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A Pilot-Scale Application of Ozone in Machine Cleaning to Replace $Na_2S_2O_4$

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An O_3 based cleaning process for removing dyestuff residues from the surface of textile dyeing machine was investigated in this study. The objective of this pilot-scale study was to compare the cleaning efficiency of new oxidative method with that of conventional reductive cleaning method containing $Na_2S_2O_4$ and NaOH. A sample dyeing machine was developed to assess the effectiveness of O_3 based cleaning carried out at the end of deep shade reactive dyeings. Pre-dyed and pre-bleached fabric samples processed after conventional and O_3 based machine cleanings were compared in terms of change in shade, fastness properties and whiteness degree (%). The new oxidative method appeared to be a promising alternative to the conventional machine cleaning. The results show that similar or better degree of cleaning can be obtained by injecting O_3 into the textile dyeing machine. The new process is environmentally acceptable because it does not use any harsh chemicals and requires low quantity of water and energy as opposed to conventional machine cleaning. Wastewater generated in O_3 cleaning exhibited reduced pollutant load in terms of COD, pH, electric conductivity, colour and total suspended solids.

Keywords: Ozone, Advanced oxidation processes, Reactive dyeing, Machine cleaning, Colour removal.

INTRODUCTION

Textile industries are responsible for the discharge of large quantities of wastewater and chemical load into natural waterways. This practice has become one of the major causes of environmental pollution because textile effluents are strongly loaded with unfixed dyes, salts and chemical auxiliaries[1]. New environmental laws for industries are imposing tighter limitations on wastewater discharges and forcing textile companies to explore new methods to reduce pollution load[2,3].

After dark shade dyeing, machine cleaning step becomes a vital process in order to clear dye deposits off the machine surface. Conventional cleaning of dyeing machines involves washing process at high temperature (80-95 ºC) using strong reducing bath usually made up of sodium dithionite ($Na_2S_2O_4$), and sodium hydroxide. The problems associated with sodium dithionite in conventional machine cleaning include strongly alkaline conditions and requirement of large amounts of water during the machine cleaning and subsequent rinsing of machine with fresh water to remove traces of sodium dithionite, which could otherwise affect next white or dyed lot. The conventional machine cleaning method not only adds cost to the process but also increase effluent load.

This study uses ozone (O_3) for removing dyes residues from the surface of dyeing machine. Ozone, an important member of advanced oxidation processes, has been extensively studied for the removal of various dyes from textile wastewater effluents[4-7].

Due to very high oxidation potential (2.07 V), O_3 is capable of breaking up most organic compounds, including dye chromophores[8]. Fig. 1 demonstrates the O_3 production wherein high voltage energy splits diatomic oxygen (O_2) molecule, allowing the formation of a 3-atom oxygen molecule-O_3.

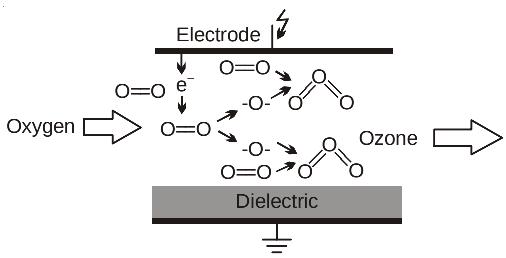


Fig. 1. Production mechanism of O_3

Moreover, the formation of O_3 is an endothermic reaction (eqn. 1):

$$3O_2 \rightleftharpoons 2O_3 \quad \Delta H^o_f \text{ at 1 atm} = +284.5 \text{ kJ mol}^{-1} \qquad (1)$$

Thus, O_3 is thermodynamically unstable gas and spontaneously reacts with most inorganic and organic substances. In an aqueous solution, O_3 can react with different materials (M) in two possible ways[9]: (1) Through direct reaction with the molecular ozone and (2) through reaction with the radical species that are formed when O_3 decomposes in water. The two basic reactions of O_3 in water are illustrated in Fig. 2

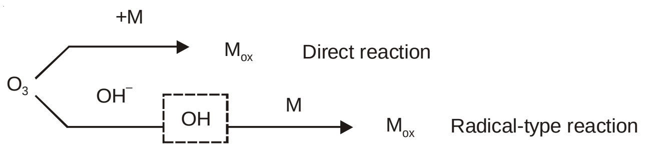


Fig. 2. Reactivity of ozone in water

Results obtained in this study indicate that the use of O_3 for cleaning textile dyeing machinery is a viable option which can replace the conventional chemical intensive cleaning process, without compromising dyeing quality. The new method not only reduces the pollution load but also saves the amount ofwater, chemicals, process time and energy used.

