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Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent

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Abstract

The effectiveness of a combined reduction–biological treatment system for the decolorization of non-biodegradable textile dyeing wastewater was investigated. In this treatment system, a bisulfite-catalyzed sodium borohydride reduction followed by activated sludge technique was used in order to remove the color at ambient temperature and pressure. This experimental study consisted of two major parts: reduction treatment and biological oxidation. Both synthetic and actual wastewater was used in this research. Synthetic wastewater was made by several groups of dyes such as direct, basic and reactive colors. Actual wastewater was collected from two different textile industries in the city of Isfahan, Iran. The characterization of raw and treated wastewater was carried out by infrared and ultraviolet spectrometers. The results of this study demonstrated that the newly developed treatment technique decreased color, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS) by 74–88, 76–83 and 92–97%, respectively. The IR and UV analyses showed that non-biodegradable dyes are converted to biodegradable organic compounds such as alkyl and alkenes. Another major advantage of this method with respect to other methods, namely, adsorption and coagulation, was that it removes color without causing any disposal problem. The optimum dosage for treatment of actual wastewater was found to be 50–60 mg/l for catalyst bisulfite and 200–250 mg/l for sodium borohydride. Finally, a bench-scale experimental comparison of this technique with other reported combined chemical–biological methods showed higher efficiency and lower cost for the new technique.

Keywords: Textile effluent; Dye; Chemical reduction; Biodegradation; Color removal

1. Introduction

The efficient removal of dyes from textile industry effluents is still a major environmental challenge. Typically, textile wastewaters consist of a variety of waste streams from different operations. Some dyestuffs are highly structured polymers and are very difficult to decompose. Currently, various chemical, physical and biological treatment methods are used to remove color. Because of the high cost and disposal problems, many of these methods for treating dye wastewater have not been widely applied in the textile industries. A literature survey shows that research has been and continues to be conducted in the areas of chemical and combined chemical–biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production.

Previous studies have shown that many of the dyes are carcinogenic, mutagenic and detrimental to the environment. As toxicity standards become more common and stringent, the development of new techniques for minimizing the concentration of dyes and their breakdown products in the wastewater also becomes necessary. Protection of human health and the environment is now perceived as more important than the profitability and efficiency of a business. The wastewater discharged from a dyeing process in the textile industry exhibits low biochemical oxygen demand (BOD), high chemical oxygen demand (COD) and is highly colored. Hence, the need for chemical treatment is necessary in order to produce a more readily biodegradable compound. Chemical color removal technologies which are reported in the literature include adsorption by activated carbon, electrochemical treatment, ozonation, chemical precipitation, membrane filtration, hydrogen peroxide, Fenton's reagent and reverse osmosis [1–8]. The high cost and disposal problems have opened the door for further investigation of new techniques. Application of conventional biological processes in the treatment of textile wastewater has been extensively reported in the literature [9–13].

The results from a literature review support the conclusion that wastewaters containing water soluble dyes are generally not decolorized effectively by the aerobic biological treatment. Shaul et al. [14] conducted a literature review

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that indicated adsorption to the sludge is the primary removal mechanism for dyes in a biological wastewater treatment system and that factors inhibiting permeation of the dye through the microbial cell membrane reduce the effectiveness of biological degradation.

Many investigators [1,13,15] have examined a wide variety of materials like fly-ash, peat, sawdust, brown coal and bagasse pith for color removal. The inability of biological treatment processes in degrading dye compounds makes chemical treatment a necessary stage prior to biotreatment in order to produce more readily biodegradable materials. Pagga and Taeger [16] used the activated sludge as biomass in the adsorption of dyestuff. With different types of activated sludge treatment methods, the following removals are normally achieved: about 90% of BOD_5, 40–50% of COD and 10–30% of color [9,13,17].

The objective of this research was to evaluate the effectiveness of a new combined chemical reduction and biological oxidation treatment system for the decolorization of non-biodegradable textile dyeing wastewater.

