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Ozonation of light-shaded exhausted reactive dye bath for reuse

M. Sundrarajan*, G. Vishnu, Kurian Joseph

Centre for Environmental Studies, Anna University, Chennai 600 025, Tamil Nadu, India

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Abstract

Exhausted reactive dye bath of light yellow and blue shades were collected from cotton knit wear dyeing units in Tirupur and ozonated in a column reactor system at the rate of 0.16 g/min to assess its efficiency in reducing the color, chemical oxygen demand and total organic carbon. The potential for repeated reuse of the decolorized dye bath was also studied. Color removal of the effluent was achieved in 5 min contact time for yellow and blue shades at an ozone consumption of 37.5 and 36 mg/L, respectively.

It is concluded that ozonation is efficient in decolorization of exhausted dye bath effluents containing conventional reactive dyes. However, the corresponding removal of COD was not significant. Maximum for yellow and blue shades, COD removal was achieved in 20 and 40 min contact time at an ozone consumption of 65.8 and 76.5 mg/L, respectively. The COD removal was 51% for blue and 48% for yellow shades, while the TOC removal efficiency was 51 and 42% for blue and yellow shades, respectively. The dyeing quality was not affected by the reuse of decolorized dye bath for two successive cycles.
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Keywords: Ozonation; Decolorization; Dye bath; Reactive dye; Reuse

1. Introduction

Textile industry is one of the most complex manufacturing industries. Various textile chemicals such as wetting agents, dyes, surfactants, fixing agents, softeners and many other additives are used in wet processes such as bleaching, dyeing and finishing processes. As a result, textile wet processing produces highly polluting wastewater [1–4]. Strong color of the textile wastewater is the most serious problem of the textile waste effluent. Textile dyeing effluents are known to present extreme variations of pH, high temperature, high COD and high concentration of dissolved salts [5–7]. Treatment of wastewater containing reactive dyes is a severe problem for the cotton textile industry [8]. Ozonation is perhaps the most advanced method ever attempted for decolorization of the textile effluents [9–12].

It is well known that ozone is a powerful oxidant and its oxidizing potential is nearly twice that of chlorine. The high oxidation potential allows ozone to degrade most organic compounds [13]. Ozone and hydroxyl radical ($OH^{\bullet}$) species generated in aqueous solution are able to open aromatic rings. Ozone alone and in combination with UV light, catalyst, ultrasound or activated carbon has been successfully applied to textile industrial effluents [14]. The advantage is that ozone can be applied directly in its gaseous state and therefore doesn't increase the volume of wastewater and sludge [4]. Typically, ozonation doesn't yield complete mineralization to CO_2 and H_2O but leads to formation of partial oxidation products such as organic acids, aldehydes and ketones [8].

This paper presents the results of the studies on ozonation for decolorization of light-shaded reactive dye bath effluents originating from cotton knit wear textile industry for potential reuse.

2. Materials and methods

A schematic of the methodology followed for decolorization and reuse of reactive dye bath is depicted in Fig. 1. The exhausted dye bath samples were collected from textile dyeing

* Corresponding author. Tel.: +91 44 22301283; fax: +91 44 2354717.
E-mail address: sundrarajan@yahoo.com (M. Sundrarajan).

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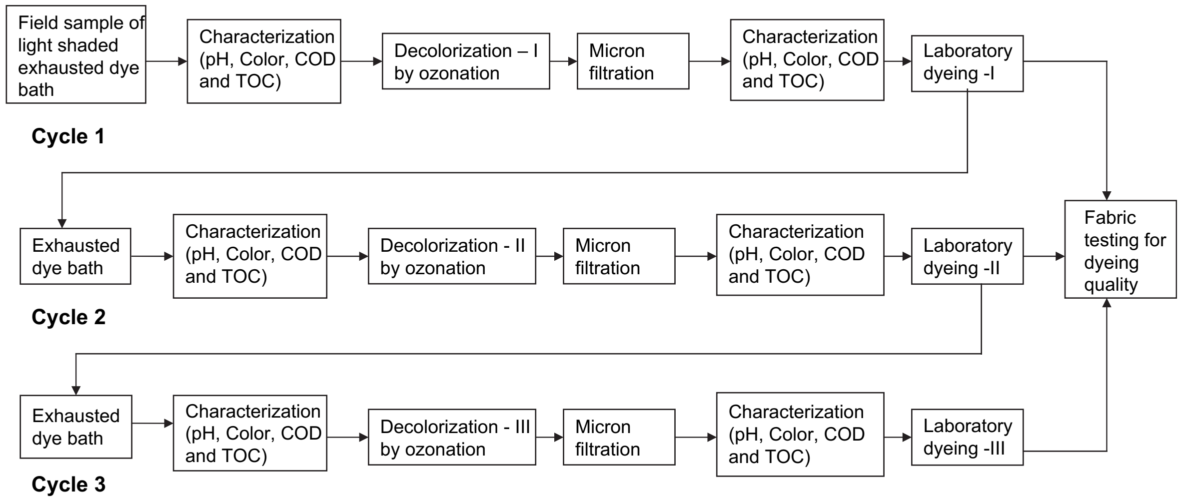

