EPA-600/2-77-136
July 1977

Environmental Protection Technology Series

AUTOMATIC EXCHANGE RESIN PILOT PLANT FOR REMOVAL OF TEXTILE DYE WASTES

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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AUTOMATIC EXCHANGE RESIN PILOT PLANT FOR REMOVAL OF TEXTILE DYE WASTES

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Grant No. R803455-01
Program Element No. 1BB610

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

ABSTRACT

The use of an automated bench scale pilot unit employing adsorption resins to remove colored dyes from textile dye wastes, and also permit the reuse and recycle of its effluent has been realized in this study. At the same time approximately 50 $\pm$ 10% of the BOD and COD was concurrently removed from these same dye wastes.

This adsorption resin pilot unit was adequately sized and automated to operate continuously at flow rates which enabled the realistic calculation of costs and design of a commercial plant to remove these dyes. For 20,000 gals/day dye waste (a typical size for most individual hosiery dye plants), the estimated capital costs would be $86,000 and operating costs would be $9,430/yr. This is equivalent to an amortized operating cost of $3.47/1000 gals. of dye bath wastes. These costs are competitive to those for three other competing processes for treatment of dye wastes: ozonation, carbon treatment, or hyperfiltration (reverse osomosis). Operating costs for these processes are approximately $1.90, $1.00 and $2.00 per 1000 gallons, respectively on a one million gals/day rate of operation. These costs would be equal to or exceed the estimated costs for the resin adsorption process when scaled down to the typical 20,000 gals/day dispersed dye hosiery plant basis. A key factor that favors this adsorption process over the other three, is the proven effectiveness in removing insoluble dispersed dyes from wastewater. The alternate processes are reported to effectively remove soluble dyes in textile wastes, however, little has been reported on how efficient they are in removing the relatively insoluble dispersed dyes. These insoluble dyes are non-responsive to biological waste treatment processes. Disperse dyes, in the amount of about 50 million lbs/yr. are used to dye man made fibers (polyester, polyamides, acetates and acrylics). More dispersed dyes are in use today than any other type.

This report was submitted in fulfillment of Project No. R-803455-01 by Bennett College, Greensboro, North Carolina under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1, 1975, to February 28, 1977, and work was completed as of April 15, 1977.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

Abs	-- absorbance
BOD	-- biochemical oxygen demand
BV	-- bed volumes
bv/hr	-- bed volumes per hour
COD	-- chemical oxygen demand
ml	-- milliliters
MGD	-- million gallons per day
ppm	-- parts per million
$P.S.^{-1}$	-- pressure switch number one
P_1	-- pump number one
SS	-- suspended solids
TOC	-- total organic carbon
V_1	-- valve number one

SYMBOLS

H_2O	-- water
MeOH	-- methyl alcohol
O_3	-- ozone

ACKNOWLEDGEMENTS

The authors are indebted to Seymour G. Hall, originally of Cone Mills and now of Chemionics Industries who provided valuable background information and made available his doctoral dissertation, "The Adsorption of Dispersed Dyes on Powdered Activated Carbon".

The advice and assistance of Mr. Ellis Pardue, Manager of Environmental Health & Safety Services and his staff, Central Research and Development, Hanes Corp., in expeditiously supplying the plant dispersed hosiery dyes which enabled us to obtain the cost engineering data necessary for completion of this project is greatly appreciated. A useful contribution was made by Mr. William Simpson, Manager of Dyeing, Glen Raven Hosiery Mills, who not only provided all the initial dispersed plant dye exhaust samples, but also rendered invaluable technical assistance related to dispersed plant dyeing operations.

The assistance given by Howard Dixon, Manager of Dyeing, Sellers Manufacturing, in supplying all the various waste samples containing non-dispersed dyes is gratefully acknowledged.

A major contribution was made by Dr. Dale Chidester of Rhom and Haas who assisted in the initial phases of the project and finalized the diagrams and special equipment for the automation of the Bench Scale Automatic Pilot Plant. Also, the assistance of Mr. Chester P. Fox, P. E., Manager of the Fluid Processes Dept., Rhom and Haas, was invaluable in supplying their exchange resins along with scale up design and engineering knowledge that resulted in optimizing the cost engineering represented in this report.

The assistance given by William F. Dixon, Colorist, Ciba-Geigy, Dyestuffs & Chemical Div., was most useful in confirming the actual chemistry and chemical structures of the dyes involved in these dye wastes.

Special thanks are due to Dr. Max Samfield, Project Officer, whose continued helpful technical advice supplied the essential costs of potential competitive proceses (granular activated charcoal, ozonation and hyperfiltration). This enabled presentation of a meaningful economic comparison of the adsorption resin process compared with the alternate processes as a means of decolorization of dye wastes. Also appreciated was the foresight and encouragement rendered for this Project by Dr. Willie Ashley and Mr. Clyde Bishop, Office of Monotoring & Technical Support, EPA, Washington, D. C.

