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RECYCLING OF ELECTROCHEMICALLY TREATED DISPERSE DYE EFFLUENT

BY A.E. WILCOCK AND S.P. HAY
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ABSTRACT

Electrochemical treatment of wastewater using sacrificial iron electrodes has been demonstrated to be effective in the removal of heavy metals and organic compounds. This technique has also been reported to be effective in the removal of acid dyes and stain blocking chemicals from carpet dye effluent. Our studies show that electrochemically treated disperse dye effluents have markedly reduced toxicity (as determined by the Daphnia magna test), suggesting that residual dyebath additives have been removed. In addition, the treated effluent can be recycled in subsequent dyeing operations to produce level dyeings with reasonable colour reproducibility.

INTRODUCTION

The economic significance of the more than 800 million litres of aqueous waste from Canadian mills each day stems from the loss of potentially reusable chemicals and the need to neutralize such wastes to protect the environment. Although dyes and pigments form a relatively small percentage of the total chemical effluent, their high cost (approximately 190 million dollars worth were used in Canada in 1989) makes the importance of their reclamation paramount (5). From the standpoint of environmental contamination, waste dyes present not only the usual problem of potentially toxic or carcinogenic chemicals entering sewage treatment facilities not specifically designed for them; merely by virtue of their colour, dyes represent an aesthetic pollutant as a problem separate from their chemical toxicity 24, 32).

Effluent from industrial dyebaths contains the dyestuffs themselves as well as the various chemical assistants. A wide variety of dyes, representing several different chemical groups, are toxic, carcinogenic, mutagenic, or teratogenic (2, 4, 6, 7, 10, 12-15, 17-21, 26, 30, 33) in various microbiologic, fish, or mammalian test systems. Each day a mixture of harmless dyes and chemicals enters the environment, separated from our lakes and streams only by whatever sewage treatment facilities are available locally. In a limited number of published studies of pure dyestuffs entering actual or simulated sewage treatment facilities (11, 22, 23) only a few dyes were shown to either damage the microbial ecology of the treatment system or escape complete detoxification. Despite this reassuring data, the recognition that the daily dyebath effluent contains a much more complex and variable mixture of dyes, dispersants, wetting and levelling agents, and trace metals (1, 9, 28, 29, 31) makes it clear that every effort should be made to minimize the volume of each effluent leaving the plant. That the threat is more than imaginary is evidenced by the strict regulations in some U.S. states requiring that textile plant effluent be pretreated prior to discharge, at great expense to the industries affected (8, 29).

In addition to these environmental concerns, the re-use of dyebath effluent seems to make good economic sense. In theory, most dyeing procedures result in an effluent that is only quantitatively different from the original formulation. All that must be done is determine the amount of dyestuff and chemical assistant required to restore dyebath effluent to full formula strength, or reformulate it to another specified dyebath recipe. When exhaustion of only the dyestuff is of concern, experienced dyers may have learned to add more or less the right amount of dye to the effluent to restore it to acceptable potency. Unfortunately, the results are often unacceptable in situations requiring rigid colour matching.

Alternatives include mathematical estimation or photometric measurement of dyebath exhaustion — both too slow to be of use in actual production — or careful scheduling of batch dyeings so the light fabric colours always precede darker colours. In this last method, the ideal is that the partially exhausted effluent from the lighter baths is so slightly coloured in comparison to the darker dyebath liquor for which it is destined that it may be considered as almost colourless in the formulation of the new dyebath. Unfortunately, the key word here is "almost", and resultant colour mismatches still present a quality control headache.

Similar manipulations may be used to partially overcome the variability in the exhaustion of other dyebath chemicals. A common and important example is the attempt to control the amount of carrier chemical in effluents from disperse dyebaths by increasing the bath temperature in order to almost completely exhaust the carrier (29). Too much carrier in reformulated dyebath liquors results in non-uniform dyeing. Too little results in too little adherence of the dye to the fabric (virtually always polyester).