Fig. 1. Schematic of methodology for decolorization and reuse of reactive dye bath.

industries using light shades of yellow (0.082%) and blue (0.083%). Conventional reactive dyestuffs were decolorized and reused for dyeing. The recipes of these dye baths are presented in Table 1. The studies were repeated in three cycles. In the cycle I, the samples were analyzed for pH, color, COD and TOC based on standard methods [15].

2.1. Ozonation

Ozonation studies were done using an experimental setup consisting of ozonator, oxygen concentrator and bubble column reactor and air diffuser as depicted in Fig. 2. Ozone was generated from concentrated oxygen by Indizone Model Ozone generator. A cylindrical Borosil glass reactor of 10 cm diameter and 200 cm height was used for the ozonation. Silicon tubing was used for the connection between ozone generator and reactor column. A tubular cylindrical porous diffuser was connected to the silicon tube and placed at the bottom of the reactor to transfer ozone gas into aqueous solution. Two reactors containing 2 L of 2% KI solution were used to trap the unreacted ozone. Sodium thiosulphate titration procedure [15] was performed to measure the ozone concentration, trapped in the KI solutions from which the ozone dose required for complete decolorization of dye bath was determined.

All experiments were performed at ambient temperature (28–30 °C). Ten liters of the exhausted reactive dye bath (blue and yellow shades) samples were initially subjected to ozonation for 5 min contact time at an ozone dose of 0.16 g/min. The samples that were decolorized during this period were turbid. These were subjected to filtration using 5 μm filter at an operating pressure of 1.0 bar. As the COD reduction during the first 5 min was not significant, the samples were further subjected to ozonation at different contact times (10, 15, 20, 25, 30, 35 and 40 min).

The exhausted dye bath and decolorized samples were analyzed for pH, color, COD and TOC based on standard methods [15]. Total organic carbon (TOC) of the exhausted dye bath and decolorized dye bath were measured using a TOC analyzer (Micro N/C Model 1997, Analytica Jena,

Table 1
Recipe of the dye baths (industrial samples)

Sl. no.	Parameter	Particulars	
1	Shade	Blue	Yellow
2	Reactive dye (%)	Reactive Red RR (0.001) Reactive Yellow RR (0.002) Reactive Blue BB (0.080)	Reactive Yellow FN2R (0.003) Reactive Yellow H4GL (0.077) Reactive Blue FNR (0.002)
3	Sodium chloride (g/L)	10	10
4	Sodium carbonate (g/L)	5	2
5	Material liquor ratio	1:15	1:15

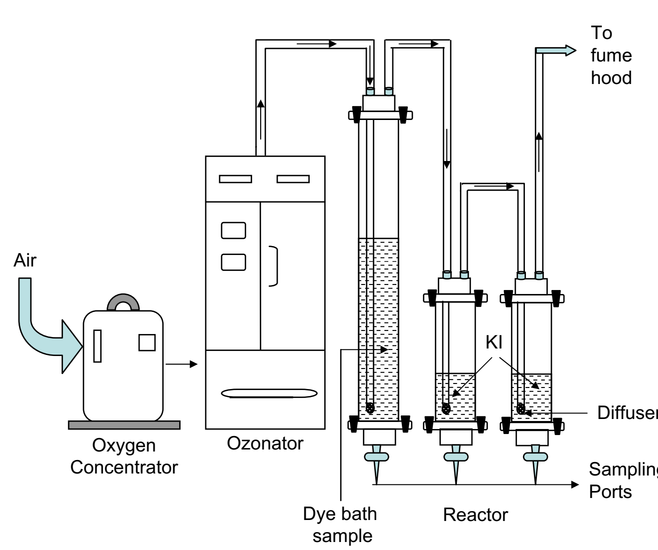

Fig. 2. Experimental setup for ozonation.

