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Studies on decolouration, toxicity and the possibility for recycling of acid dye effluents using ozone treatment

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Abstract

Investigations carried out to study the feasibility of application of ozone technology for decolouration, toxicity and towards recycling of acid dye effluents for dyeing of silk fabric are reported in this paper. The dyes Acid Red 88, Acid Red 18, Acid Orange 7, Acid Orange 10 and Acid Red 73 were used in this study. The used dye baths were treated with ozone till complete colour removal and reused. For all the dyes two successive recycling processes were carried out. Characteristics of effluents and ozone treated effluents were assessed in terms of total dissolved solids (TDS) and chemical oxygen demand (COD). *Gambusia affinis* was used for the bioassay tests to find the LC_{50} value of the treated effluents. The effect of recycling on quality of dyeing was determined using colour difference (ΔE^*) and relative unlevelness index (RUI). This study reveals that treatment of acid dye effluents with ozone does not have an effect on TDS reduction. But it reduces the COD of effluents including the effluents obtained in recycling processes. The toxicity of the ozone treated effluents increases with increasing time. A dye having a greater number of sulphonic acid groups in its structure reveals higher toxicity. Resulting effluents from the application of Acid Red 88 and Acid Red 73 on silk fabric can be recycled twice and those from Acid Red 18 and Acid Orange 10 can be recycled once with acceptable ΔE^* values. Acid Orange 7 effluent is found to be unsuitable for recycling because of its higher colour difference values. The levelness of the shade determined on the basis of RUI, produced on the silk fabric in the recycling processes, is either excellent or good in all the cases, which include those producing higher colour difference.

Keywords: Ozonation; Colour removal; Acid dyes; Recycling; Toxicity; Colour difference; Relative unlevelness index

1. Introduction

Reuse of water in textile processes has been the subject of research and development work in recent years [1–11]. The incentives for reuse of water are great, since there is a potential for reduction of both water requirements and wastewater treatment costs. One of the approaches to reuse the dye bath is to reconstitute the dye bath by adding the required amount of dyes and chemicals after analysing the dye liquor. This method is applicable only if the dyeing process does not change the character of the residual dye in the bath. Another approach is to remove the residual colouring matter prior to reuse. This method is applicable to any class of dye provided sufficient colour is removed.

Vandevivere et al. and Skelly [7,9] reviewed the efficiency of the recycling process in textile wet processing industries and they found that reuse of the treated dye baths saves chemicals and water. Perkins et al. [2,4] reported that the dye bath water was suitable for repeated dyeing if it is treated by chlorination. Also, they assessed the performance of the reuse by colour difference (ΔE^*) values of the dyed samples obtained from the treated effluent and found that 4 out of 10 samples were of less than the acceptable level. Perkins and Reed [3] reported that reusing ozone treated water for dyeing with vinyl sulphone dyes shows excellent colour reproducibility.

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The effluents from textile dyeing industries contain a variety of chemicals and dyes, which are carcinogenic and mutagenic [12,13]. The nature and extent of pollution depend on the biochemical oxygen demand (BOD) and dissolved oxygen (DO) in the aquatic bodies [14]. The chemicals present in the dye effluents deplete DO and increase the BOD, which can cause heavy fish mortality by interfering with respiratory physiology [15–17].

Hence, an investigation was carried out to study the feasibility of application of ozone technology towards recycling of acid dye effluents for dyeing of silk fabric and the toxicity of the ozone treated effluents. The dyes Acid Red 88, Acid Red 18, Acid Orange 7, Acid Orange 10 and Acid Red 73 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, two successive recycling processes were carried out. The results, namely, total dissolved solids (TDS) and chemical oxygen demand (COD) of the effluents before and after treatment, colour difference (ΔE^*), relative unlevelness index (RUI) of the dyed fabrics and LC_{50} of the ozone treated effluents, 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 consists of a 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.

Multivoltine plain-woven raw silk fabric used for dyeing studies was obtained from Central Silk Technical Research Institute, Central Silk Board, India. The chemicals and dyes used were of analytical and commercial grades, respectively. Ground water having a hardness of 82 mg/l was used in the dyeing processes.

