yellow RNL
CI Reactive Red 22	0.50	2.0	0.50	1.0	Remazol Red RR
CI Reactive Blue 220	0.50	0.25	-	-	RemazolBrillian Blue BB
CI Reactive Black 5	-	-	4.0	-	Remazol Black B
Mixed dye	-			5.0	Remazol Black N
Common Salt (NaCl)	40	60	80	90	
Soda Ash (Na_2 CO_3)	15	20	15	20	
Caustic Soda (NaOH)	-	-	0.5	1.0	

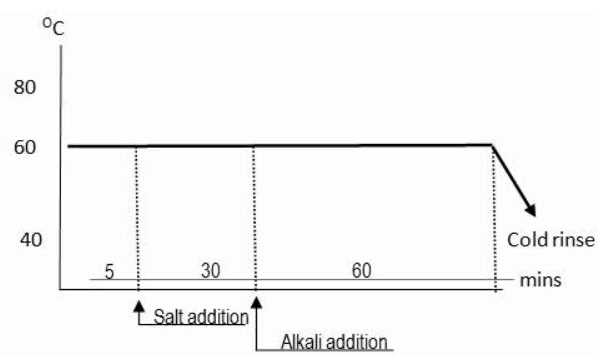

FIG. 1. DYEING PROCESS USED IN THE STUDY

not disclosed here. Wastewater was sampled at regular interval time (10 minutes) for the evaluation of decolouration(%). Ozone oxidation was continued until 95-100% decolouration was attained. This was calculated using difference of absorption values of waste water. Decrease in colour strength of wastewater was regarded as an indication of removal efficiency of the treatment to remove unfixed dyed from the fabric because fabric was being continuously washed in the same liquor under treatment. Ozone gas was generated by a corona discharge generator (OZ-50 Kaufman). Concentration of ozone in ozone/air mixture was determined using ozone analyzer (UVP 200 Ozonova). The ozone production rate was 50g O_3 h^{-1}. All experiments were carried out at ambient temperature and at original pH of wastewater. Unutilized ozone coming out of the dyeing machine was destructed in the catalyst destructor due to its poisonous nature.

2.4 Analyses

A reflectance spectrophotometer (Datacolor, USA) was used to calculate the colour reflectance values of dyed samples in terms of ΔL*, Δa*, Δb*, Δc*, Δh*, and ΔE*. This difference (Δ) denotes colour difference properties between sample and standard, and it has no unit. The measurements were taken under illuminant D65, using a 10^o standard observer with specular component excluded and UV component included. Each fabric was folded to achieve four thicknesses and an average of four readings was taken. Washfastness, crockfastness, and perspiration tests were conducted according to AATCC Test Methods 61-2A, 8, and 15, respectively. The pH and electric conductivity of the aqueous solution was measured using a multi-meter model (HI 9829, Hanna Instruments). The changes in pH and conductivity indicate chemical degradation of dye molecules present in the solution.

TABLE 2. CONVENTIONAL WASH-OFF STEPS

Step	Operation	Temp (^{0}C)	WaterLiters (L:R 1:8)	Time (Minutes)
1	Cold rinse	30	40	10
2	Cold rinse	30	40	10
3	Neutralization with Acetic Acid	30	40	10
4	Hot Wash	80	40	10
5	Soaping / Boil-off	95	40	10
6	Cold rinse	30	40	10
	Total		**240**	**60**

3. RESULTS AND DISCUSSIONS

3.1 Determination of Optimum Ozone Dose

Determination of the required ozone dose for the decolorization of wash-off liquor in the presence of textile material was essential to avoid discolouration of fixed dyes. At constant experimental settings (pH =10.5, exposure time 45 minutes, ozone/air flow 600 l/h), a pre-dyed fabric was subjected to ozone treatment using varied ozone doses.

The impact of ozone concentration on fabric properties was determined in terms of change of shade. The results were summarized in Fig. 2, which clearly showed that that major change of shade was noticed when elevated amount of ozone gas was utilized in the treatment of washing wastewater. This change of shade was also accompanied with white marks throughout the fabric that showed discoloration of dyes already fixed on the fabric. As the ozone production rate (output) was reduced, the change of shade was also reduced. When ozone dose was set to 166.7 mg/m (zone output 10g/hr, airflow 600LPM), no significant change of shade was noticed. Consequently, this amount of ozone gas was regarded as a safe dosage for this particular experimental setup (5kg fabric; 40L liquor quantity).