Germany). COD was measured according to standard methods [15]. Color of the samples was determined by absorbance measurements using Spekol 1200 model spectrophotometer at three different wavelengths (436, 525 and 620 nm) based on German method [4].

2.2. Laboratory dyeing – cycle I

The dye bath samples after decolorization (5 min ozonation + filtration) and after 40 min ozonation were used for dyeing 10 g sample of bleached and fluorescent brightener free knitted cotton fabric in a laboratory dyeing machine. The dyes used in this study, their color index generic name, λ_{max}, chemical constitution and type are provided in Table 2. The recipe for the dyeing studies and quantity of dyes for the dyeing of 10 g knitted cotton fabric are given in Table 3. The dyeing studies were also repeated using tap water and salt for comparison of dyeing quality.

A laboratory dyeing machine with 12 numbers of 250 mL stainless steel tumblers was used for dyeing. The tumblers were filled with 200 mL of decolorized dye bath or tap water and heated to 40 °C. The dyestuff and exhausting agent (NaCl) were added in the case of tap water (based on the dyeing recipe) while for the decolorized dye bath, only dyestuff was added.

Fabric was wetted and immersed in the dye bath and dyeing was done as temperature gradually increased from 40 to 60 °C in 30 min. At this temperature, alkali (Na_2CO_3) was added and dyeing was continued at 80 °C for 60 min. After dyeing, the fabric was removed from the dye bath and hot wash (90 °C for 10 min) was done twice. Then the fabric was neutralized using 0.1 g/L glacial acetic acid at 27–30 °C for 10 min. Soaping with 2 g/L soap solution at 90 °C for 10 min was done followed by two cold washes at 27–30 °C for 10 min after which the dyed fabric was air dried.

2.3. Fabric testing for dyeing quality

The dyed fabric was tested for color strength using UV–visible Spectrophotometer U-3210 (make: Hitachi). The *K/S* value as per Kubelka–Munk equation has a linear relationship with the concentration of colorant and is calculated using the equation,

Table 2
Properties of the dyes used in dyeing studies

Sl. no.	CI name	λ_{max} (nm)	Chemical constitution	Type
1	CI Reactive Red 120	510	Diazo, dichlorotriazine	Salt controllable high substantivity
2	CI Reactive Yellow 84	420	Diazo, bisaminochlorotriazine	Salt controllable high substantivity
3	CI Reactive Blue 5	620	Diazo, bis(sulphatoethylsulphonate)	Alkali controllable low substantivity

Table 3
Recipe for reactive dyeing

No.	Parameter	Values
1	Shade	Blue and yellow
2	Weight of knitted fabric (g)	10
3	Material liquor ratio	1:20
4	% of shade	0.1%
5	Dye (mg)	0.01
6	Dyeing time (min)	90
7	NaCl (g/L)	10[a]
8	Na_2CO_3 (g/L)	5
9	Temperature (°C)	70–80

[a] Only for tap water.

$$K/S = \frac{(1-R)^2}{2R},$$

where *R* is the reflectance (%).

Wash fastness of dyed sample was measured using ISO Test 3 (ISO 105-C03: 1989, Geneva) testing method. Dyed fabric sample (10 cm × 4 cm) was taken, stitched with one of the shorter sides of the adjacent bleached fabric and put into the water bath at 60 °C for 30 min. Then the specimen was washed with hot water, cold water and dried.

2.4. Decolorization and reuse studies for cycles II and III

After dyeing (cycle I), the exhausted dye bath samples from laboratory dyeing were analyzed for pH, color, COD and TOC, and subjected to ozonation for 5 min and micron filtration. The decolorized samples were used for dyeing (cycle II) and the procedure repeated once again (cycle III).

3. Results and discussion

3.1. Decolorization by ozonation

The color of yellow shade dye bath was reduced by 23, 29 and 47% at 436, 525 and 620 nm, respectively, at an ozone contact time of 5 min (Fig. 3). The ozone consumption during the period was 37.5 mg/L. Micron filtration of this sample improved the overall color removal to 80, 82 and 79% at the

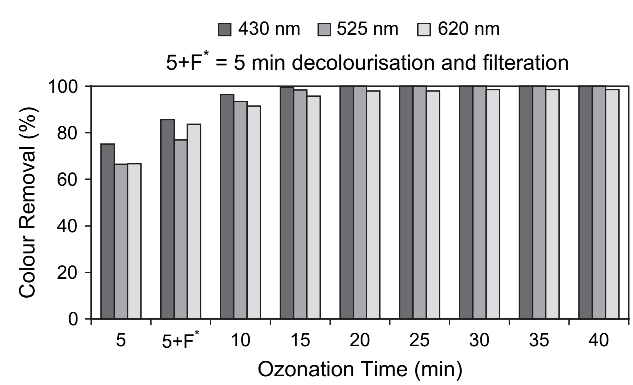

Fig. 3. Decolorization of light yellow shade dye bath by ozonation.

three wavelengths. Complete decolorization was achieved after ozonation for 40 min at an ozone consumption of 76.5 mg/L.