EXPERIMENTAL

Cotton knitted fabric having 200 g/m^2 was used throughout this study. Scoured fabric (prepared for dyeing) was used to dye fabrics in deep shades. Selected commercial dyes commonly used in dark reactive shades were used in experiments (Table-1). Chemicals like sodium sulphate (Na_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium dithionite ($Na_2S_2O_4$) were of commercial grade.

Dyeing procedure: Three dark shades, Black, Red and Navy were dyed using C.I. Reactive Black 31, C.I. Reactive Red 194 and C.I. Reactive Blue 19, respectively. Dyeings (7 % o.w.f) were carried out using a standard isothermal dyeing method shown in Fig. 3. In all cases, liquor ratio (L:R) of 1:10, 80 g/L of Na_2SO_4, 20 g/L of Na_2CO_3 and 1.0 g/L of NaOHwere used. At the end of dyeing cycle, only twocold rinses (fill and drain) of 10 min each were given to the dyed fabric so that dyeing machine is not completely cleaned by the fabric wash-off process.

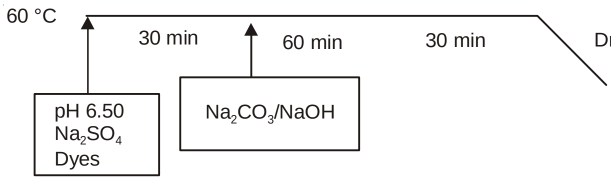


Fig. 3. Dyeing process used in the study

Conventional machine cleaning: Conventional machine cleaning was carried out by a hot reductive treatment at 90 ºC containing 6 g/L $Na_2S_2O_4$ and 4 g/L NaOH for 1 h. This process ensures destruction of dyestuffs residues stuck to the machine walls. The bath is then dropped and rinsed with warm water twice to ensure no residues of $Na_2S_2O_4$ are left in the machine. Pre-bleached (OBA treated) and pre-dyed (light coloured) fabric samples were then run in the machine for 0.5 h in plain water at ambient temperature. The acquired whiteness degree of bleached fabric and colour properties of dyed fabrics were regarded as reference.

Ozone treatment for machine cleaning: Ozone application was carried out using a pilot-scale experimental setup consisting of sample jet machine (Thies GmbH & Co. KG, Germany), ozone generator (Kaufman, OZ-50), Ozone analyzer (Ozonova, UVP 200), injector pump, ozone catalyst (destroyer), Ozone gas leak detector, ORP meter and ambient air O_3 monitor (Gfg, Micro III). The exact drawing of the machine is not disclosed here owing to the commercial confidentiality. O_3 gas was generated using the ozone generator capable of producing up to 50 g of O_3/h. The O_3 flow rate was maintained at 500 L/min. The ozone generator was kept cooled by using cooling water. Ozone gas was transferred from ozone generator to the dyeing machine with the help of an injector pump through 2 inch diameter stainless pipe. The O_3 was introduced at the bottom of the jet dyeing machine, just prior to the suction of main pump to achieve homogenous mixing of O_3 with the receiving liquor, ensuring maximum mass transfer of O_3 gas

TABLE-1
STRUCTURE AND PROPERTIES OF DYES

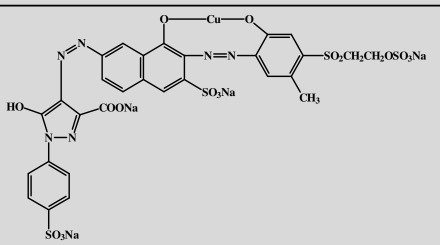
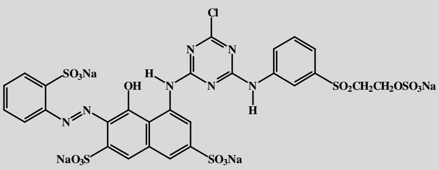
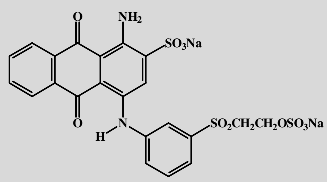
Name of dye	Chemical structure	Molar mass	λ_{max} (nm)
C.I. Reactive Black 31		1006.25	575
C.I. Reactive Red 194		984.21	523
C.I. Reactive Blue 19		626.55	593