If these hit-and-miss approximations are a headache in batch or piece dyeing operations, they are complete disasters in continuous dyeing operations in which the reclaimed effluent from even a single station along the production line may contain several different chemicals. The chance of the "eyeball"

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Alternatives include mathematical estimation or photometric measurement of dyebath exhaustion — both too slow to be of use in actual production — or careful scheduling of batch dyeings so the light fabric colours always precede darker colours. In this last method, the ideal is that the partially exhausted effluent from the lighter baths is so slightly coloured in comparison to the darker dyebath liquor for which it is destined that it may be considered as almost colourless in the formulation of the new dyebath. Unfortunately, the key word here is "almost", and resultant colour mismatches still present a quality control headache.

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If these hit-and-miss approximations are a headache in batch or piece dyeing operations, they are complete disasters in continuous dyeing operations in which the reclaimed effluent from even a single station along the production line may contain several different chemicals. The chance of the "eyeball"

approach to restitution of such effluents being successful is remote. In those instances in which recycling of these effluents is essential, membrane filtration (3) may result in a chemically defined end product that may then be reformulated to a standard dyebath recipe. This procedure is extremely expensive and cannot be justified on economic grounds alone.

Despite the obvious savings in water and dyebath chemicals that a recycling program would create (3, 25, 29, 31), the actual initiation of these programs has been limited. Manufacturers have been reluctant to invest in the equipment and personnel retraining when the results may not be instantly rewarding. The colour computer system deals only with the dyes themselves, not with the variables in the exhaustion or build-up of other chemicals during the dyeing procedure. In simple batch or piece dyeing, one assumes that the few other dyebath constituents consumed are inactivated to the same extent as the dyestuff. In the more complex continuous dyeing procedure, only trial-and-error will eventually correct the error caused by those few critical chemicals that are not consumed in direct proportion to dyestuff exhaustion.

A recently developed method used for the separation of organic compounds and heavy metals in the electroplating, metal polishing, and circuit board manufacturing industries is an electrochemical system composed of sacrificial iron electrodes (16). Wastewater is circulated between the electrodes, allowing electrical current to flow between them and slowly dissolve the anode. The reaction releases ferrous ions which are converted into ferrous hydroxide upon contact with the water. The ferrous hydroxide is then precipitated from the solution along with organic and/or heavy metal contaminants which were adsorbed to its surface. The precipitate is subsequently removed by flocculation and solid/liquid separation.

When applied to textile dyeing, the electrochemically treated effluent should be able to be recycled as though it were water because the treatment removes any residual organic dyeing assistants. If recycling is not a consideration, electrochemical treatment may still be of interest because of its potential to reduce the environmental toxicity of the effluent (again, because of removal of the organic content). Ideally, the dyestuffs will be separable from the residue so that they may be reused in subsequent dyeing processes.

It is the purpose of this project to: (a) demonstrate the environmental safety of the supernatant "water" following electrochemical separation; (b) test the efficiency of an electrochemical treatment system for dyebath effluent using a laboratory simulation of commercial disperse dyeing of polyester fabric, and (c) extend the laboratory model to actual industrial application. This paper is a report on the first phases of the research — the effects of the treatment on the toxicity of the effluent and on the ability to recycle used disperse dyebaths.

MATERIALS AND METHODS

Dyes and Carriers

The sales managers of five large dye suppliers were contacted for data on the most commonly used disperse dyes in Ontario. The two most popular reds, blues, and yellows were screened for their environmental toxicity and the more toxic of each colour was used. Those three dyes were C.I. Disperse Blue 56, C.I. Disperse Red 177, and C.I. Disperse Yellow 34. Each of these dyes was used in combination with each of three carriers which are commonly used in Canada (Table 1).

TABLE 1: Characterization of dyes and carriers.

Product	C.I. Number (if applicable)	Chemical Type
C.I. Disperse Blue 56	63285	anthraquinone
C.I. Disperse Red 177	60756	anthraquinone
C.I. Disperse Yellow 34	not available	not available
Carrier A	not applicable	methyl naphthalene
Carrier B	not applicable	biphenyl/ chlorotoluene
Carrier C	not applicable	isopropyl alcohol

Fabric

One hundred percent Dacron polyester (Testfabrics style #777) was used as the substrate to which the dyes were applied. Each specimen weighed 10 ± 0.2 grams. Four specimens were used in all cases to improve the accuracy of the results.