2. Materials and methods

Both synthetic and actual wastewaters were used in this research. Synthetic wastewater was prepared by dissolving measured quantities of different types and groups of dyes in deionized water, such as direct red 23, disperse yellow 5, acid yellow 17, basic blue 41, and reactive orange 13 (Merk). Actual wastewaters were collected from two different textile companies in Isfahan, Iran.

The actual wastewaters were characterized before and after they were subjected to the combined chemical reduction and biological oxidation treatment system. The BOD, COD, total suspended solids (TSS), volatile suspended solids (VSS), oil and grease and pH were measured according to the American Public Health Association standard methods for the examination of water and wastewater [18], methods nos. 5210-B, 5220-D, 2540-D, 4500-H and 5220-B, respectively. ASTM-E450-82 approved method was used to measure color. Also the chemical characterization of raw and treated actual wastewaters were carried out by IR (infrared) and UV (ultraviolet) spectrometers. The instruments used for IR and UV analyses were Shimadzu 435 and 240.

Two separate 2.5 l continuous stirred tank reactors (CSTR) were utilized to carry out the chemical reduction and biological oxidation reactions. In the chemical reactor bisulfite ($Na_2S_2O_5$, Merk) and sodium borohydride ($NaBH_4$, Aldrich, catalog no. 19801-2) were used as the catalyst and reduction agent, respectively. All operating conditions for each of the reactors, such as pH, mixing, food/microorganisms, amount of catalyst and reducing agent, subsurface aeration and residence time, were monitored throughout the experiments.

For IR analysis, color materials were separated from wastewater through complete water evaporation. The potassium bromide (KBr, Fisher Scientific IR grade) was oven-dried to complete dryness and was then stored in a desiccator until use. The dye material–KBr mixture was prepared by weighing the KBr and color materials. Dry KBr powder (450 mg) and 50 mg dye material were weighed to obtain a total mixture of 500 mg. All amounts were adjusted to within 0.2 mg of the desired weight and weighed to a precision of 0.1 mg. The mixture was quantitatively transferred to a mortar and ground with a pestle for 20–30 min to obtain a homogenous mixture. The 500 mg amount color material–KBr mixture was placed between two highly polished, stainless steel dies inside a pellet press, where it was compressed at 25,000 psi for 1 min to make a small pellet approximately 0.5 in. in diameter. Prepared pellets were stored in a desiccator to prevent the KBr from absorbing moisture. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons. Analyses were made for both the blank and the sample pellets. Prior to analyses, the instrument sample compartments were purged with nitrogen for at least 20 min. In order to obtain UV spectra, first color materials were dissolved in water and then the prepared solution was analyzed by a Shimadzu-240 model analyzer.

3. Results and discussions

The results obtained from this research are classified into two parts: synthetic and actual wastewater.

3.1. Synthetic wastewater

The main objective of the series of experiments carried out with synthetic wastewater samples was to understand the nature of the chemical reactions leading to color reduction. Therefore, 17 wastewater samples were synthetically prepared with 20 ppm concentrations. The dyes were selected from five main different color categories, namely, basic, direct, disperse, acid and reactive. Tables 1 and 2 show the results of these color reduction experiments. In Table 1 $NaBH_4$ was very effective in removing 81–99% of the color for seven different dyes. The optimum dose of $NaBH_4$ required was quantitatively determined utilizing the jar test technique. In the case of the 10 remaining dyes for which $NaBH_4$ was ineffective, selection and addition of bisulfite sodium ($Na_2S_2O_5$) as an appropriate catalyst to the reducing agent was necessary. The important operating parameters optimized were pH, $NaBH_4$ concentration, $Na_2S_2O_5$ dosage and contact time. The reaction was carried out at the ambient temperature and pressure. A comparison of the two tables reveals an important finding in regard to the required $NaBH_4$ dosage. For instance, for reactive red 120 dye, the addition of only 0.15 g/l of $Na_2S_2O_5$ decreased the amount of $NaBH_4$ by 99% due to the direct effect of catalyst on the reaction activation energy.