TABLE-2
COLOUR DIFFERENCE VALUES OF REFERENCE AND SAMPLES RAN AFTER O_3 BASED MACHINE CLEANING

Deep shade dyeing	Sample ran after O_3 cleaned machine	Colour difference values					
		ΔL*	Δa*	Δb*	Δc*	Δh*	$\Delta E^*_{cmc\ (2:1)}$
Black	Light grey	0.51	0.26	0.16	-0.15	0.27	0.29
	Light green	-0.39	-0.03	0.10	0.10	-0.01	0.17
	Light yellow	-0.15	0.29	0.50	-0.19	0.04	0.24
Navy	Light grey	-0.71	-0.01	-0.23	-0.21	0.11	0.35
	Light green	-0.22	0.19	0.30	-0.15	0.09	0.34
	Light yellow	0.171	-0.11	-0.49	-0.18	0.34	0.45
Red	Light grey	0.15	0.22	-0.37	-0.10	0.38	0.28
	Light green	0.22	0.25	-0.19	-0.45	0.17	0.33
	Light yellow	-0.31	0.53	0.41	-0.08	0.31	0.41

into the liquor. Machine cleaning was carried out at ambient temperature for 0.5 h. Unused O_3 coming out of the dyeing machine was destroyed in the catalyst destructor. After-wards, pre-bleached (OBA treated) and pre-dyed (light-coloured) fabric samples were run in the machine for 1 h in plain water at ambient temperature. These samples were then compared with reference samples.

Machine cleaning efficiency: Machine cleaning efficiency of O_3 based washing method was determined and compared with that of conventional method in terms of COD and spectrophotometric absorbance. Determination of COD was carried out by using closed reflux titrimetric method[10]. Using a UV/VIS spectrometer (Perkin Elmer, Lambda 25), the absorbance of the washing liquors was measured under the maximal absorption peak (λ_{max}). Colour removal (%) of two wastewaters was determined using eqn. 2:

$$\text{Colour removal (\%)} = \frac{A_0 - A_1}{A_0} \times 100 \qquad (2)$$

where A_0 is the absorbance of wastewater of the conventional machine washing and A_1 is the absorbance of wastewater from O_3 based machine washing. Evaluations regarding wash fastness (ISO 105-C06), change in colour (ISO 105-A02), colour staining (ISO 105-A03) and change in CIE whiteness index (AATCC 110-2011) of fabrics processed in the machines were also made.

RESULTS AND DISCUSSION

Effect of ozone based machine cleaning on dyeing quality: The colour differences between reference (fabric processed after conventionally-washed machine) and samples (fabric processed after ozone washed machine) were summarized in Table-2. Overall results indicate that the colour difference in all cases was negligible (ΔE* ≤ 1.0). In case of machine cleaning with O_3 after black shade dyeing, the results show that the final shade of light gray sample was identical to that of reference because only minor differences in lightness (ΔL* = 0.51), chroma (Δc* = -0.15), hue (Δh* = 0.27) and total colour difference (ΔE* = 0.29) were observed. Compared to the reference, the shade of light green fabric was found to be bit darker (ΔL* = -0.39), slightly brighter (Δc* = 0.10) and within acceptable total colour difference (ΔE* = 0.17). For light yellow shade, O_3 based machine cleaning imparted slight changes to lightness (ΔL* = -0.15), chroma (Δc* = -0.19), hue (Δh* = 0.04) and total colour difference (ΔE* = 0.24). For rest of the shades, similar trend was observed and lower values of ΔL*, Δc*, Δh* and ΔE* indicated that there was no significant colour difference between reference and samples processed in O_3washed dyeing machine. Total colour difference (ΔE*) values of all shades are summarized in Fig. 2.

Table-3 displays a comparison of fastness properties of reference and sample fabrics. It is evident from the results that both conventional and O_3 cleaning of jet dyeing machine exhibited similar washing and crocking fastness properties with minimum change in shade. In all cases, fastness properties were found to be excellent (4.5-5.0) showing that no residues of dyes were carried forward at the time of the switchover of dyeing lots.