SECTION I

INTRODUCTION

BACKGROUND

One of the major problems faced by the textile industry is the pollution of streams by dye wastes. Previous laboratory research, "Application of Exchange Resins for Treatment of Textile Dye Wastes", Report No. EPA - 660/75-016, Project No. R80-2586 had shown the potential feasibility of the application of polymeric exchange resins to remove colored dyes from textile dye wastes. Among the vast array of industries contributing to the pollution of our environment, textile mills are perhaps the most conspicuous. Not only are their discharges characterized by persistent and obnoxious colors, but also by high concentrations of BOD, COD, TOC, SS. Elevated temperatures, extreme pH and substantial levels of heavy metals (e.g. chromium, copper, zinc) also are typical of these effluents. The discharge of intensely colored industrial wastes into natural waters immediately brings to one's attention a deterioration of the aesthetic quality of these receiving waters. However, three less obvious but equally important effects also result from color pollution. (1) The presence of light absorbing compounds decrease light penetration and hence the rate of production of oxygen by photosynthesis. The net result can be an oxygen deficiency accompanied by a loss of marine life and algae growth. Because of this relationship the EPA is seeking to limit the discharge of color pollutants into natural waters at levels which cause less than a 10% change in oxygen production by photosynthesis vs oxygen production by respiration.[1] (2) Color substances also chelate metal ions. This phenomenon increases both the cost of water treatment and the probability of contaminants of heavy metals. (3) The condensed aromatic polyringed color compounds which usually contain nitrogen are generally highly toxic and are suspect carcinogens, particularly so after the usually standard post chlorinated treatment by most municipal plants. For these reasons the EPA has proposed that color in water before treatment be less than 75 APHA[2] color units, and perhaps quite less, in terms of micrograms per liter because of later toxic findings as related to halogenated polyringed structures.[3,4]

OBJECTIVES

The same chemistry that gives fabric colorfastness and resistance to bleaching, sunlight, and oxidation makes these dyes similarly resistant to clean-up processes that depend upon degradation (BOD, chlorination, and even at times the ozonation of dispersed dyes) as a means of decolorization.

The objectives of this study is to demonstrate an automatic bench scale pilot unit using polymeric resins to remove dyes from textile wastes. The size and flow rates of the unit will be appropriately sized to obtain the necessary data to ascertain costs and technical feasibility of a full scale resin exchange.

In the latter studies of this project our Project Officer, Dr. Max Samfield, suggested that we show an economic comparison between ion exchange resins (this study) vs granular activated charcoal, ozonation and hyperfiltration as a means of decolorization. Under separate cover he has supplied us with the essential cost data of the latter three technologies (see Appendices), thus providing the basis for a cost comparison as a further objective of this project.[7]

SECTION II

CONCLUSIONS

Removal of color from dispersed dyeing wastes by adsorption resin technology is a practical and effective procedure. Capital and operating costs for such a process are favorable when compared to other proven processes, viz: activated charcoal, ozonation, and hyperfiltration. This is especially so in that the resulting effluent appears to be reusable and can be recycled in the same plant dyeing operation.

This finding is relevant to dispersed dye wastes since the particular type of macroreticular polar adsorption resins used herein were tailored to efficiently adsorb the surfactant and dispersants that held the colored dispersed dyes in suspension. Thereupon these dyes readily become agglomerated and attracted by Van der Waals forces to porous surfaces of the resin.

The findings showed that 120 bed volumes of dyeing wastewater could be passed and decolorized before the resin bed had to be regenerated. At least five cycles of regeneration were accomplished with no decrease in adsorption efficiency of the resin. The most efficient arrangement, representing the lowest capital and operating costs, was when two XAD-7 type resin beds were used in a "flip-flop" sequence in series. The projected capital cost is $86,500. Operating costs, including amortization, for this arrangement to remove the color from 20,000 gals/day of hosiery plant dye wastewater would be $3.47/1000 gals. Ozonation at the same processing rate (20,000 gals/day) would require capital costs of $55,000 and an amortized operating cost of $3.21/1000 gals. The other two processes, carbon treatment and hyperfiltration, are impractical because of technical difficulties with <u>Disperse</u> dye wastes.

Disperse dye waste removal is important because these nonsoluble type of dyes are either non or only partially biodegradable refractory compounds which pass through biological treatment systems relatively unchanged. Use of dispersed dyes, similarly for dyeing man-made fibers (polyester, polyamides, acetates and acrylics), totals 50 million pounds plus per year. More dispersed dyes are used than any other type.

Though disperse dyes are effectively removed by the Adsorption Resin Process, the other three competitive processes have almost solely reported on soluble dye removal rather than insoluble dispersed dyes. The reasons for this situation are technical limitations inherent in each of the processes: (1) Hyperfiltration- easy clogging of small membrane pores with suspended dispersed dyes with extra maintenance and energy usuage; (2) Carbon treatment has been reported to be not effective for dispersed dye removal; (3) Ozonation- assuredly a build up of decolorized oxidized dyes and additives which may impair continuous reuse and recycle of effluent and which when purged to the wastewater environment will have an increased BOD.

