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Studies on the possibility of recycling reactive dye bath effluent after decolouration using ozone

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Abstract

In this study, the possibility of recycling of reactive dye bath for dyeing of cotton fabric after decolouration using oxidation technique was assessed. Cold brand reactive dyes namely Red 5MR and Golden Yellow MR were used and the oxidation was carried out by ozone. The dyed effluents were reused five times. Time required for decolouring the dye effluent and the effect of decoloured dye effluent on tonal variation of the cotton fabric were analysed. Ozone was found to be more effective on decolouring the dye effluent. The samples produced from the decoloured dye effluents were examined by comparing the spectral reflectance values of the samples with control using colour difference (ΔE^*) and relative unlevelness index values. Based on the colour reproduction ability, it has been found that effluents produced in Red 5MR and Golden Yellow MR can be recycled thrice. The levelness of the shade produced in the recycling of effluents is either excellent or good in all the cases, which includes the samples that produce higher colour difference.

Keywords: Ozonation; Recycling; Decolouration; Reactive dyes; Colour difference

1. Introduction

One of the important technical and economic challenges facing the dyeing industry concerns the efficient use of water. In a typical dyeing and finishing plant, about 120–280 l of water is consumed on an average for every kilogram of cloth processed [1]. The increasing cost of water, energy and wastewater treatment and the limitations imposed on wastewater disposal by changing environmental regulations dictate needs for water recycle in the textile industry on a large scale.

Treatment of textile effluent is a major problem faced today especially by dyeing and processing units. To prevent the environment from the hazard of pollution it is necessary that they have to be treated before they are let out to land or waterways. Prior to dyeing, sizing, desizing, scouring, bleaching and mercerisation are done and as a colouring process, dyeing and/or printing are done. So textile effluents contain size ingredients, desizing agents, scouring agents, bleaching agents and dyestuffs. Amongst all, removal of colour is very difficult. For colouring, varieties of dyes are used viz. acid, basic, direct, vat, sulphur, reactive, disperse, etc. But for dyeing cotton goods, which accounts for almost 50% of the world's total fibre consumption, reactive dyes are widely used in the industry. Also the reactive dye has lower percentage of the dye up-take implying that quantity let out as waste is larger than the other class of dyes.

For the removal of colour, the existing methods such as activated carbon or membrane technology or coagulation/flocculation may be used [2–4]. Among all the possible treatment systems that were proposed for textile wastewaters, oxidative treatments seem to be promising [1,5–11] because they involve a degradation process of the pollutants contained, although never complete. They are moreover very effective towards the oxidation of chromophoric structures of the

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dyes, removing colour, which is the main disturbing factor for water recycle in textile industry. Colour removal by ozone oxidation is the best option as it does not leave any sludge and so the consequent removal and disposal costs and time are reduced [12–15].

Vandevivere et al. [16] and Skelly [17] reviewed the efficiency of recycling process in textile wet processing industries and found that reuse of the treated dye baths saves chemicals and water. Perkins et al. [18,19] reported that the dye bath water was suitable for repeated dyeing if it is treated by chlorination. While numerous reports of water recycle have been reported in the literature a very little information is available on the quality of recycle water utilized for successful process reuse and the quality of the fabrics in terms of colour difference and levelness of dyeing.

Hence an investigation was carried out to study the feasibility of application of ozone technology towards recycling of reactive dye effluents for dyeing of cotton fabrics. Dyes namely Red 5MR and Golden Yellow MR were selected for this study. The used dye baths were treated with ozone until entire colour was removed. The resulting liquor was used for further dyeing studies. For all the dyes five successive recycling processes were carried out. The result such as time taken for complete decolouration, chemical oxygen demand (COD) and pH of the effluents before and after treatment, lightness difference (ΔL^*), colour difference (ΔE^*) and relative unlevelness index (RUI) of the dyed fabrics are reported along with suitable discussions.

2. Experimental

2.1. Apparatus

The experimental set-up consisted of an oxygen concentrator (Sim O_2 plus, Italy) ozone generator (Ozonetek Ltd., India), ozonation chamber and ozone destructor (Ozonetek Ltd., India). A controlled flow rate of 2 l/min of oxygen was used to produce 2 g/h of ozone. The concentration of ozone was analysed using an ozone analyzer (BMT 201, Berlin). The ozonation chamber consisted of 1850 mm glass column with 50 mm inner diameter having a capacity to hold 1000 ml of effluent. It was provided with a sample port at various points, an ozone gas inlet at the bottom with a ceramic diffuser over the inlet port to diffuse the oxygen/ozone gas mixture through the column and a closed top with a collection port to collect the unreacted ozone gas for analysis and to the thermal vent ozone destructor before venting it out. A PTFE tube was used for connecting the ozone outlet port from the ozone generator to the ozone reaction chamber.