The color of blue shade was reduced by 75, 66 and 67% at 436, 525 and 620 nm, respectively, at an ozone contact time of 5 min (Fig. 4). The ozone consumption during the period was 37.5 mg/L. Micron filtration of this sample improved the overall color removal to 86, 77 and 84% at the three wavelengths, respectively. Complete decolorization was achieved after ozonation for 20 min at an ozone dose of 65.8 mg/L.

These results are in line with the decolorization efficiency of 95% [8], 71% [16] and 90% at 5 min ozonation time [17] at ozone dose of 15 and 14 g/L, respectively. Complete color removal of dye bath at 60 min ozonation time has also been reported [18,19] at an ozone dose of 35 mg/L.

3.2. COD and TOC removal

It was observed that the COD removal (18%) and TOC removal (23%) for yellow shade dye bath was low at a contact time of 5 min (Fig. 5). Micron filtration improved it to 31% for COD and 29% for TOC removal. It was observed that the COD reduction increased to 48% and TOC reduction increased to 42% after further ozonation of 35 min.

It was observed that the COD removal (22%) and TOC removal (35%) for blue shade dye bath was low at a contact time of 5 min (Fig. 6). Micron filtration improved it by 32% for COD and 44% for TOC removal. It was observed that the COD and TOC reduction increased to 51% after further ozonation of 40 min.

It was reported [20] that though ozonation is an efficient process for dye removal, COD removal was rather inefficient, usually not exceeding 54%. The reduction of COD and TOC for yellow and blue shade dye baths was low and did not show much variation. Approximately, a reduction of 50% COD was achieved after 40 min of ozonation. This was comparable with the reported values for COD reduction of 11–29% [21], 50% [22], 27–87% [23] and 5–20% [8], respectively. A TOC reduction of 5% at 5 min contact time and 43% at 60 min contact time was reported [18]. In other

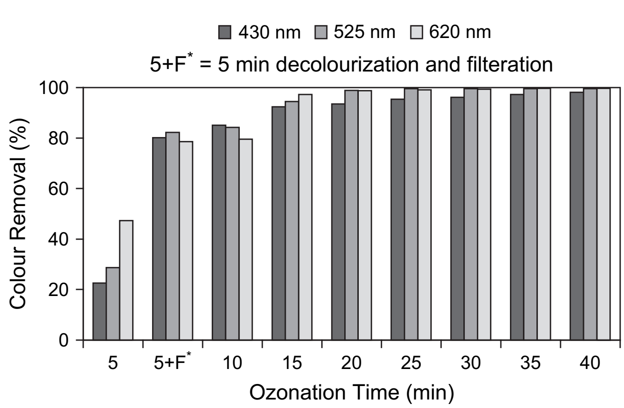

Fig. 4. Decolorization of light blue shade dye bath.

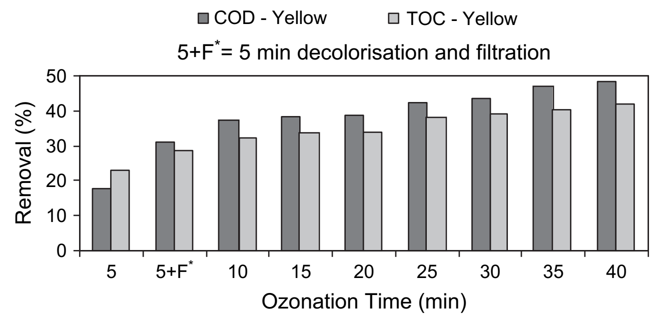

Fig. 5. COD and TOC removal of yellow shade dye bath.

studies, 50% TOC removal [24], and 48–62% removal at 5 min contact time has been reported [25].