Finally, a unique practical advantage is that the relatively non-aqueous highly concentrated BOD and COD oily dye waste from the resin process can be readily burned as fuel at the plant site while the other three processes still have to dispose of the dilute aqueous polluted BOD and COD dye waste by more expensive methods.

SECTION III

RECOMMENDATIONS

It is suggested that a typical textile mill using dispersed dyes be the site of a Demonstration Resin Adsorption Plant to treat colored dye waste effluent for reuse and recycle in a closed loop system.

In particular a hosiery dyeing plant should be selected where there is currently an active program going on to both remove waste dyes and reuse the resulting effluent instead of discharging said wastes into a municipal treatment plant which is not prepared to handle this type refractory wastes.

It is suggest that such an arrangement be considered and explored with a textile company that has several similar hosiery plants in the Southeast using dispersed dyes, which would be applicable to the same technology of treating their colored dye wastes and reuse of the resulting effluent.

It may be valuable to demonstrate and evaluate the amortized operating costs of the ozone vs the resin adsorption process using the same Disperse dye waste.

SECTION IV

EXPERIMENTAL PROCEDURES

PREPARATION OF ION-EXCHANGE RESINS

Some ion-exchange resins require little pretreatment if any. In some cases the pretreatment of the resins are specific only to the application.

For example, the treatment of an acid dye waste influent is best accomplished by alkalizing Duolite A-7, which is shipped in its hydrochloride salt form, with one bed volume of 5% sodium hydroxide solution at 5 bv/hr followed similarly with a water rinse. The sodium hydroxide treatment of the resin is replaced with 5% sulfuric acid, when the influent is basic.

XE-275 was pretreated by the following method in all applications. The resin was soaked in water and transferred to columns by the slurry method. XE-275 used in our work was shipped in its weak basic form.

The pretreatment of XAD-7 in all application is accomplished by soaking the resin in methanol and transferring it to columns by slurry methods. The resin bed was expanded 50% with a water backwash for a minimum of ten minutes. The bed was allowed to settle and was ready to accept the influent dye waste.

AUTOMATION

The automatic bench scale pilot unit, Figure 1, was designed to ascertain the cost and technical feasibility of a full scale resin exchange plant to remove textile dye waste. Plans for the unit were made after careful discussion with engineers of Rhom and Haas and using several related reference reports. The consideration for minimal standards to obtain appropriate data to be able to scale up findings to plant size are: the resin bed in the columns must be at least two feet high, minimum diameter of column = one inch, and a flow rate of at least four bed volumes per hour. Experimental conditions were set at bed height of three feet and flow rate at 4 bv per hour.

Kimex beaded glass pipes, four feet long by one inch (i.d.) coupled with industrial flanges to reducing glass tube fittings were used as columns.

The automatic control equipment used was composed of the following components:

Stepping Switch, Model 2420, Tenor Company
Multi Range On-Delay Reset Timers, Model 551, Tenor Company
Ten Multi Head Metering Pumps, Model 7189, Cole Palmer Company
Automatic Solenoid Switching Valves, Automatic Switching Company

Universal 3-Way Valves, Red Hot, No. 832043
2-Way Valves, Red Hot (NC) No. 8262C6

Pictorial Wiring Diagram, shows the electrical circuits to the above equipment to automatically carry out the 22 steps of the operation, Figure 2.

Automation 1

Steps of Automation of Bench Scale Unit for 2 columns of different resin material. The following refer to Figure 3.

Step 1 Removal of Dyes and Additives in Dye Waste--
P_1 (pump 1) starts dye waste by P.S.-1 (safety pressure switch) through column 1, V_3, V_4, column 2, V_5, V_6 to effluent.

Step 2 Rinsing of Resin in Column 1 (C-1)--
P_1 stops. P_2 starts H_2O through V_2, V_1, column 1, V_3, to Semi-Continuous Stripping Still or Used Regenerant.

Step 3 Regeneration of Resin in Column 1 (C-1)--
V_2 changes. Methanol is pumped by P_2 through V_2, V_1, column 1 to Semi-Continuous Stripping Still or Used Regenerant.

Step 4 Rinsing of Resin in C-1--
V_2 changes. H_2O is pumped by P_2 through V_2, V_1, C-1 to Semi-Continuous Stripping Still or Used Regenerant.

Steps 1, 2, 3 and 4 are repeated four more times in sequence as shown above and respectively called steps (5, 6, 7, 8), (9, 10, 11, 12), (13, 14, 15, 16), (17, 18, 19, 20).

Step 21 Rinsing of Resin in Column 2--
P_2 is still running V_3 closes, V_2 changes, V_4 opens, V_5 changes and H_2O flows through V_2, V_4, C-2, V_5 to Used Regenerant of Semi-Continuous Stripping Still.

Step 22 Regeneration of Resin in C-2--
V_2 changes, methanol is pumped by P_2 through V_2, V_4, C-2, V_5 to Semi-Continuous Stripping Still or Used Regenerant.