2.2. Procedure

Reactive Red 5MR and reactive Golden Yellow MR dyes are obtained from Atul Limited, India and plain cotton fabric was used for this study. Known weight of scoured and bleached cotton fabric was dyed at 3% shade on weight of material (OWM) with the dyes selected using a liquor ratio of 100:1. Dye bath was prepared by adding necessary quantity of dye and 100 g/l of sodium chloride salt in fresh water. Pre-wetted fabric was introduced in the dye bath at room temperature and worked for 30 min. Finally, the material was removed from the dye bath and squeezed in such a way that the liquor falls back in the bath itself. The liquor so obtained was actual effluent of the respective dye.

The fabric taken from the dye bath was introduced in the fixation bath, which contained 2% w/v sodium carbonate and the liquor ratio used was 50:1 at room temperature and it was kept for another 20 min. Then the fabric was removed from the fixation bath and soaping was done using 2 g/l of soap with liquor ratio of 50:1 for 20 min at a temperature of 70 °C.

The effluents obtained above were subjected to complete decolouration using the apparatus described, in order to use it in further dyeing. The complete decolouration of the effluents was ascertained using UV–visible spectrophotometer (Hitachi, U-3210, Japan). The treated effluents were reused; the same dyeing procedure given above was used except the addition of sodium chloride in the bath. Dyed samples produced using the treated effluents were assessed for its quality of dyeing using the spectrophotometer by integrating sphere column. The wavelength measured ranged from 400 to 700 nm with an interval of 10 nm. Eight readings were taken from different places of the fabric.

2.3. Characterisation of effluents and dyed materials

Characteristics of effluents generated in each process and the corresponding ozone treated effluents were assessed in terms of pH and COD using standard methods for analysis of wastewater [20]. The effect of recycling of ozone treated dye effluents on colour reproduction and lightness on cotton fabric was analysed using ΔE^* and ΔL^* values, respectively, calculated with the help of 1976 CIE L^*, a^* and b^* (CIELAB) equations [21]. A relative unlevelness index (RUI) value of dyed samples was calculated by using the equation proposed by Chong et al. [22].

3. Results and discussion

3.1. Effect of recycling on characteristics of effluents

The time required for decolouration of dye liquor obtained from different recycling processes for the dyes used in this study is given in Table 1. The results show that as the number of recycling processes increases the time required for decolouration increases. This reveals that the formation of by-products during ozone oxidation may interfere with the decolouring mechanisms, which leads to increasing time for complete colour removal.

The %COD reduction of ozone treated effluents is also given in Table 1. It reveals that the ozone treatment of dye effluent and those obtained from recycling operations result in reduction of COD. But the reduction in COD does not show any specific trend with respect to increase in number

Table 1
Time taken for complete decolouration and %COD reduction of reactive dye effluents

Number of recycling processes	Red 5MR			Golden Yellow MR		
	Time (min)	% COD reduction	pH after treatment	Time (min)	% COD reduction	pH after treatment
First	15	58	4.23	18	62	4.38
Second	25	52	3.96	19	60	4.25
Third	29	53	4.19	20	60	4.35
Fourth	32	48	4.58	26	56	3.98
Fifth	34	50	4.12	32	54	4.08

of recycling operations. Lopez et al. [23] have observed a reduction in COD in their study on ozone treatment of industrial textile effluents and stated that it was due to the reduction of total organic carbon (TOC) and partial oxidation of organic substrates. Koynnchu and Afsar [24] and Perkins et al. [25] have also observed a similar trend in the treatment of reactive dye and acid dye effluents, respectively.

After ozone treatment, it was observed that the pH decreased for all the effluents (Table 1), which were obtained from all the recycling processes. This indicates that the formation of acidic by-products during ozonation makes the effluent acidic in nature. Muthukumar [26] observed the decreasing pH in acid dye effluents during ozone oxidation and it was reported that ozonation rarely produces complete mineralisation to CO_2 and water, but leads to production of partial oxidation products such as organic acids, inorganic acids, aldehydes and ketones during ozonation. Shu and Huang [6] and Lopez et al. [23] have reported on the generation of acidic compounds during ozonation. Similar kinds of observations, in this study, show that the formations of acidic by-products cause the decrease in pH of the effluents.

3.2. *Effect of recycling on quality of dyeing*

3.2.1. *Effect on colour reproduction*

Dyed materials are generally accepted when the ΔE^* values are between 0 and 1.5 and the ΔL^* values are between −0.7 and 0.4. If the ΔE^* value is above 1.5 the colour difference between sample and control is very high to be rejected. If the ΔL^* values are less than −0.7 the samples are darker in shade and if it is greater than 0.4 the samples are lighter in shade compared to that of control sample [21]. The objective of this work was to determine the colour reproducibility of dyeing in ozonated water rather than to match the standard shades provided by the company. Therefore, the original dyeing performed in fresh water was used as the target shades by which reproducibility was judged. ΔE^* and ΔL^* values of the dyed samples produced in the present study are given in Table 2. The L^*, a^* and b^* values of control and samples obtained from various recycling processes are given in Table 3. It is observed from Table 2 that as the number of recycling processes increases, the ΔE^* values increase. In Red 5MR, as the number of recycling processes increases, the ΔE^* values increase from 0.32 in first recycling to 2.68 in fifth recycling process. Similarly in Golden Yellow MR, the ΔE^* values increase from 0.31 in first recycling to 2.016 in fifth recycling process.