Electrochemical Treatment

The system used in this study was a laboratory-scale electrochemical cell obtained from Andco Environmental Processes, Amherst, New York. Wastewater was circulated around iron electrodes to which an electric current was applied. Iron was released from the anode, with the following reaction occurring:

Anode (oxidation):

$$\mathrm{Fe} \longrightarrow \mathrm{Fe}^{++} + 2e^-$$

Cathode (reduction):

$$2\mathrm{H_2O} + 2e^- \longrightarrow \mathrm{H_2} + 2\mathrm{OH}^-$$

Overall Reaction

$$\mathrm{Fe} + 2\mathrm{H_2O} + \text{Electrical Energy} \longrightarrow \mathrm{Fe(OH)_2} + \mathrm{H_2}$$

The freshly produced iron hydroxide facilitated adsorption of the dye from the effluent.

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Cathode (reduction):

$$2H_2O + 2e- \text{ ----> } H_2 + 2OH-$$

Overall Reaction

$$Fe + 2H_2O + \text{Electrical Energy} \text{ ----> } Fe(OH)_2 + H_2$$

The freshly produced iron hydroxide facilitated adsorption of the dye from the effluent.

The cell was operated at 0.4 amperes for eight minutes in order to release sufficient iron (approximately 280 mg/l) to optimize removal of the residual dyestuff from the effluent. After passage through the cell, the pH was raised to 8.5 using sodium hydroxide and a small amount of polyacrylamide polymer added to stimulate flocculation and precipitation of the iron hydroxide and adsorbed dyestuff. The treated dyebath was then filtered (Whatman #2) twice with suction. Representative samples of the treated effluent were analyzed for iron content using atomic absorption spectrophotometry. The colour of the treated samples was not measured because of the inability to determine whether residual colour (if present) was due to the presence of disperse dyestuff or iron.

Dyeing and Colour Measurement

The dyebath formulation was as follows:

Disperse dyestuff	1%
Carrier	6% owf
Liquor-goods ratio	20:1
pH	5

In accordance with the manufacturer's recommendations (and in contrast to the dyebath concentration of Carrier A and B), Carrier C was used at a concentration of 12% owf. Deionized water was used for the purpose of laboratory control.

The fabric swatches were wet out with deionized water containing a few drops of Triton X-100 (Rohm & Haas, Philadelphia, PA). Dyeing was done in a rotary laboratory dyeing machine (Atlas Launder-Ometer), beginning at a temperature of approximately 22°C. The temperature was raised to 50°C over 30 minutes. The appropriate amount of carrier was then added. The temperature was raised to the boil where it remained for 1 hour. The samples were removed from the dyebath, rinsed in hot (75°C) deionized water, and then dried at room temperature. The used dyebath and rinse water were combined and 1 litre was passed through the electrochemical cell and filtered.

The filtered effluent was used to formulate a new dyebath within 96 hours following filtration. This reconstituted dyebath had the same formulation as the initial dyebath except that the recycled effluent was used instead of deionized water. The pH was lowered to equal that of the initial dyebath (4.5-5.0) using acetic acid, and the dyeing was performed as before.

Each dye solution was applied to fabric and the effluent electrochemically treated in ten consecutive dye-treatment cycles. The colour of the samples (composed of four replicate specimens) which had been dyed using the recycled liquor was compared to that of the initial sample (of four replicate specimens) dyed with fresh dye liquor, using the formula $\blacktriangle E = (\blacktriangle L^2 + \blacktriangle a^2 + \blacktriangle b^2)^{\frac{1}{2}}$. Five colour measurements were obtained on each specimen using a ColorQUEST spectrocolorimeter.