There are two main advantages in using the newly developed technique: (1) The fact that using $Na_2S_2O_5$ is very cost

Table 1
Different synthetic wastewater samples amenable to $NaBH_4$ reduction reaction

Dye	Dye concentration (mg/l)	Chemical group	Required $NaBH_4$ (g/l)	ΔE (% color reduction)
Acid blue 9	20	Triphenylmethane	1.05	98.8
Reactive red 120	20	Azo	2	81.4
Reactive orange 13	20	Mono-azo	1.01	91.4
Reactive black 5	20	Di-azo	2.5	83.7
Reactive yellow 28	20	Metin	0.08	98.6
Basic green 4	20	Triarylmethane	0.01	98.7
Basic blue 41	20	Mono-azo	2	99.2

Table 2
Effect of catalyst ($Na_2S_2O_5$) on the operating conditions of the color reduction

Dye	Dye concentration (mg/l)	Type	Optimum pH	$NaBH_4$ concentration (g/l)	$Na_2S_2O_5$ concentration (g/l)	Contact time (min)	Final pH	ΔE (% color reduction, $NaBH_4 + Na_2S_2O_5$)
Direct yellow 12	20	Di-azo	8.5	0.03	0.12	10	6.5–7.5	96.2
Direct black 122	20	Azo	8.5	0.1	0.8	60	4.5–5.5	76.9
Direct red 23	20	Di-azo	8.5	0.1	0.8	40	4.5–5.5	88.8
Direct blue 168	20	Di-azo	8.5	0.1	0.8	45	4.5–5.5	95
Direct blue 15	20	Di-azo	8.5	0.05	0.4	45	5–5.5	85.3
Direct orange 26	20	Di-azo	8.5	0.05	0.4	50	5–6	94
Disperse yellow 5	20	Azo	8.5	0.05	0.2	20	6.5–7	82
Acid yellow 17	20	Mono-azo	8.5	0.05	0.2	10	6–7	98.5
Acid blue 9	20	Mono-azo	8.5	0.03	0.12	15	6–7	98.8
Basic blue 41	20	Mono-azo	8.5	0.1	0.4	45	6–7	99.2
Basic yellow 28	20	Metin	8.5	0.04	0.2	15	6–7	98.7
Basic green 4	20	Triarylmethane	8.5	0.05	0.035	10	7.5–8.5	98.7
Basic blue 9	20	Tri-azin	8.5	0.04	0.04	10	7.5	–
Reactive orange 13	20	Mono-azo	8.5	0.03	0.12	10	6.5–7.5	91.5
Reactive black 5	20	Di-azo	8.5	0.02	0.15	20	5–5.5	83.7
Reactive red 120	20	Azo	8.5	0.02	0.15	15	5–6	81.4
Reactive brown 33	20	Azo	8.5	0.05	0.4	15	4.5–5.5	94

effective ($NaBH_4/Na_2S_2O_5$ cost ratio = 7) with respect to $NaBH_4$, and thus the addition of the catalyst minimizes the operating cost significantly. (2) The color reduction capability of the technique comprising the addition of a catalyst to the reducing agent can cover a broad range of dyes compared to the reducing agent technique alone.

Moreover, in order to investigate the environmental engineering parameters such as BOD and COD as well as color reduction, a new series of experiments were conducted with synthetic wastewaters made out with selected dye from each main color category. Tables 3 and 4 show the results of these studies. The important parameters studied were BOD, COD, COD/BOD and color reduction.

The most important findings related to the significant decrease in color and the COD/BOD after the chemical reduction reaction, which also indicated the theoretical feasibility of the application of biological oxidation for further treatment. Consequently, the combined chemical–biological treatment system was applied to the actual wastewaters.