Automation 2

Steps of Automation of Bench Scale Unit for 2 columns of the same resin. The following description of steps refers to Figure 4.

Step 1 Removal of Dyes and Additives in Dye Waste--
P_1 starts column 1 (C-1) dye waste by P.S.-1 (safety pressure switch) through V_7, V_1, C-1, V_3, C-2, V_4, V_5, V_6 to effluent.

Step 2 Rinsing of Resin in (C-1)--
V_7, V_3, V_5, V_6 change, Pump 1 (P-1) stops and P-2 starts H_2O through

V_2, V_7, V_1, C-1. V_3, V_5, V_6, to Semi-Continuous Stripping Still or Used Regenerant.

Step 3 Regeneration of Resin in (C-1)--
V_2 changes, methanol is pumped by P_2 through V_2, V_7, V_1, C-1, V_3, V_5, V_6 to Semi-Continuous Stripping Still or Used Regenerant.

Step 4 Rinsing of Resin in Column 1--
V_2 changes and H_2O is pumped by P_2 through V_2, V_7, C-1, V_3, V_5, V_6 to Semi-Continuous Stripping Still or Used Regenerant.

Step 5 Removal of Dyes and Additives in Dye Waste Through Column 2 (C-2)--
V_7, V_1, V_6 change. Pump 2 stops and Pump 1 starts dye waste through V_7, V_1, C-2, V_4, C-1, V_3, V_5, V_6 to effluent.

Step 6 Rinsing of Resin in C-2--
V_7, V_4, V_5, V_6 changes. Pump 1 stops and Pump 2 starts H_2O through V_2, V_7, V_1, C-2, V_4, V_5, V_6 to Semi-Continuous Stripping Still or Used Regenerant.

Step 7 Regeneration of Resin in C-2--
V_2 changes and methanol is pumped by P_2 through V_2, V_7, V_1, C-2, V_4, V_5, V_6 to Semi-Continuous Stripping Still or Used Regenerant.

Step 8 Rinsing of Resin in C-2--
V_2 changes and H_2O is pumped by P_2 through V_2, V_7, V_1, C-2, V_4, V_5, V_6 to Semi-Continuous Stripping Still or Used Regenerant.

STILL FOR METHANOL RECOVERY

A semi-continuous column stripping still was set up to remove methanol from the methanol dye regenerant. A five-liter round bottom three neck glass jointed flask fitted with a Vigreux distilling column over an Oldershaw sieve plate column composed the still, see Figure 5. Methanol regenerant and water rinse mixture (Used Regenerant) was fed through a side adapter tube connected between the two columns. The flask was heated with a heating mantle to 102-105°C. Temperature was monitored with a thermometer placed in one of the three neck glass joints of the flask. Pure methanol distilled over at its boiling point of 64°C while the dark mixtures of dyes, additives and water continued down the sieve plated column to the flask. The pure methanol was collected in a five gallon glass bottle from which it was drawn and reused as the regenerant for removing the absorbed dyes from the exchange resin columns. The still was operated manually. The used regenerant was collected and later distilled.

COLOR REMOVAL

Visual Photography

A Nikon F-2 Photomic camera with filters and a tripod was used to visually show the removal of color by the use of color photography. This was deemed necessary to prove the actual removal of color from the colored dye wastes.

As shown below, the use of a Bausch and Lamb's Spectronic-20 not only registers the remaining color, but also any white emulsified polyethylene registers as color.

Spectronic-20, Readings for Color Removal

The wavelength in which each dye waste effluent is monitored is determined by scanning the influent over the visible region. However, the thin white emulsified polyethylene also registers as absorbance at the wavelength used to detect the dye color. The white thin turbidity is clearly not due to the dyes in the influent. Treatment with sulfuric acid or sodium hydroxide solution had no visible effect, when the pH was changed from 1 to 13. Most of the problem was overcome by diluting the influent, one to ten with water, and measuring the dilute solution at the desired wavelength on the Spectronic 20. This gave a good indication of the removal of color, but not as absolute as the actual color photos shown herein. The percent of color removed from the influent was calculated as follows:

$$\% \text{ Color Removed} = \frac{\text{Abs. influent} - \text{abs. effluent} \times 100}{\text{Absorbance of influent}}$$

COD and BOD

Samples were taken usually every 10 bed volumes for COD and BOD determinations. Samples were preserved by refrigeration.

The BOD values were determined by the dissolved oxygen Probe Method using a YSI Model 54 ARC Dissolved Oxygen Meter and YSI 5720 self stirring bottle probe. The manufacturer's instructions were followed in calibrating the meter. The air calibration method was used and checked against the Saturated Water Method. Repeated readings of saturated water gave 8.4 ± 0.1 ppm using both methods at 28°C after correcting for barometric pressure. The solubility of oxygen in fresh water for calibration was taken from Table 281 page 480, Standard Methods for Examination of Water and Waste Water, 1971.