3.3. Testing of fabric – cycle I

The *K/S* value and wash fastness of the fabric dyed with tap water and decolorized dye bath obtained in the cycle I and presented in Table 4 showed little variation with a difference of 0.0013 for yellow shade and 0.0084 for blue shade. A similar trend was observed for wash fastness, as the grey scale value of tap water (5) when compared with yellow shade (4–5) and blue shade (4) did not vary significantly.

3.4. Decolorization and reuse studies for cycles II and III

For cycle II, decolorization of 47, 47 and 45% was observed for yellow shade dye bath, at 5 min contact time which increased to 92, 82 and 60% at 436, 525, 620 nm, respectively, after micron filtration (Fig. 7). A similar increase was observed for cycle III. For blue shade dye bath, at 5 min contact time, decolorization of 45, 38 and 48 was observed which increased to 93, 87 and 86% at 436, 525, 620 nm, respectively, after micron filtration for cycle II (Fig. 8). A similar increase was observed for cycle III.

Characteristics of the exhausted and decolorized dye bath from laboratory dyeing are presented in Table 5. The TOC of the yellow shade exhausted dye bath increased from 1080 mg/L in cycle I to 1305 and 1300 mg/L after cycles II and III, respectively. The COD also increased from 3024 mg/L in cycle I to 3254 and 3325 mg/L after cycles II

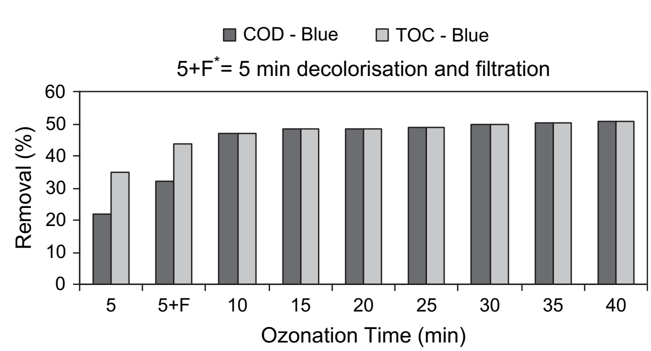

Fig. 6. COD and TOC removal of blue shade dye bath.

Table 4
K/S and wash fastness of dyed fabrics

Sl. no.	Number of cycles	Shade	*K/S*	Wash fastness	
				Change in shade	Change in stain
1	Standard	Yellow	0.0100	5	5
	(tap water)	Blue	0.0737	4–5	4–5
2	Cycle I (5 min decolorization	Yellow	0.0087	4–5	4
	+ filtration – dye bath)	Blue	0.0653	4	4
	Cycle I (5 min decolorization	Yellow	0.0093	4–5	4–5
	+ filtration and 35 min	Blue	0.0691	4–5	4–5
	decolorization – dye bath)				
3	Cycle II (5 min decolorization	Yellow	0.0082	3–4	3
	+ filtration – dye bath)	Blue	0.0592	3–4	3
4	Cycle III (5 min decolorization	Yellow	0.0065	3	3
	+ filtration – dye bath)	Blue	0.0521	3	3

and III, respectively. After decolorization of the dye bath obtained from cycles I, II and III, TOC decreased from 1080 to 830 mg/L for cycle I, 1305 to 945 mg/L for cycle II and 1300 to 1144 mg/L for cycle III. A similar trend was observed for COD. As the dye bath obtained from 5 min decolorization was turbid, micron filtration was done after which the TOC decreased from 830 to 772 mg/L for cycle I, 945 to 737 mg/L for cycle II and 1144 to 810 mg/L for cycle III, respectively. A similar trend was observed for COD.

The TOC of the blue shade exhausted dye bath increased from 1262 mg/L in cycle I to 1350 mg/L after cycles II and III, respectively. The COD also increased from 3155 mg/L in cycle I to 3512 and 3598 mg/L after cycles II and III, respectively. After decolorization of the dye bath obtained from cycles I, II and III, TOC decreased from 1262 to 820 mg/L for cycle I, 1350 to 960 mg/L for cycle II and 1350 to 1190 mg/L for cycle III. A similar trend was observed for COD. As the dye bath obtained from 5 min decolorization was turbid, micron filtration was done after which the TOC decreased from 820 to 712 mg/L for cycle I, 960 to 717 mg/L for cycle II and 1190 to 845 mg/L for the cycle III, respectively.