Table 2
Colour difference (ΔE^*) and lightness (ΔL^*) values with respect to control

Samples	Red 5MR		Golden Yellow MR	
	ΔE^*	ΔL^*	ΔE^*	ΔL^*
First recycle	0.32	0.27	0.31	0.05
Second recycle	0.87	0.55	0.57	0.15
Third recycle	1.39	0.89	1.01	0.28
Fourth recycle	2.06	1.45	1.51	0.40
Fifth recycle	2.68	1.79	2.16	0.52

Perkins et al. [19] reported that 10 target shades were dyed on cotton fabric using ozone treated water out of which only four shades met the acceptable limits. They suggest that the dark shades can be reproduced in ozonated water still containing up to 40% of the spent dye from previous cycle. It can be inferred from Table 2 that for Red 5MR and Golden Yellow MR dyes, usage of recycled effluents can be carried out three times. This shows that even though we decolourised the dyes completely in the fourth and fifth cycles we could not achieve the acceptable limits. This reveals that the formation of acidic by-products during ozonation may interfere with the affinity of the dye to the fabric, which reflects increasing colour difference values. Also the oxidizing agent can affect the finished fabric quality as a result of chemical reaction with fibres which might cause an increase in ΔE^* values. The samples produced by recycling process results in lighter shade compared to that of the samples obtained from fresh water process. Positive ΔL^* values indicate that the samples are lighter in shade compared to that of control sample. It can be observed that in Red 5MR the ΔL^* values fall in acceptable limits in only first recycling process, whereas in Golden Yellow MR the ΔL^* values are within acceptable limits in the first four recycling processes.

Table 3
L^*, a^*, and b^* values of control and samples obtained from various recycling processes

Samples	Red 5MR			Golden Yellow MR		
	L^*	a^*	b^*	L^*	a^*	b^*
Control	55.60	54.45	−11.53	83.40	9.87	57.14
First recycle	55.88	54.35	−11.66	83.46	9.92	56.85
Second recycle	56.16	54.43	−12.20	83.55	9.94	56.60
Third recycle	56.49	53.84	−12.40	83.69	9.79	56.18
Fourth recycle	57.06	53.36	−12.50	83.80	9.81	55.69
Fifth recycle	57.20	53.20	−13.08	83.92	9.78	55.04

Table 4
Relationship between relative unlevelness index (RUI) and visual appearance of levelness

RUI values	Visual appearance of levelness
<0.2	Excellent levelness (undetectable unlevelness)
0.2–0.49	Good levelness (noticeable unlevelness)
0.5–1.0	Poor levelness (apparent unlevelness)
>1.0	Bad levelness (conspicuous unlevelness)

Chong et al. [22].

3.3. Effect on level dyeing character

The differences between the visual assessment and instrumental determination of levelness are important issues. The eye is not equally sensitive to light at all wavelengths. Therefore, the levelness results from the visual observation do not always agree with the data determined by the instrument [27]. Therefore the levelness was assessed using spectrophotometer and calculated using the equation proposed by Chong et al. [22]. The level dyeing characteristics of dyed fabrics are explained with the help of RUI. It has been proved as an indicator of levelness, an important parameter of the dyeing process. This index can accurately indicate degree of levelness of any dyeing. The relationship between RUI and visual appearance of levelness is given in Table 4. The RUI values of dyed samples produced in the study are given in Table 5. It is observed from the results that all the dyed samples produced from recycling processes show excellent to good levelness, which is comparable to that of dyed samples produced using fresh water. An observation to be pointed out here is that even in the cases where the dyed samples are rejected based on ΔE^* values (Table 2), the levelness obtained is either excellent or good. This indicates that the dye effluents produced in these cases can still be recycled, provided alteration in tone is acceptable.

4. Conclusions

The study reveals that ozonation can be used to remove completely colour and chemical oxygen demand to an extent, which is sufficient for water reuse even in critical conditions as dyeing with light tones. Reuse of ozonated water saves chemicals mainly salt, water, wastewater treatment expense and energy. Based on the colour reproduction ability, it has been found that effluents produced in Red 5MR and Golden Yellow MR can be reused three times.

Table 5
Relative unlevelness index (RUI) of dyed samples

Samples	Red 5MR	Golden Yellow MR
Control	0.052 (EL)	0.037 (EL)
First recycle	0.091 (EL)	0.040 (EL)
Second recycle	0.099 (EL)	0.047 (EL)
Third recycle	0.120 (EL)	0.059 (EL)
Fourth recycle	0.136 (EL)	0.071 (EL)
Fifth recycle	0.261 (GL)	0.085 (EL)

EL – excellent levelness; GL – good levelness.

The levelness of the shade produced in the recycling of effluents is either excellent or good in all the cases, which includes the samples that produce higher colour difference. Production of good levelness in dyed samples which have shown higher colour difference compared to that of control sample indicates that in these cases the recycling can still be carried out to produce goods with alteration in tone, if accepted. So ozonation shows to be a promising method for purification aimed at reuse of textile wastewater resulting in direct environmental and economic costs.

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