Flow Rates

Flow rates for loading columns were usually 4 bv/hr. The most feasible flow rate for regeneration was 2 bv/hr. This allowed maximum contact time between resin and methanol at a practical operation rate. The flow rates for all rinses were 2 bv/hr.

Regeneration

Regeneration of the adsorption resin was all downflow through the columns because of difficulties in backflow operation. The major problem in backflow regeneration was the occasional creation of voids in the column that allowed the methanol to channel, resulting in a loss of efficiency for dye color removal. The advantage of Backflow operation would allow the column to clean up more rapidly with less methanol extraction, however, downflow regeneration was deemed more practical in everyday operation of the pilot unit.

SECTION V

DISCUSSION AND RESULTS

GENERAL

The main Dispersed dyes used by the textile mills mentioned in the report are of the structures shown in Figure 6. Though these dyes are used for dyeing nylon hosiery, other Dispersed dyes used in dyeing polyester, acrylics, and acetates are not that much different and would be expected to have the same adsorption characteristics.

A recently published article[5] deals with research conducted at the Wastewater Research Center. The report is timely in that it describes deficiencies in the removal of Disperse dyes by activated carbon, ozone and biological treatment.

The Major Conclusions as stated were:

1. The organic constituents in dyeing wastewater are relatively biodegradable, and BOD and TOC can be effectively reduced by biological treatment.

2. Color, in general, is not readily removed by biological waste treatment, suggesting that dye molecules are not readily biodegradable.

3. BOD and TOC removal by physical-chemical treatment techniques, i.e. coagulation, carbon adsorption and ozonation, is not very effective.

4. Disperse, vat and sulfur dyeing wastewaters can be readily decolorized by coagulation with alum, but are not readily decolorized by activated carbon.

5. Reactive, basic, acid and azoic dyeing wastewaters can be readily decolorized by activated carbon.

6. Reactive dyes can be decolorized most effectively by ozone; Dispersed dyes are decolorized least by ozone.

As previously planned for this study, and before finalizing on a set of operating conditions to otbain data for calculating costs, numerous phone conversations were had with the engineers of Rhom and Haas Company and the Hanes Company Legg's Division. This included a two day consultation visit with Rhom and Haas in Philadelphia and several day visits with Hanes in Winston-Salem, North Carolina. The purpose of these discussions was to interpret the experimental data to date, and to finalize the operating conditions to provide data for determining a most practical process with minimum capital and operating costs requirements for the removal of Disperse dyes from wastes in plant hosiery dyeing operations. These same capital and operating cost estimates could be applied to other Disperse dyeing operations in the textile industry. Most hosiery dyeing operations are made with Disperse dyes only. Some industries use a small percentage of acid dyes along with Disperse dyes when they are dyeing certain types of panty hose.

From an engineering standpoint the use of two columns in series containing the most efficient adsoprtion resin regenerated by methanol in both columns would reduce the capital and operating costs as well as simplify the controls of the operation. This would also avoid the use of acid and basic regenerants (pollutants in their own right) in the process.

Hanes Disperse Dye Wastes

As shown in Figure 7, complete removal of all color was obtained after 120 bv were passed through both columns containing resin XAD-7 only. After about 30 bv, a slight white milkiness was present in the effluent which was probably the white emulsified polyethlene softener that was dispersed by the surfactant system used in the original plant dye formula. Spectronic-20 readings of color removal are reported in Table 1 and shown graphically in Figure 8. Also shown in Figure 9 and Table 1 is the removal of approximately 50% of the COD. The BOD content removal was 54% at 60 bv.

The above conditions were used in the Flip-Flop arrangement which is as follows: The dyes waste is passed through Column 1 and Column 2 in series as usual, containing the same resin. When the 120 bv has passed through both columns, the first column is relatively completely saturated (complete coloration of first resin columm with dye color noticeably in its effluent).

At this stage only one-fifth of the second resin in series is colored in the second column; the rest of it is white and yet capable of adsorbing more dyes. The waste dye loading cycle is stopped. then, only the first colored saturated column is desorbed completely by regeneration with two bv of methanol and then washed with one bv of water. The dye loading cycle is started and the Flip-Flop arrangement takes place in that the two columns are reversed in their order of receiving the dye waste. Thus, the original second column now becomes the first to receive the dye waste and the original first column that has just been regenerated becomes the back-up column. This Flip-Flop sequence occurs after each 120 bv of dye waste are passed and regeneration of the leading column. There was no degeneration or apparent lessening of efficiency of color removal of the XAD-7 resin after five complete cycles or regeneration. In our main work earlier we have already demonstrated that XAD-7 resin could be regenerated at least 25 cycles and still continued to be as efficient. This is shown below with Glen Raven's Disperse dyes which are the same as Hanes. Using XAD-7 followed by A-7 gave fairly good color and COD removal, but only up to when 20 bv was passed, and then the resin had to be regenerated, Figure 10 and Table 2.

