SEPARATIONS TECHNIQUES FOR RECOVERY
AND/OR REMOVAL OF TOXIC METALS FROM
SPENT TEXTILE DYEBATHS

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Handout

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Summary

The Textile Resource Conservation Project (TReC) is a major initiative of the American Textile Partnership (AMTEX) focusing on energy and the environment. The largest proposed project in the TReC is Raw Material Recovery and Reuse. The main task within the Raw Material Recovery and Reuse Project is Textile Chemical Recovery. The initial focus of this task is the separation/removal of colorants from solution. Screening studies were performed at a number of U.S. Department of Energy National Laboratories to identify promising technologies for the treatment and recovery of dyes containing toxic metals. These dyes were chosen because of the environmental concern associated with their disposal.

The research group at Pacific Northwest Laboratory (PNL) took two approaches to the removal and recovery of the toxic metals in the dyes. One approach was to react or destroy the organic fraction of the dye, releasing the metals for conventional separation such as ion exchange. PNL evaluated the Rapid Thermal Decomposition of precursors in Solution (RTDS) and Corona Discharge processes for metal release. The other approach was to separate and concentrate the dye, metal-complex intact, from the bulk of the spent solution. Membrane separation was evaluated for recovery of the dyes with the metals left intact.

The RTDS process was found to be effective for destroying color and releasing or precipitating metals for recovery. Corona Discharge was effective at selectively destroying color, but the metals were not sufficiently released to allow recovery with a chelating resin. Ultrafiltration membranes were effective for separating and recovering the metal-containing dye as a potentially reusable concentrated stream.

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Introduction

The U.S. Integrated Textile Industry and the U.S. Department of Energy (DOE) have created the American Textile Partnership, AMTEX, enacted by the joint signing of a Cooperative Research and Development Agreement (CRADA) by Secretary of Energy, Hazel O'Leary and industry representatives. AMTEX will serve as a national model of excellence for productive research and development collaborations between government and industry in serving national needs. The mission and purpose of AMTEX is to engage the unique technical resources of the DOE national labs to develop and deploy technologies that will increase the competitiveness of the industry.

The AMTEX program has been divided into four technical areas: Analysis, Simulation and Integration; Improved Materials and Processes; Automation; and Textile Resource Conservation (TReC). A screening of separation technologies for dye recovery was led by Argonne National Laboratory as part of the effort to develop a research focus of the Raw Material Recovery and Reuse Task of the TReC project. The specific focus of the effort was on the colorant recovery portion of this task.

This paper summarizes the results of a study conducted by Pacific Northwest Laboratory (PNL)^(a) in conjunction with the screening efforts. PNL has extensive capabilities in the area of separation and treatment related to energy and environment. Two technologies, recently developed at PNL, were evaluated for dye treatment and recovery: Rapid Thermal Decomposition of precursors in Solution (RTDS) and Corona Discharge. Membrane separation using ultrafiltration, a method also being studied extensively by PNL, was evaluated along with these two processes.

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Screening Studies

The results of the screening studies using ultrafiltration membranes, RTDS, and Corona Discharge are given below. Dye samples were provided by two different sources, Russell Corporation and Collins and Aikman. Table 1 presents results from characterization of the spent dye samples.

Table 1. Characterization of Spent Dye Samples

	Russell Corporation	Collins and Aikman	Collins and Aikman
pH	10.36	4.33	3.97
Heavy Metal Present	Copper	Copper	Chromium
Metal Concentration (mg/L)	17.6	69.0	72.7
Density (g/mL)	1.067	0.998	0.988
Suspended Solids (ppm)	46	418	1230

Membrane Filtration

Polymer-assisted membrane separation (PAMS), using water-soluble polymers and ultrafiltration membranes, was originally proposed for the removal of the metal-containing dye from solution. Ultrafiltration experiments showed that polymer addition was not required. Suspended solids were first removed by microfiltration. Experiments on solids removal by 0.2- μ m membrane filters are shown in Table 2. Metal concentrations were reduced for the Collin and Aitken samples. The 0.2- μ m filtrate was then treated by ultrafiltration. Ultrafiltration effectively removed the metal-containing dyes from solution. Results from the evaluation of a variety of different membranes are presented in Table 3. Batch separations were performed with a targeted 10-fold volume reduction (filtrate/retentate). Color removal appeared to correlate with metals removal for the membrane separations, but this was not quantified by UV-Vis analyses.