In order to investigate the applicability of the experimental findings obtained in the previous section, actual wastewater was subjected to the newly combined method in a series

Table 3
Characteristics of treated synthetic dyeing wastewater (200 mg/l)

Dye	Type	$NaBH_4$ (g/l)	$Na_2S_2O_5$ (g/l)	Reaction time (min)	ΔE (initial color)	ΔE (final color)	ΔE (% color reduction)	Concentration (mg/l)
Direct red 23	Di-azo	0.2	0.8	35	135.71	20.46	84.92	200
Disperse yellow 5	Azo	0.15	0.6	30	50.21	7.88	84.31	200
Acid yellow 17	Mono-azo	0.06	0.25	15	92.36	1.75	98.01	200
Basic blue 41	Mono-azo	0.15	0.6	15	127.15	2.86	97.75	200
Reactive orange 13	Mono-azo	0.03	0.12	10	131.4	7.53	94.27	200
Mixture of direct red 23, acid yellow 17 and reactive orange 13	Mono-azo	0.1	0.4	30	136.29	15.9	88.33	210

Table 4
BOD and COD of synthetic dyeing wastewater before and after reduction process

Dye	Type	Concentration (mg/l)	Before reduction			After reduction		
			COD (mg/l)	BOD (mg/l)	COD/BOD	COD (mg/l)	BOD (mg/l)	COD/BOD
Direct red 23	Di-azo	200	149	11.2	13.3	185	84.3	2.2
Disperse yellow 5	Azo	200	288	27.9	10.3	310	96.5	3.2
Acid yellow 17	Mono-azo	200	124	8.2	15.1	125	37.5	3.3
Basic blue 41	Mono-azo	200	146	20	7.3	67.2	23.4	2.9
Reactive orange 13	Mono-azo	200	110	6.2	17.8	98.6	25.7	3.8
Mixture of direct red 23, acid yellow 17 and reactive orange 13	Mono-azo	210	133	10	13.1	154	64	2.4

Table 5
Experimental results before and after chemical reduction reaction

Actual effluent samples	$NaBH_4$ concentration (g/l)	$Na_2S_2O_5$ concentration (g/l)	Optimum pH	Final pH	Before chemical treatment				After chemical treatment				ΔE (% color reduction)
					BOD (mg/l)	COD (mg/l)	COD/BOD	ΔE (color)	BOD (mg/l)	COD (mg/l)	COD/BOD	ΔE (color)	% COD reduction	
1	0.06	0.25	4	4–5	163	770	4.7	27.1	214	619	2.5	6.54	11.81	72.5
2	0.05	0.2	4	4–5	157	616	3.9	25.2	227	565	2.5	3.64	8.08	85.5

Table 6
Experimental results of biological and combined chemical–biological treatment system

Sample number	Biological treatment (after reduction)				Combined chemical–biological treatment			
	% COD removal	% BOD removal	% TSS removal	% Color removal	% COD removal	% BOD removal	% TSS removal	% Color removal
1	73.3	98.2	–	6.5	76.5	96.9	92	74.3
2	72	97.8	–	9.5	74.3	96.8	97	86.9

of experiments. The chemical reduction reaction followed by biological oxidation was carried out in the two CSTRs connected in series. The results are shown in Tables 5 and 6. The expected results derived from synthetic wastewater experiments were verified for actual wastewaters.

The combined treatment system decreased color, BOD, COD and TSS by 74–88, 97–100, 76–83 and 92–97%, respectively. The experimental results of this study are reported within a 5% error. As shown in Table 6, BOD increased by 41 and 31% after chemical reaction for samples 1 and 2, respectively. Further analyses were necessary to understand and explain the modification in the chemical structure of the color-causing materials. Therefore, the actual wastewaters were characterized before and after treatment using IR and UV spectrometers.