As the single resin in both columns, the use of XE-275 or Duolite A-7 in either their weak base or salt form also failed to give as many satisfactory

TABLE 1. HANES DISPERSE DYE (2XAD-7 COLUMNS)

Effluent		Color Absorbance				COD		
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed	Influent	Effluent	% Removed
1	5	1.75	.019	360	99.0	8160	600	93
	10		.020		99.0		720	91
	20		.060		97.0		850	90
	30		.100		95.0		1760	78
	40		.130		93.0		2500	69
	50		.190		89.0		3500	57
	60		.230		87.0		5900	27
	70		.280		84.0		6570	19
	80		.300		83.0		7196	11
	90		.660		62.0		7380	8
	100		1.080		38.0		7500	8.1
2	10	1.75	.020	360	99.0	8160	580	93.0
	20		.060		99.0		600	92.0
	30		.100		96.0		835	90.0
	40		.140		94.0		1560	81.0
	50		.180		93.0		2300	72.0
	60		.230		89.0		3400	58.0
	70	1.75	.290	360	87.0	8160	5700	30.0
	80		.300		85.0		6450	20.0

(continued)

TABLE 1 (continued)

Effluent		Color Absorbance				COD		
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed	Influent	Effluent	% Removed
	90		.660		63.0		7200	11.0
	100		1.080		38.0		7300	10.0
3	10	1.75	.023	360	99.0	8160	590	93.0
	20		.050		97.0		600	92.0
	30		.090		95.0		840	90.0
	40		.150		92.0		2530	69.0
	50		.180		90.0		3250	60.0
	60		.230		87.0		6080	26.0
	70		.290		83.0		6670	18.0
	80		.300		83.0		7300	9.0
	90		.660		62.0		7400	9.0
	100		1.080		38.0		7530	7.0
4	10	1.75	.020	360	99.0	8134	800	90.0
	20		.070		96.0		856	90.0
	30		.080		95.0		1860	77.0
	40		.160		91.0		2600	68.0
	50		.200		89.0		3500	57.0
	60		.240		86.0		6000	26.0
	70		.300		83.0		6600	19.0

(continued)

TABLE 1 (continued)

Effluent		Color Absorbance				COD		
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed	Influent	Effluent	% Removed
	80		.310		82.0		7100	12.0
	90		.660		62.0		7400	9.0
	100		1.100		37.0		7600	6.0
5	10	1.75	.020	360	99.0	8134	830	90.0
	20		.080		96.0		856	90.0
	30		.090		95.0		1893	76.0
	40		.160		91.0		2680	67.0
	50		.210		88.0		3570	56.0
	60		.240		86.0		6070	26.0
	70		.310		82.0		6673	18.0
	80		.310		82.0		7190	11.0
	90		.660		62.0		7480	8.0
	100		1.100		37.0		7670	6.0

TABLE 2. HANES DISPERSE DYE (XAD-7 FOLLOWED BY A-7 COLUMN)

Effluent		Color Absorbance				COD		
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed	Influent	Effluent	% Removed
1	5.2	1.75	0	360	100.0	8160	3000	63
	10.4		.06		99.4		3600	55
	14.7		.58		67.0		4100	50
	25.0		.38		78.0		7200	12
2	5.0	1.75	.02	360	99.0	8160	2900	64
	10.0		.07		98.0		3600	55
	20.0		.60		85.0		3700	54
	30.0		.38		78.0		4100	50

bv of color removal as the neutral XAD-7 resin above. Only about 30 bv of the dye waste could be passed before the effluent became noticeably colored.

Glen Raven Disperse Dye Wastes

The main thrust here was to evaluate the long lasting qualities and retention of efficiency of dye removal after each regeneration for resins XAD-7 and A-7 in tandum. As many as 25 complete cycles of regeneration with methanol still gave good color removal, Figure 11, (about 90% removal of color by Spectronic data) and 50% BOD and COD removal, Figures 12, 13, 14 and Table 3. In this series before each regeneration 25 to 30 bv were passed, while still maintaining about 85% color removal. The main goal here was to find out how long these resins could retain their efficiency after numerous regenerations before being seriously overloaded. Note, in the field these resins are reported to last several years of continuous use before they are replaced.[6]

TABLE 3. GLEN RAVEN DISPERSE DYE WASTE (XAD-7 FOLLOWED BY A-7 COLUMN)

Effluent		Color (absorbance)			COD			BOD		
Cycle	1000 ml cuts	Influent	Effluent	% Removed	Influent	Effluent	% Removed	Influent	Effluent	% Removed
1	1	3.51*	.85	75	1049	861	18	6400		
	2		.38	89		900	14		2950	53
	3		.42	88		815	22		2750	57
	4		.48	86		961	8		2850	55
	5		.50	86		715	32		2300	64
	6		.68	81		930	11		3000	53
	7		.25	93		961	8		3850	40
	8		.16	95		976	7		3775	41
	9		.23	94		1122			3200	50
2	1	2.90	.15	95	1434	898	37	6300	3075	51
	2		.14	95		837	41		3100	50
	3		.25	91		1089	24		3600	42
	4		.26	91		1154	20		3750	40
	5		.23	92		1182	18		3725	40
	6		.22	92		1170	18		3850	38
	7		.24	91		1227	14		4182	33
	8		.24	92		1142	20		4100	34
	9		.22	92		1182	18		3275	48
4	1	1.30	.21	84	748	307	59	4850	1575	67
	2		.20	85		358	52		1750	64
	3		.20	85		436	42		1750	64
	4		.14	89		524	30		2200	55
	5		.13	90		480	36		2500	48
	6		.13	90		544	27		2425	50

*Wavelength used was 480 namometers for Cycles 1 through 5.