2.2. Procedure

2.2.1. Recycling of actual effluent

Known weight of degummed silk fabric was dyed to 2% shade on weight of material (OWM) with the dyes selected using a liquor ratio of 20:1. The dye bath was prepared by adding the necessary quantity of dye (dyes, namely, Acid Red 88, Acid Red 18, Acid Orange 7, Acid Orange 10 and Acid Red 73) and 20% OWM of sodium sulphate salt in fresh water. Pre-wetted fabric was introduced in the dye bath having a temperature of 40 °C and worked for 10 min. Then 3% OWM formic acid was added and the temperature was raised to 85 °C and the dyeing was continued for further 45 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 the actual effluent of the respective dye.

The effluents obtained from the above process were subjected to 100% decolouration using the apparatus described, in order to use them in first recycling. The complete decolouration of the effluents was ascertained using a UV–visible spectrophotometer (Hitachi, U-3210, Japan). The treated effluents were used for first and second recycling following the same dyeing procedure as given above but without the addition of sodium sulphate salt in the bath. Dyed samples produced using the treated liquors were assessed for the quality of dyeing.

2.2.2. 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, TDS and COD using standard methods for analysis of wastewater [18]. The effect of recycling of ozone treated dye effluents on colour reproduction and lightness on silk fabric was analysed using ΔE^* and ΔL^* values, respectively, calculated with the help of 1976 CIE L^*, a^* and b^* (CIELAB) equations [19]. A relative unlevelness index (RUI) value of dyed samples was also calculated by using the equation proposed by Chong et al. [20].

Bioassay studies were carried out following the APHA [18] recommended procedure to determine LC_{50} values of the ozone treated effluents. The fish *Gambusia affinis* was used for the experiment. Preliminary bioassay test was carried out using a wide range of toxicant concentration; the fish mortality was taken for 48 h for concentrations ranging from 10 to 100% by volume of toxicant preceding the final narrow range of toxicant concentration. In these tests, fish mortality was taken for 24 h, 48 h, 72 h and 96 h. The test medium was replaced daily with a freshly prepared one in order to maintain the effect produced by the various contents in the toxicants. During the removal, 80% of the test medium was siphoned out and equal quantity of freshly prepared similar effluent was added back with least disturbance.

3. Results and discussion

3.1. Effect of recycling on characteristics of effluents

The characteristics of effluents and ozone treated effluents are given in Table 1. It reveals that the treatment results in a very slight reduction in TDS values. This indicates that the ozonation does not have an effect on the removal of dissolved solids from acid dye effluents. Further, it can be observed that the ozone treatment of dye effluent and those obtained from recycling operations results in reduction of chemical oxygen demand (COD). But the reduction in COD does not show any specific trend with respect to increase in number of recycling operations. Lopez et al. [8] 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. Koyunchu and Afsar and Perkins et al. have also observed a similar trend in the treatment of reactive dye and acid dye effluents, respectively [21,22].

3.2. Toxicity of ozone treated acid dye effluents

The bioassay tests were conducted by taking the ozone treated dye effluents as obtained. The safe pH range for the test organism *G. affinis* used in the test was between 5.5 and 8.5 [23]. Since the pH of the bioassay effluents is within these values, the contribution by the pH of the above test liquors to their toxicity has not been taken into account.

Figs. 1–3 show the plots drawn using the results obtained after converting the % mortality to probit scale and the concentration to log scale. From the plots, LC_{50} values were determined by finding the corresponding value of concentration for 50% mortality. The LC_{50} values for the different ozone treated effluents are given in the same figures.

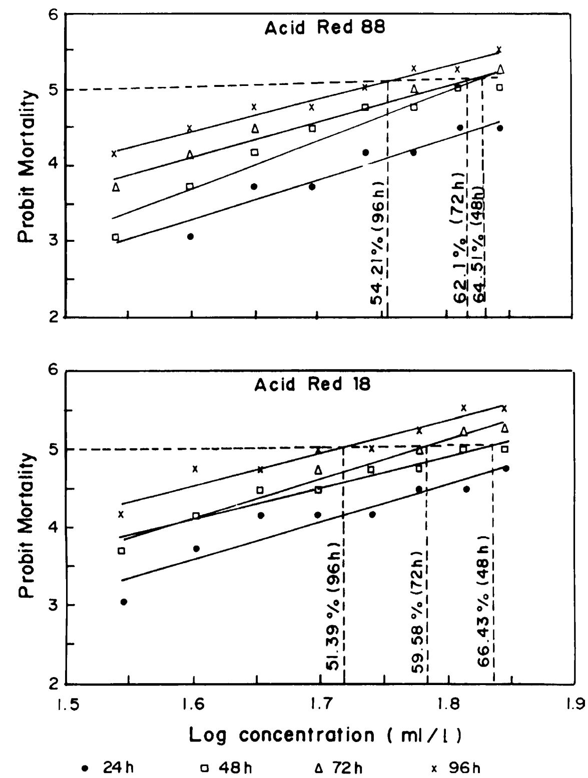

Fig. 1. Log probability plots of % mortality against concentration of ozone treated Acid Red 88 and Acid Red 18 dye effluents.