3.2. Chemical characterization

Infrared spectroscopic analyses of the original and two treated actual wastewaters are shown in Figs. 1–3. The infrared absorption bands of the three samples and their intensities were compared, and possible assignments for the absorption bands are also listed in Tables 7 and 8. The IR analyses showed that non-biodegradable dyes are converted

Table 7
IR absorption intensities of original and treated actual wastewaters

Band numbers	Absorption wavelength (cm^{-1})	Peak intensity		
		Original actual wastewater	After chemical reaction	After combined chemical–biological treatment
1	3450–3600	Medium	Medium	Medium
2	3100–3400	Medium	Medium	Medium
3	1380–1470	Medium	Weak	–
4	1030–1230	Strong	Strong	Strong
5	920–1000	–	Medium	–
6	570–650	Medium	Strong	Medium

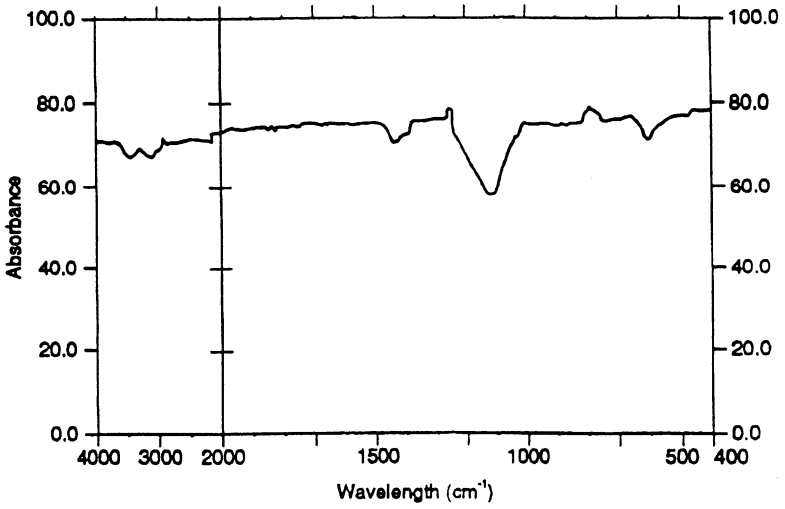

Fig. 1. IR spectrum of actual wastewater sample before treatment.

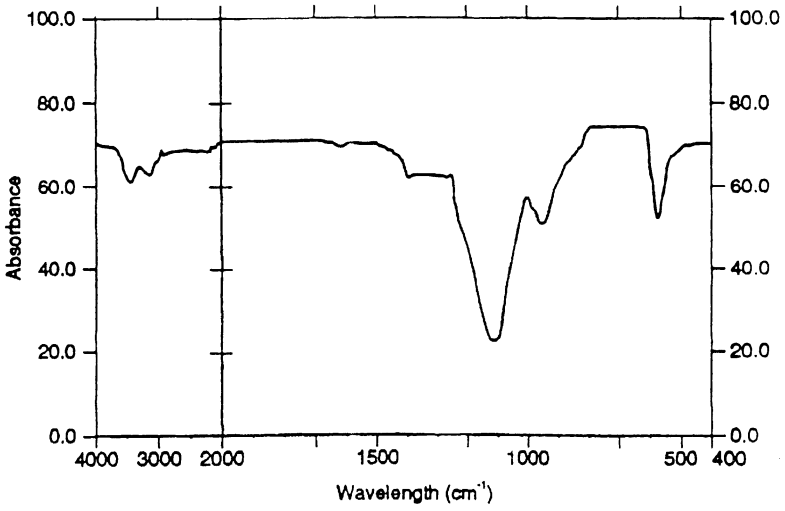

Fig. 2. IR spectrum of actual wastewater sample after chemical treatment.