(Continued)

TABLE 3 (continued)

Effluent Cycle	1000 ml Cuts	Color (absorbance) Influent	Effluent	% Removed	COD Influent	Effluent	% Removed	BOD Influent	Effluent	% Removed
4	7	1.30	.12	91	748	495	34	4850	2150	56
	8		.11	92		583	22		1900	60
	9		.10	93		590	21		2175	55
5	1	1.30	.21	84	748	209	72	4850	2350	52
	2		.20	85		238	68		2375	51
	3		.18	86		321	57		2400	50
	4		.16	88		304	59		2300	53
	5		.16	88		321	57		2925	40
	6		.18	86		521	30			
	7		.14	89		585	21			
	8		.14	89		604	19			
	9		.12	91						
	10		.11	92						
6	1	1.30	.10	92	1235	1000	19	5700	2250	61
	2		.11	92		1113	10		2475	57
	3		.12	90		1146	7		2650	54
	4		.11	92		1121	9		2775	51
	5		.11	92		1138	8		3150	46

(Continued)

TABLE 3 (continued)

Effluent		Color (absorbance)					COD			BOD		
Cycle	BV**	Influent	Effluent	Wave length*	% Removed	Avg.	Influent	Effluent	% Removed	ppm Influent	ppm Effluent	% Removed
7	5	3.80	.95	640	75		1809	880	51	7500	3250	57
		4.50	1.00	520	78	73	"			"		
		4.60	1.50	480	67		"			"		
	25	3.80	.86	640	78		1809	754	58	7500	3450	54
		4.50	1.00	520	78	74	"			"		
		4.60	1.50	480	67		"			"		
9	5	3.80	.75	640	80		1809	870	52	7500	3620	52
		4.50	.95	520	79	79	"			"		
		4.60	1.00	480	78		"			"		
	30	3.80	.85	640	78		1809	763	58	7500	3333	56
		4.50	1.00	520	78	74	"			"		
		4.60	1.50	480	67		"			"		
11	5	3.80	.75	640	80		1809	893	51	7500	3333	56
		4.50	1.20	520	73	77	"			"		
		4.60	1.00	480	78		"			"		
	15	3.80	.85	640	78		1809	631	65	7500	4000	53
		4.50	1.10	520	76	76	"			"		
		4.60	1.20	480	74		"			"		

* Average of the three wavelength readings used for Cycles 7 through 25.
**Data was taken at number of BV (bed volumes) passed for remaining cycles.

(Continued)

TABLE 3 (continued)

Effluent Cycle	BV**	Color (absorbance) Influent	Effluent	Wave length*	% Removed	Avg.	COD Influent	COD Effluent	% Removed	BOD ppm Influent	BOD ppm Effluent	% Removed
11	25	3.80	.80	640	79		1809	786	57	7500	3450	57
		4.50	.95	520	79	77	"			"		
		4.60	1.20	480	74		"			"		
	30	3.80	.75	640	80		1809	750	59	7500	3320	56
		4.50	.90	520	80	79	"			"		
		4.60	1.00	480	79		"			"		
13	5	3.80	.81	640	79		1809	830	54	7500	3500	53
		4.50	1.00	520	78	78	"			"		
		4.60	1.00	480	78		"			"		
	25	3.80	.86	640	77		1809	790	56	7500	3550	53
		4.50	1.00	520	78	79	"			"		
		4.60	.82	480	82		"			"		
15	5	3.80	.96	640	75		1809	850	53	7500	3400	55
		4.50	1.20	520	74	77	"			"		
		4.60	.85	480	81		"			"		
	25	3.80	.80	640	79		1809	750	59	7500	3650	51
		4.50	1.00	520	78	77	"			"		
		4.60	1.20	480	74		"			"		
16	5	1.50	.36	640	76		1144	562	51	6300	2980	53
		2.80	.52	520	81	79	"			"		
		3.00	.61	480	80		"			"		

(Continued)

TABLE 3 (continued)