TABLE-3
COMPARISON OF COLOUR STAINING OF FABRICS PROCESSED IN DYEING MACHINE AFTER CONVENTIONAL AND OZONE BASED MACHINE CLEANINGS

Fabric samples	Crocking		Multi-fiber staining			Change of shade
	Dry	wet	Cotton	nylon	polyester	
Light grey						
Reference	5	5	5	5	5	–
Sample	5	5	5	5	5	5
Light green						
Reference	5	4.5	5	5	5	–
Sample	5	5	5	5	5	4/5
Light yellow						
Reference	5	5	5	5	5	–
Sample	5	5	4.5	5	5	5

Effect on whiteness degree: Whiteness degree (%) of white (bleached) fabrics, processed after dark shade dyeing and subsequent machine cleaning, can indicate the efficacy of cleaning method. The overall results (Fig. 4) indicate that both conventional and O_3 based cleaning systems did not alter or reduce the whiteness degrees of fabrics. In case of machine cleaning after black shade dyeing, % whiteness degree of bleached fabric was found to be 150 for both conventional and O_3 based machine cleanings. For bleached samples ran after navy and red dyeings, the whiteness values of conventional and O_3 washing were found to be in the range of 148-149 and 153-155, respectively.

Ecological analysis: Physico-chemical characteristics of wastewater generated during O_3 based machine cleaning was compared with that of conventional machine cleaning and reported in Table-4. The comparison clearly illustrates that wastewater from O_3 based machine cleaning was found to be

TABLE-4
CHARACTERISTICS OF WASTEWATER FROM MACHINE CLEANINGS

Parameter	Wastewater samples					
	After black dyeing		After navy dyeing		After red dyeing	
	Conventional	Ozone	Conventional	Ozone	Conventional	Ozone
COD (mg/L)	671	16	585	13	667	18
pH	12.3	7.6	11.9	7.9	12.1	7.1
EC (µS/cm)	4875	25	4323	36	5010	29
Temp. (ºC)	80	34	82	32	82	35
TSS (mg/L)	130	10	165	17	135	15
Water usage (L/kg)	45	15	45	15	45	15
Colour difference (%)	–	95	–	98	–	96

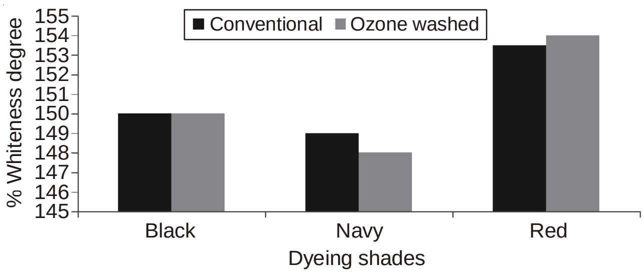


Fig. 4. CIE whiteness index of white fabric processed in O_3 washed dyeing machine and compared with reference

satisfactory. The COD level in wastewater resulted from conventional machine cleaning varied from 585 to 671 mg/L, whereas COD levels in O_3 based machine cleaning were found to be in the range of 13-18 mg/L. The pH values of wastewaters from conventional and O_3 based machine cleanings were found to be around 12 and 7.5, respectively. Due to the use of large quantities of chemicals ($Na_2S_2O_4$ and NaOH) in the conventional machine cleaning, electric conductivity and solid content in wastewater were found to be on the higher side. Compared to the colour of wastewater coming from the conventional machine cleanings, the O_3 based machine cleaning generated the wastewater having 95-98 % less colour strength. O_3 based cleaning dyeing machine also brings reduced energy costs by using water at ambient temperature, which lowers the energy necessary to heat water. Conventional machine cleaning requires several rinsing steps to clear off residues of $Na_2S_2O_4$ and NaOH. No rinsing is required in ozone based machine cleaning, thus resulting into water savings. Ozone based machine cleaning does not release any objectionable odour during application, thus working conditions and workplace hygiene are better than those of conventional machine cleaning using $Na_2S_2O_4$ based reducing agents.

Conclusion

This pilot-scale study investigated a new washing method to remove dye residues from the surface of textile dyeing machine. Instead of using conventional cleaning method employing hot alkaline solutions of $Na_2S_2O_4$, the new method used ozone gas at ambient temperature for the destruction of dyestuff that stains the interior of dyeing machinery. The performance of ozone based washing was investigated for number of shades and the results showed that O_3 based machine cleaning was capable to achieve similar results in terms of shade difference and colour fastness properties. Compared to the conventional machine washing, new method showed a reduction of 67 % water consumption, 97 % COD and 92 % TSS. Moreover, new method did not use any heating during machine washing and hence proved to be less energy intensive compared to the conventional process.

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