The increase in COD and TOC in successive cycles could be attributed to increased residual by-products of ozonation

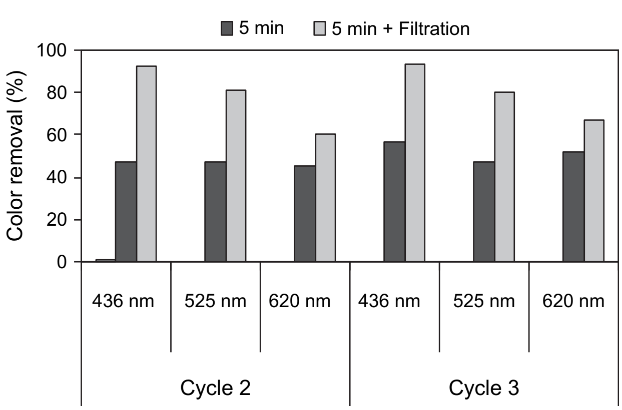

Fig. 7. Color removal for reusability studies using yellow shade dye bath.

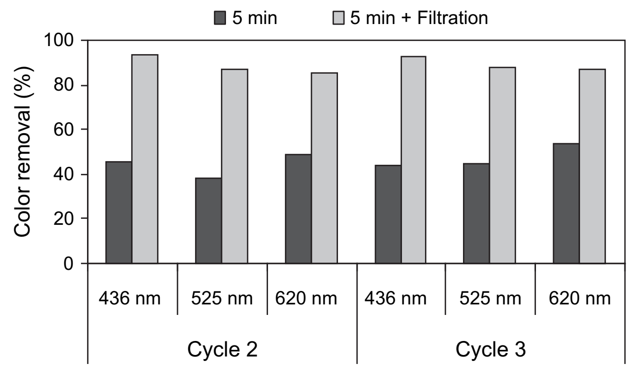

Fig. 8. Color removal for reusability studies using blue shade dye bath.

with each cycle of reuse. Significantly, the high COD and TOC of the decolorized dye bath obtained in cycle I did not affect the quality of the subsequent dyeing, while the increase of COD and TOC in cycle II affected the quality of cycle III.

When the *K/S* value of the fabric dyed with tap water and decolorized dye bath obtained from cycles II and III were compared (Table 5), there was a significant deterioration of quality in cycle III. The difference was 0.0018 for cycle II and 0.0035 for cycle III for yellow, and 0.0145 for cycle II and 0.0216 for cycle III for blue shade, respectively. A similar trend was observed for wash fastness, as the grey scale value was lower for cycle III when compared with other shades/cycles. Cycles II and I produced good wash fastness when compared to cycle III.

4. Conclusions

The results of the present studies show that ozonation is effective in complete decolorization of light-shaded dye bath effluent. The associated COD and TOC reduction was low. At a short contact time of 5 min and ozone consumption of 37.5 mg/L for yellow and 36 mg/L for blue, almost 90% of the color was removed. Micron filtration played an important role in removing the turbidity that interfered with color measurement.

The average COD removal for the blue and yellow shades of exhausted reactive dye bath was 50% while TOC removal was 46%. This implies that ozonation alone is not a satisfactory method for removal of COD and TOC. Though the color is removed effectively, the by-products are still present in the decolorized dye bath and contribute to COD and TOC.

The results from the reusability studies of decolorized dye bath indicate that the dyeing quality was not affected for two successive cycles. The increase in residual COD and TOC affected the dyeing quality in the third cycle implying that ozonation was feasible for decolorization of light-shaded dye bath for two cycles of reuse. Further COD reduction is needed for its repeated reuse in more than two dyeing cycles. Studies are in progress to assess ozonation of dark- and medium-shaded exhausted dye baths for reuse.

Table 5
Characteristics of exhausted and decolorized dye baths from reuse studies

Sl. no.	Number of reuse	Sample name	Yellow			Blue		
			pH	TOC (mg/L)	COD (mg/L)	pH	TOC (mg/L)	COD (mg/L)
1	Cycle I	A	10	1080	3024	10	1262	3155
		B	9.8	830	2491	9.8	820	2460
		C	9.8	772	2084	9.8	712	2136
2	Cycle II	A	10.3	1305	3254	10.2	1350	3512
		B	10.2	945	2466	10.2	960	2376
		C	10.2	737	2189	10.1	717	2168
3	Cycle III	A	10.3	1300	3325	10.4	1350	3598
		B	10.2	1144	2860	10.3	1190	2980
		C	10.2	810	2400	10.3	845	2116

A − Exhausted dye bath, B − decolorized dye bath, C − decolorized dye bath after micron filtration.

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