Table 2. Metal Removal from Dye Sample by 0.2- μ m Filtration

Dye Sample	Metal	Initial Conc. (μ g/mL)	Final Conc. (μ g/mL)	% Reduction of Metal
Russell Corp.	Copper	17.57	17.86	-1.65
Collins & Aikman	Copper	59.00	45.87	33.52
Collins & Aikman	Chromium	72.70	54.92	24.46

Table 3. Metal Removal from Dye Sample by Ultrafiltration after 0.2- μ m Filtration

Sample	Membrane*	%REJ	FLUX (mL/min/cm ²)	Filtration Pressure (psi)
Russell-Cu	YC05	97.46	4.57E-03	55
Russell-Cu	YM1	95.68	0.02	55
Russell-Cu	YM10	72.32	0.06	30
C&A-Cu	YM1	75.97	0.02	55
C&A-Cu	YM10	66.67	0.09	30
C&A-Cr	YM10	98.21	0.08	30

* YC05: 500 MW cut-off membrane
 YM1: 1000 MW cut-off membrane
 YM10: 10000 MW cut-off membrane

Rapid Thermal Decomposition of Precursors in Solution

RTDS is a hydrothermal treatment/material synthesis process. Hydrothermal destruction of selected organic compounds occurs at temperatures as low as 200°C. Refractory organics can be quite stable up to temperatures of 400°C and require a catalyst or other reactant for destruction. The approach was to hydrothermally treat the dye samples containing the bound or complexed metal to determine if the metal could be released and precipitated as a hydroxide/oxide. The dye samples were treated at temperatures ranging from 250°C to 325°C with a 1.3 second residence time. Solids were removed after treatment using 0.2- μ m membrane filters. Lower temperatures resulted in less metal removal with maximum removal at temperatures above 300°C. Selected results are presented in Table 4. Note that the metal was not always precipitated but could be removed if followed by chelating ion exchange (IX) with Chelex 100.

Table 4. Metal Removal from Dye Samples by RTDS Followed by Ion Exchange

Dye Sample	Initial Conc. ($\mu\text{g/mL}$)	% Removed by RTDS	% Removed by Ion Exchange	Total % Removed
Russell-Cu	17.6	55	79 (90)	90
C&A-Cu	69.0	57	98 (99)	99
C&A-Cr	72.7	91	57 (93)	93

RTDS also effectively destroyed the dye color. Figure 1 shows that 99+% of the blue color in the Russell dye sample could be destroyed. The UV band at 260 nm was only partially destroyed. This is probably from aromatic ring structures which are more difficult to destroy.

Corona Discharge

The three dye samples were treated by point to plane corona discharge. The samples were diluted from between 1 and 50 times before treatment to allow easy analysis. The Russell sample was also neutralized to pH 7 before treatment. The metal concentration of the treated solutions was determined by atomic absorption after filtration by 0.2- μm membrane. The percent removal of metal was low by corona alone. Following corona treatment, metal removal was increased using a chelating ion exchange resin, Chelex 100. The results presented in Table 5 show the metals removal was still much lower than the targeted 90% level. This is probably due to incomplete destruction of the organic compounds in the dye.

Figure 1. RTDS Destruction of Color for Russell Dye Sample

Table 5. Metal Removal from Dye Samples by Corona Followed by Ion Exchange

Dye Sample	Initial Conc. ($\mu\text{g/mL}$)	% Removed by Corona	% Removed by Ion Exchange	Total % Removed
Russell-Cu	17.6	1	48	49
C&A-Cu	69.0	24	19	38
C&A-Cr	72.7	11	5	15

The Russell sample and product were diluted 25 times and analyzed by UV-Vis. Figure 2 shows the results of color destruction for the Russell dye sample. Based on the reduction in absorbance from 500 to 750 nm, 99+% color removal was obtained. The reduction appears to be somewhat selective with less color removal in the UV range.

Figure 2. Corona Destruction of Color for Russell Dye Sample

Conclusions

The RTDS treatment and membrane separations were effective at color and metals removal. The membrane separation has the advantage of recovering the dye intact for potential reuse. The corona effectively removed color but did not free the complexed or chelated metals. These results are specific to the dyes tested; complete testing of other classes of dyes should be performed to determine if these technologies are broadly applicable.

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