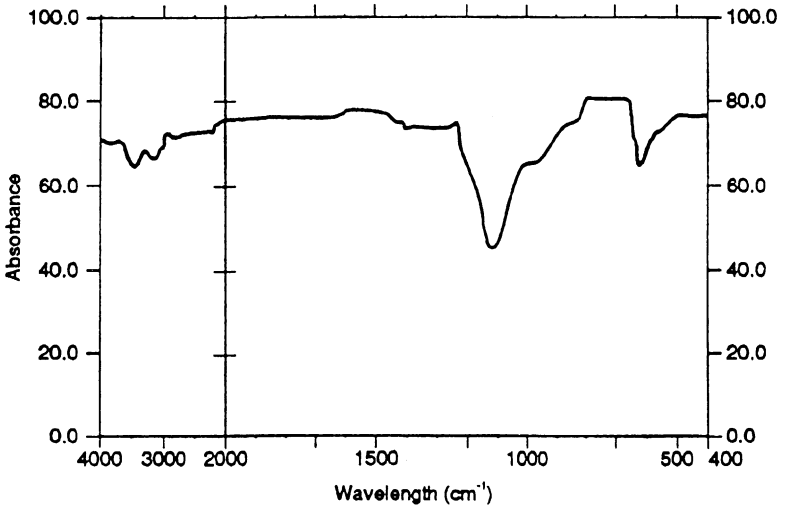

Fig. 3. IR spectrum of actual wastewater sample after combined chemical reduction and biological oxidation treatment.

Table 8
IR absorption assignments of original and treated actual wastewaters

Band numbers	Absorption wavelength (cm^{-1})	Possible assignments	Functional group
1	3450–3600	Phenol	Ar–OH
2	3100–3400	Amine	=NH
3	1380–1470	Alkyl (C–H stretching)	Weak
4	1030–1230	Ester and lactones (C–O stretching)	CH–COOR
5	920–1000	Alkenes	$R_2C{=}CH_2$
6	570–650	Alkenyl	*Cis*-RCH=CHR

Table 9
The possible assignments of UV signals of original and two treated actual wastewaters

UV signal number	Wavelength (cm^{-1})	Peak intensity			Possible assignment	Functional group
		Original actual wastewater	After chemical reaction	After combined chemical–biological treatment		
1	245	Strong	Medium	Weak	Monosubstituted aromatic ring	Ar–R
2	280	Strong	Medium	Weak	Monosubstituted aromatic ring	Ar–R
3	325	Strong	Medium	Weak	Disubstituted aromatic ring (*ortho* isomer)	R–Ar–R′, MeO–Ar–CHO

Table 10
Comparison of reduction–biological technique with other conventional methods

Treatment technique	Sample 1			Sample 2		
	% COD removal	Sludge disposal problem	Color removal	% COD removal	Sludge disposal problem	Color removal
Reduction–biological technique	76.5	Slight	High	82.2	Slight	High
Coagulation with alum	49.5	Severe	Low–medium	61.1	Severe	Low–medium
Activated carbon	53.2	Severe	Medium–high	48.2	Severe	Medium–high
Biological method	47.8	Medium	Low	56.9	Medium	Low

during the course of chemical reaction to biodegradable organic compounds such as alkyl and alkenes, which verifies the experimental data on BOD. Consequently, the biodegradable material formed in the first reactor was oxidized completely by the aerobic bacteria in the second reactor.

The same chemical characterization was conducted using spectra. The possible assignments of UV signals of original and two treated actual wastewaters are shown in Table 9. Comparison of the UV signals shows significant absorbance reduction in the treated sample by the chemical and the combined techniques. These results may have contributed to the elimination of unsaturated organic compounds such as aromatic rings, ketone, benzylic and phenolic substances. Thus, UV spectral data confirm the observed experimental results on BOD, COD and color reduction.

4. Economics

The operating cost due to disposal problems and efficiency of the developed technique was compared with other conventional treatment methods as shown in Table 10. Not only does the new technique have higher color and COD removal capability, it also does not create any sludge disposal problems in contrast to the coagulation with alum and activated carbon techniques.

5. Conclusions

The results of this study indicate that a combined reduction–biological treatment method is a viable technique to effectively decrease the color, BOD, COD and TSS by 74–88%, 97–100, 76–83 and 92–97%, respectively. The major difference between this newly developed technique with other conventional methods is the key step of converting non-biodegradable dyes into biodegradable materials via reduction reaction with sodium borohydride as the reducing agent and bisulfite as the catalyst. The main economic advantage of this system is the lack of a serious sludge disposal problem and consequently much less operating cost.

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