Toxicity Tests

The toxicity of the samples to **Daphnia magna** was assessed following the protocol of the Ontario Ministry of the Environment (27) for an LC_{50} for 48 hours. The test consists of placing three **Daphnia magna** organisms of less than 24 hours of age in 50 ml of test liquor in each of four glass test tubes. The temperature is maintained at 18-20°C and the tubes are not aerated, nor the organisms fed, for the 48 hour duration of the test. Mortality is recorded at 0, 1, 2, 4, 24, and 48 hours. Each test is conducted on a series of five concentrations (and a water control), with the concentrations being selected on the basis of prescreening bioassays.

The effluent from the initial dyeing of each of the nine dye-carrier combinations (3 dyes x 3 carriers) was tested immediately prior to, and following, electrochemical treatment.

RESULTS AND DISCUSSION

The iron contents of selected samples of the electrochemically treated disperse dye effluent are presented in Table 2. The data show that, in the majority of the cases, the electrochemical treatment removed all but trace amounts of the iron added to the effluent by the electrodes. It was considered essential that the iron be eliminated prior to re-use of the effluent because of the possibility that it would cause a shade change in subsequently dyed specimens.

The specimens dyed sequentially with each of the dye-carrier combinations were level with no dyespots, and would be considered commercially acceptable. The difference in colour between recycled and initial dyeings was virtually always somewhat greater than that among replicate specimens.

The colour of each of the samples dyed using recycled effluent was compared to the corresponding sample dyed using fresh effluent. The colour differences for each dye-carrier combination fluctuated throughout the nine times the effluent was recycled, but did not show a steady increase with the number of times it was reused (Table 3). This is consistent with the belief that no contaminants are accumulating in the effluent over time.

In general, there were smaller colour differences among the samples dyed with either C.I. Disperse Blue 56 or C.I. Disperse Red 177 than with C.I. Disperse Yellow 34 (Table 3, Figures 1-3). It appears that even trace amounts of iron in the dyebath can cause the large colour differences with C.I. Disperse Yellow 34. Interestingly, however, these dyed samples were neither unlevel nor did they contain dyespots as might be expected to occur in the presence of iron.

The carrier appeared to have an effect on how accurately the colour could be reproduced in samples dyed using the recycled effluent. Typically, the samples dyed with the assistance of Carrier C showed optimal colour reproducibility. When compared to the sample dyed using fresh liquor, only one of the samples dyed sequentially with C.I. Disperse Blue 56 had a colour difference greater than one. The same trend was apparent when Carrier C was used in baths with either C.I. Disperse Red 177 or C.I. Disperse Yellow 34 (Figures 1-3).

TABLE 2: Iron content of representative samples of dye effluent after electrochemical treatment. *

Sample Description (Dye/Carrier**)	Number of Re-uses	Iron Content (mg/l)
C.I. Disperse Blue 56/Carrier A	2	0.33***
C.I. Disperse Blue 56/Carrier A	4	<0.01
C.I. Disperse Blue 56/Carrier A	6	<0.01
C.I. Disperse Blue 56/Carrier B	2	<0.01
C.I. Disperse Blue 56/Carrier B	4	0.03***
C.I. Disperse Blue 56/Carrier B	6	<0.01
C.I. Disperse Blue 56/Carrier B	8	<0.01
C.I. Disperse Blue 56/Carrier C	2	<0.01
C.I. Disperse Blue 56/Carrier C	4	<0.01
C.I. Disperse Blue 56/Carrier C	6	<0.01
C.I. Disperse Blue 56/Carrier C	8	<0.01
C.I. Disperse Red 177/Carrier C	2	<0.01
C.I. Disperse Red 177/Carrier C	4	<0.01

***As determined by atomic absorption spectrophotometry.**

****Carrier A = methyl naphthalene; Carrier B = biphenyl/chlorotoluene; Carrier C = isopropyl alcohol.**

*****Cause of high iron content is unknown. Note relationship between high iron content and large colour difference in dyeing (Figure 1).**

The cell was operated at 0.4 amperes for eight minutes in order to release sufficient iron (approximately 280 mg/l) to optimize removal of the residual dyestuff from the effluent. After passage through the cell, the pH was raised to 8.5 using sodium hydroxide and a small amount of polyacrylamide polymer added to stimulate flocculation and precipitation of the iron hydroxide and adsorbed dyestuff. The treated dyebath was then filtered (Whatman #2) twice with suction. Representative samples of the treated effluent were analyzed for iron content using atomic absorption spectrophotometry. The colour of the treated samples was not measured because of the inability to determine whether residual colour (if present) was due to the presence of disperse dyestuff or iron.