Perkins et al. [22] pointed out that salinity increases the toxicity and especially toxicity contributed by sulphates is more than that of chlorides. The results obtained on the effect of ozonation of acid dye effluents on total dissolved solids (TDS) show that ozonation does not have an appreciable effect on reduction of TDS of the effluents. Hence, it can be said that the sodium sulphate concentration remains more or less the same after ozonation. So in the present situation, the toxicity of bioassay test liquors is also to an extent due to the sulphate salinity, which is over and above the

Table 1
Characteristics of effluents obtained after dyeing and after ozone treatment

Names of the dyes used	Parameters analysed	Dyeing with fresh water		1st Recycling		2nd Recycling	
		After dyeing	After ozone treatment	After dyeing	After ozone treatment	After dyeing	After ozone treatment
Acid Red 88	TDS[a]	858	842	860	858	868	862
	COD[a]	288	146 (49)	264	158 (40)	280	162 (42)
Acid Red 18	TDS	842	838	846	840	842	836
	COD	296	162 (45)	242	118 (51)	234	138 (41)
Acid Orange 7	TDS	828	820	830	826	830	820
	COD	312	172 (44)	224	168 (25)	208	156 (25)
Acid Orange 10	TDS	838	832	852	846	840	832
	COD	248	142 (43)	186	138 (27)	196	124 (37)
Acid Red 73	TDS	862	856	866	858	870	862
	COD	276	152 (48)	246	154 (37)	258	162 (37)

[a] TDS and COD values are given in mg/l and the values within the parentheses indicate % reduction in COD.

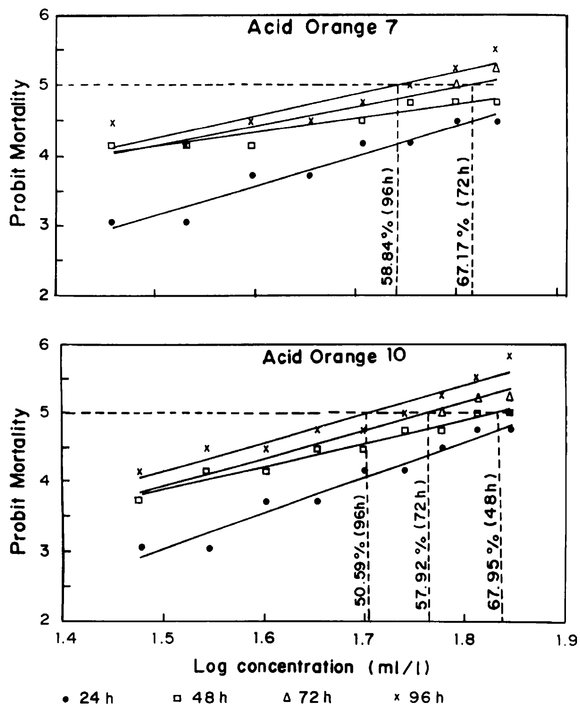

Fig. 2. Log probability plots of % mortality against concentration of ozone treated Acid Orange 7 and Acid Orange 10 dye effluents.

contribution made by the other agents. The LC_{50} values of all ozone treated effluents prepared from different dye effluents indicate that the toxic effect of the ozone treated effluent increases with increase in time. Hence, it is necessary to dilute the treated effluent to minimum 50% of fresh water before discharging to the water bodies. Further, it can be seen from the plots that the LC_{50} value for Acid Red 73 shows higher toxicity compared to the remaining dyes. This indicates that effluents of acid dyes with different azo group content behave differently i.e., the higher the azo group content, the higher the toxicity of the effluent.