3.2 Decolorization of Hydrolyzed Dyes

Table 3 shows the decolourationefficiency of ozone gas for various washing wastewater. It can be seen that ozone oxidation was effective technique for the removal of all dyes. The results also indicated that the decolourationwas largely dependent on ozone

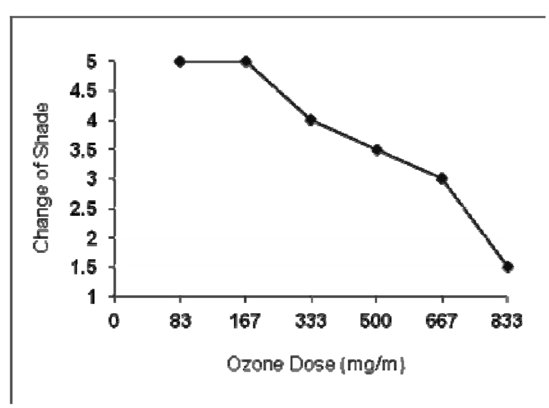

FIG. 2. INFLUENCE OF OZONE DOSE ON CHANGE OF SHADE OF FABRIC

exposure time. In all wastewaters, it was observed that the pH of washing wastewater decreased during the ozonation process. Several researchers had reported the formation of acidic products which cause a reduction in pH of the liquor [18-19]. The increase in conductivity was also observed which is due to the degradation of dye molecules present in the wastewater.

Decolorization of dyes in the wastewater of grey shade was 98% after 30 min of ozonation at ozone dose of 83 mg/m. During ozonation, the pH decreased from 9.7-7.6 whereas the conductivity increased from 13-27 µS/cm. The color of Red shade wash-off liquor was reduced by 80, 86 and 91% after 10, 20, and 30 minutes of ozonation respectively. Compared to Grey shade, it was a dark shade and hence ozone dose was increased to 167 mg/m. The pH of the liquor dropped from 9.8-8.1 after 30 minutes of ozonation. An increase in conductivity, from 58-78 µS/cm, also indicates that wash-off liquor has been decolorized. In the case of Navy shade, predominantly composed of classical CI Reactive Black 5 dye, 99% decolorization efficiency was achieved only after 20 minutes of ozone treatment at ozone dose of 167 mg/m. This shows that CI Reactive Black 5 is prone to quick degradation by ozone. These results are also in line with other decolorization studies on CI Reactive Black 5 using Ozone [20]. For Black shade, wastewater underwent 97% decolorization after 30 minutes of ozonation, accompanied by drop in pH, 10.5-7.9 and increase in conductivity, 13-27 µS/cm. COD values also decreased between 81-95%.

3.3 Effect of Ozone Dyeing Quality

The color differences between reference fabric and those washed-off using ozone were summarized in Table 4, in terms of ΔL^*, Δc^*, Δh^* *and* $\Delta E_{cmc\ (2:1)}$. Overall results show that color difference in all cases is close to commercial tolerance ($\Delta E_{cmc\ (2:1)} \leq 1.0$). The results of Grey dyeing clearly indicate that 30-minute of ozone treatment did not alter the final shade compared to that of reference. Negligible differences in lightness (ΔL^*= -0.26), chroma(Δc^*= 0.12), Hue (Δh^*= 0.10), and total difference ($\Delta E_{cmc\ (2:1)}$=0.58) confirm the fact that color properties of ozone treated fabric are similar to those of reference. In the case of Red shade dyeing, the shade of ozone treated sample was found to be slightly darker (ΔL^*= -0.98), slightly

TABLE 3. PROCESS CONDITIONS AND REMOVAL EFFICIENCIES OF OZONE GAS

Shade	Ozone Production (g/hr)	Ozone Dose (mg/m)	Ozone Concentration (mg/l)	Ozonation Period (min.)	Conductivity (µS/cm)	pH	COD Removal (%)	Color Removal (%)
Grey	5	83	0.14	0	13	9.7	-	-
				10	15	9.4	47	90
				20	20	8.9	87	95
				30	27	7.6	91	98
Red	10	167	0.28	0	58	9.8	-	-
				10	62	9.5	50	80
				20	66	8.6	62	86
				30	78	8.1	81	91
Navy	10	167	0.28	0	38	10.1	-	-
				10	38	9.8	82	95
				20	45	8.8	87	99
				30	48	8.7	95	100
Black	10	167	0.28	0	13	10.5	-	-
				10	15	9.5	42	87
				20	20	9.3	77	93
				30	27	7.9	83	97