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The colour of each of the samples dyed using recycled effluent was compared to the corresponding sample dyed using fresh effluent. The colour differences for each dye-carrier combination fluctuated throughout the nine times the effluent was recycled, but did not show a steady increase with the number of times it was reused (Table 3). This is consistent with the belief that no contaminants are accumulating in the effluent over time.

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TABLE 3: Comparison of the variation among replicate dyeings to variation between recycled and initial dyeings.

Sample Description (Dye/Carrier*)	Number of Reuses	DE Between Replicates**	DE Compared to Initial Dyeing
C.I. Disperse Blue 56/ Carrier A	0	1.00	—
	2	0.70	0.49
	4	0.29	1.71
	6	1.40	0.61
	8	0.14	0.90
C.I. Disperse Blue 56/ Carrier B	0	1.00	—
	2	0.45	1.78
	4	0.53	2.21
	6	0.12	1.08
	8	0.60	1.15
C.I. Disperse Blue 56/ Carrier C	0	0.25	—
	2	0.27	0.93
	4	0.25	0.64
	6	0.17	0.72
	8	1.77	1.29
C.I. Disperse Red 177/ Carrier A	0	0.88	—
	2	0.26	0.47
	4	0.72	2.09
	6	0.63	1.46
	8	0.59	3.57
C.I. Disperse Red 177/ Carrier B	0	0.22	—
	2	0.61	0.97
	4	0.11	1.59
	6	0.41	1.68
	8	0.58	2.14
C.I. Disperse Red 177/ Carrier C	0	0.50	—
	2	0.44	1.04
	4	0.86	2.29
	6	0.52	0.53
	8	0.90	2.44
C.I. Disperse Yellow 34/ Carrier A	0	1.09	—
	2	2.36	3.37
	4	0.95	3.60
	6	0.08	3.94
	8	1.55	2.01
C.I. Disperse Yellow 34/ Carrier B	0	1.52	—
	2	2.84	6.56
	4	0.58	4.16
	6	1.05	3.85
	8	0.27	0.50
C.I. Disperse Yellow 34/ Carrier C	0	2.23	—
	2	2.83	2.14
	4	1.77	1.70
	6	0.53	2.45
	8	2.77	5.03

*Carrier A = methyl naphthalene; Carrier B = biphenyl/chlorotoluene; Carrier C = isopropyl alcohol.

**Colour difference among replicates was calculated by comparing colour differences of pairs of specimens.

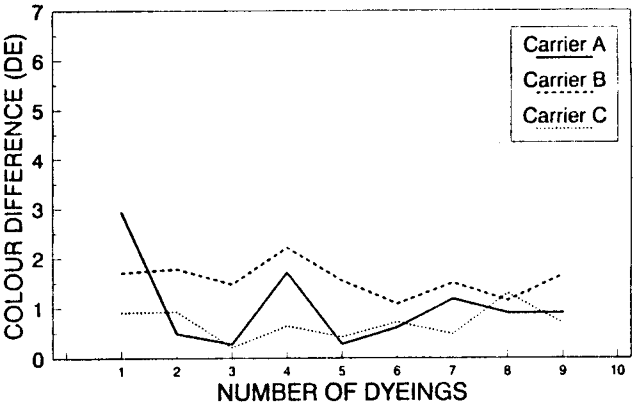

FIGURE 1: Colour differences following repeated dyeings — C.I. Disperse Blue 56.