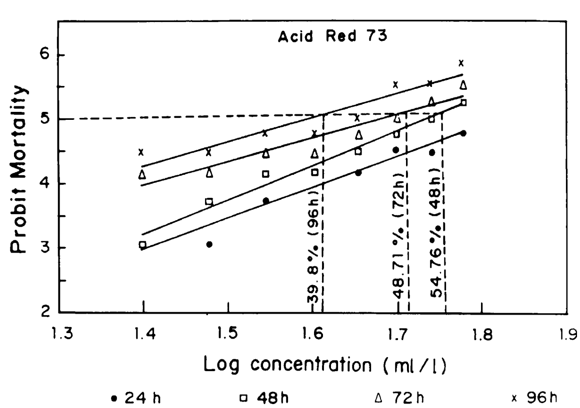

Fig. 3. Log probability plots of % mortality against concentration of ozone treated Acid Red 73 dye effluent.

3.3. Effect of recycling on quality of dyeing

3.3.1. 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 and it is to be rejected. If the ΔL^* values are less than −0.7, the samples are darker in shade and if they are greater than 0.4, the samples are lighter in shade compared to the control sample [19]. ΔE^* and ΔL^* values of the dyed samples produced in the present study are given in Table 2. It is observed from the table that with increase in the number of recycling processes, the ΔE^* value increases. This reveals that the formation of acidic by-products during ozonation may interfere with the affinity of the dye to the fabric [24], which is reflected in increasing colour difference values. The samples produced by the recycling process have a lighter shade than the samples obtained from the fresh water process. Negative ΔL^* values of Acid Red 18 and Acid Orange 7 indicate that the samples are darker in shade compared to the control sample. It can be inferred from Table 2 that for Acid Red 88 and Acid Red 73 dyes, usage of recycled effluents can be carried out twice but this is not the case with Acid Red 18 and Acid Orange 10, which

Table 2
Colour parameters of dyed samples

Names of the dyes	Parameters analysed	Dyed samples from fresh water	Dyed samples from 1st recycling	Dyed samples from 2nd recycling
Acid Red 88	L^*	38.06	38.98	38.68
	a^*	57.08	57.46	58.02
	b^*	22.69	22.08	23.36
	ΔL^*	–	0.92	0.62
	ΔE^*	–	1.16	1.30
Acid Red 18	L^*	53.89	53.13	53.47
	a^*	57.15	58.19	59.40
	b^*	20.41	20.55	21.49
	ΔL^*	–	−0.76	−0.42
	ΔE^*	–	1.29	2.53
Acid Orange 7	L^*	61.58	60.04	62.04
	a^*	48.35	48.69	49.29
	b^*	67.02	67.47	68.71
	ΔL^*	–	−1.54	0.46
	ΔE^*	–	1.64	1.98
Acid Orange 10	L^*	71.54	72.04	72.26
	a^*	29.32	30.54	30.42
	b^*	63.96	64.25	62.61
	ΔL^*	–	0.50	0.72
	ΔE^*	–	1.34	1.88
Acid Red 73	L^*	47.88	48.9	49.03
	a^*	61.92	62.08	61.96
	b^*	34.19	33.55	33.82
	ΔL^*	–	1.02	1.15
	ΔE^*	–	1.21	1.21

Table 3
Relationship between RUI values 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. [20].

can be used only once. Acid Orange 7 cannot be reused even once due to the increasing ΔE^* values. It indicates that the chosen dye is probably very sensitive to the acidic by-products produced during the ozonation of the effluent.

3.3.2. Effect on level dyeing character

The level-dyeing characteristics of dye liquors are explained with the help of RUI. The relationship between RUI and visual appearance of levelness is given in Table 3 [20]. The RUI values of dyed samples produced in the study are given in Table 4. It is clear from the results that all the dyed samples produced from first and second 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 does not have an effect on reducing the TDS content present in the acid dye effluents. But it reduces the COD of the control and recycling process effluents. All the ozone treated effluents are safer to aquatic life if they are diluted by 50% with fresh water. Diazo dyes are more toxic than monoazo dyes.

Table 4
RUI values of dyed samples

Names of the dyes used	RUI values		
	Dyed samples from fresh water	Dyed samples from 1st recycling	Dyed samples from 2nd recycling
Acid Red 88	0.11	0.31	0.14
Acid Red 18	0.12	0.12	0.22
Acid Orange 7	0.26	0.30	0.09
Acid Orange 10	0.24	0.13	0.13
Acid Red 73	0.11	0.14	0.31

Based on the colour reproduction ability, it has been found that effluents produced in Acid Red 88 and Acid Red 73 applications can be recycled twice whereas only once with respect to Acid Red 18 and Acid Orange 10. Effluents resulting from Acid Orange 7 are not suitable for recycling.

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 the control sample indicates that in these cases, the recycling can still be carried out to produce goods with alteration in tone, if accepted.

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