brighter (Δc*= 0.51), and within acceptable total color difference ($\Delta E_{cmc\ (2:1)}$= -1.17). The results pertinent to Navy shade show that 20 minutes of ozone based wash-off treatment imparted minor changes to lightness ($\Delta E_{cmc\ (2:1)}$=0.58), chroma (Δc*=0.56), hue (Δh*= -0.26), and total color difference ($\Delta E_{cmc\ (2:1)}$ = 0.85). Also, in the case of Black shade, identical trend was observed and lower values of ΔL*, Δc*, Δh*, and $\Delta E_{cmc\ (2:1)}$suggested that there is no significant color difference between reference and ozone treated fabric samples.

3.4 Fastness properties

Table 5 illustrates a comparison of fastness properties of reference and ozone treated dyed samples. It is clear from the data that both reference and ozone treated samples exhibited similar colourfastness properties in terms of washing, perspiration and rubbing fastness. In the case of grey dyeing, fabric sample washed-off with ozonated water showed similar fastness properties (washing, perspiration and rubbing) mostly in the range of 4.5-5.0.

In red shade, the wash fastness rating was found to be half point inferior compared to that of reference sample. This result could be attributed to the general difficulty of washing-off deep red shades. The obtained results suggested an extended treatment time, probably further 10-20 minutes, in order getting required wash fastness in red shade fabrics. The last two shades, navy and black, showed almost identical fastness properties on both reference and ozone treated. dyed. samples.

TABLE 4. COLOUR DIFFERENCE VALUES OF REFERENCE AND OZONE TREATED FABRICS

Shade	ΔL*	Δa*	Δb*	Δc*	Δh*	$\Delta E_{cmc\ (2:1)}$
Grey	-0.26	0.12	-0.10	0.12	0.10	0.58
Red	-0.98	0.49	-0.17	0.51	-0.02	1.17
Navy	0.58	-0.40	-0.47	0.56	-0.26	0.85
Black	0.76	-0.09	-0.52	0.51	-0.14	0.93

4. CONCLUSION

This study investigated a new treatment method to clear unfixed reactive dyes from cotton knitted fabric as well as from washing wastewater. The new method seems to be promising alternative to conventional process. The ozone gas was used in jet dyeing machine during final washing process to remove both colour and COD from the washing wastewater. The performance of the method under investigation was found to be excellent because significant level of decrease in colour (91-100%) and chemical oxygen demand (81-95%) was achieved. Consequently, the new ozone based wastewater treatment can be regarded as ZLD dyeing method. This technique also considerably reduced the process time and the quantity of wastewater generated, and thus proved to be an eco-friendly process.

TABLE 5. COMPARISON OF FASTNESS PROPERTIES

Shade	Fabric Sample	Colour Fastness Properties										
		Washing Fastness			Perspiration Fastness						Rubbing Fastness	
					Acidic			Alkaline				
		Staining			Staining			Staining			Wet	Dry
		Cotton	Polyester	Nylon	Cotton	Polyester	Nylon	Cotton	Polyester	Nylon		
Grey	Reference	4.5	5.0	4.5	4.5	4.5	4.0	4.0	5.0	4.5	4.5	4.5
	New Method	4.5	5.0	4.5	4.5	4.5	4.0	4.5	4.5	4.5	4.5	4.5
Red	Reference	4.0	4.5	4.0	4.0	5.0	4.0	4.5	3.5	4.0	4.0	4.5
	New Method	3.5	4.5	4.0	4.0	4.5	4.0	4.5	4.0	4.0	4.0	4.5
Navy	Reference	4.5	5.0	5.0	4.5	4.5	4.0	4.5	4.5	4.0	4.5	5.0
	New Method	4.5	5.0	5.0	4.5	4.5	4.0	4.5	4.5	4.0	4.5	5.0
Black	Reference	4.5	4.5	4.5	3.5	4.5	4.0	4.0	4.0	4.0	3.0	4.5
	New Method	4.5	4.5	4.0	4.0	4.5	4.0	3.5	4.0	4.0	3.0	4.5

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