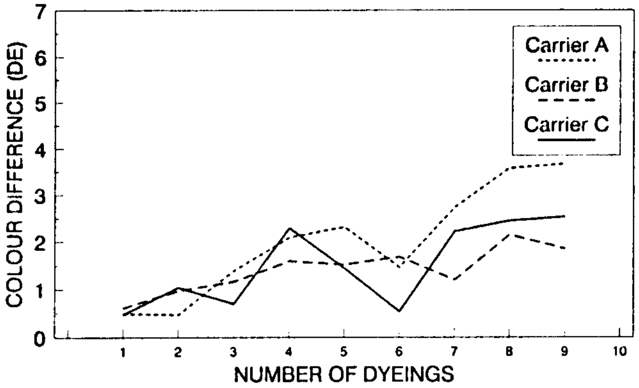

FIGURE 2: Colour differences following repeated dyeings — C.I. Disperse Red 177.

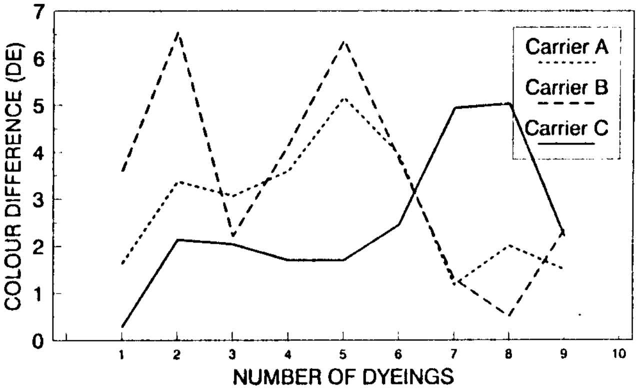

FIGURE 3: Colour differences following repeated dyeings — C.I. Disperse Yellow 34.

The acute toxicities of the three dyes, when used in combination with the three carriers, were determined following the initial dyeing, both before and after a single electrochemical treatment. The data show that the samples were consistently less toxic after electrochemical treatment than they were prior to it (Table 4). Following the treatment, there was an average increase in LC_{50} values of 158.4%.

The effectiveness of the treatment varies with the dyestuff (Table 4). Increases in LC_{50} values after treatment ranged from

27.3% (C.I. Disperse Red 177) to 431% (C.I. Disperse Yellow 34) when used in combination with the same carrier. Unfortunately, it was not possible to separate the individual contributions by dye or by carrier to the overall toxicity since the tests were conducted on the formulated dyebath after use.

SUMMARY

The electrochemical treatment used in this study was highly effective in removing colour from the disperse dye effluents tested. Toxicity of the effluent was reduced substantially by the treatment. Re-use of the treated effluent resulted in first quality dyeings, although there were colour differences in specimens dyed using the fresh and recycled liquor. We believe that recycling of electrochemically purified, filtered disperse dyebath effluent can give commercially acceptable results provided that the dyes and carriers are properly selected.

ACKNOWLEDGEMENTS

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TABLE 4: Acute toxicity to ***Daphnia Magna*** *of first-use dyes before and after a single electrochemical treatment.*

Dyestuff	Carrier*	LC_{50}** Before Treatment	After Treatment	% Decrease in Toxicity
C.I. Disperse Blue 56	A	52.6	70.7	34.1
C.I. Disperse Red 177	A	19.9	35.4	77.9
C.I. Disperse Yellow 34	A	18.0	55.4	207.8
				$\bar{x}$ = 106.7
C.I. Disperse Blue 56	B	35.4	70.7	99.7
C.I. Disperse Red 177	B	27.8	35.4	27.3
C.I. Disperse Yellow 34	B	12.0	63.7	430.8
				$\bar{x}$ = 185.9
C.I. Disperse Blue 56	C	13.7	21.8	59.1
C.I. Disperse Red 177	C	10.3	31.8	208.7
C.I. Disperse Yellow 34	C	16.2	61.4	279.0
				$\bar{x}$ = 182.3

*Carrier A = methyl naphthalene; Carrier B = biphenyl/chlorotoluene; Carrier C = isopropyl alcohol.

**LC_{50} = concentration required to kill 50% of test organisms. The lower the number, the more toxic the effluent.

27.3% (C.I. Disperse Red 177) to 431% (C.I. Disperse Yellow 34) when used in combination with the same carrier. Unfortunately, it was not possible to separate the individual contributions by dye or by carrier to the overall toxicity since the tests were conducted on the formulated dyebath after use.

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