Effluent Cycle	BV**	Color (absorbance) Influent	Effluent	Wave length*	% Removed	Avg.	COD Influent	COD Effluent	% Removed	BOD ppm Influent	BOD ppm Effluent	% Removed
16	25	1.50	.23	640	85		1144	528	54	6300	2630	58
		2.80	.45	520	84	81	"			"		
		3.00	.54	480	82		"			"		
18	5	1.50	.35	640	77		1144	576	50	6300	2800	56
		2.80	.44	520	84	81	"			"		
		3.00	.49	480	81		"			"		
	25	1.50	.22	640	85		1144	542	53	6300	2850	55
		2.80	.38	520	86	85	"			"		
		3.00	.49	480	84		"			"		
20	5	1.50	.21	640	86		1144	498	56	6300	3100	50
		2.80	.33	520	88		"			"		
		3.00	.40	480	87		"			"		
	25	1.50	.18	640	88		1144	445	61	6300	3130	50
		2.80	.30	520	89	88	"			"		
		3.00	.43	480	86		"			"		
22	5	1.50	.19	640	87		1144	520	55	6300	2820	55
		2.80	.30	520	89	87	"			"		
		3.00	.44	480	85		"			"		
	25	1.50	.20	640	87		1144	561	51	6300	2816	55
		2.80	.35	520	88	87	"			"		
		3.00	.46	480	85		"			"		

(Continued

TABLE 3 (continued)

Effluent		Color (absorbance)					COD			BOD		
Cycle	BV**	Influent	Effluent	Wave length*	% Removed	Avg.	Influent	Effluent	% Removed	ppm Influent	ppm Effluent	% Removed
24	5	1.50	.17	640	89		1144	443	61	6300	2910	53
		2.80	.31	520	89	88	"			"		
		3.00	.39	480	87		"			"		
	25	1.50	.18	640	88		1144	540	60	6300	2856	55
		2.80	.36	520	88	87	"			"		
		3.00	.45	480	85		"			"		
25	5	1.50	.18	640	88		1144	500	56	6300	2910	53
		2.80	.36	520	87	88	"			"		
		3.00	.35	480	88		"			"		
	25	1.50	.16	640	89		1144	489	57	6300	2851	55
		2.80	.34	520	88	88	"			"		
		3.00	.38	480			"			"		

Hanes Acid Dye Wastes

Recently some work was done with Hanes acid dye wastes. Previously, only Dispersed dyes were encountered in hosiery dyeing operations. However, now, up to about 30% of Acid dyes may be used in sequence dyeing along with Disperse dyes at some hosiery plants. In this case, one column was used and the resin was Duolite A-7. Excellent color removal is shown in Figure 15. Seventy bv was passed through the columns and the column was then methanol regenerated and water rinsed for the next cycle in the usual way. As shown in Table 4, there was no reduction efficiency of color removal through three regeneration cycles. Color removal was 80% after 70 bv was treated. The COD removal went from 60% to 30%, the average being about 45% by the time 70 bv was passed. The BOD removal at 20 bv was 53%. A preliminary run using one column containing XAD-7 resin was about one-half as effective as Duolite A-7 in removing the color in the initial cycle and the work was discontinued.

Sellers Reactive Dye Wastes

As usual, the dye wastes samples were taken just prior to discharging (at their most concentrated stage and not diluted with rinse waters). Sellers has a conventional type of package dyeing operation. The conditions used were with XAD-7 in one column followed by A-7 in the second column. A total of 30 bv of reactive dye wastes could be passed, as shown in Figure 16, with no visual loss in color removal. As shown in Figure 17 and Table 5, color removal dropped only to 80% after a total of 30 bv was passed, while 40% BOD and 55% COD were removed at 20 bv. Also it can be seen, with the limited time at hand, at least three complete cycles could be run with no loss of resin efficiency for color removal.

Comparison of Technical Efficiencies and Costs with Other Dye Removal Processes

Since hosiery dyeing plants normally operate at a rate that produces 10,000 to 20,000 gals/day of Disperse dye wastes, it is difficult to compare cost data with the other three competitive processes for treating soluble wastes at the normal large volume of 1 million gals/day, see Appendices. However, of three potentially competitive processes, ozonation appears to be the only practical competitor to the polymer adsorption process. Carbon treatment and hyperfiltration are considered impractical on the basis of technical diffculties of dealing with nonsoluble Disperse dyes making their process removal steps difficult and thus more costly. For instance, in hyperfiltration the minute pores in the membrane have become clogged and rendered inoperative. Carbon treatment has been reported to be efficient for removal of soluble dyes but not effective for Disperse dyes.[5] Also, with carbon treatment regeneration of the adsorbent would be difficult and quite costly.

TABLE 4. HANES ACID DYE (ONE A-7 COLUMN ONLY)

Effluent		Color Absorbance				COD		
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed	Influent	Effluent	% Removed
1	10	1.00	.005	200nm	99.5	5512	2016	63
	20		.009		90.0		2516	54
	30		.100		89.3		2935	46
	40		.107		83.9		3018	45
	50		.110		89.0		3118	43
	60		.156		84.0		3519	36
	70		.196		80.0		3916	30
2	10	1.00	.006		99.4	5618	2173	61
	20		.099		90.0		2468	56
	30		.100		90.0		2955	47
	40		.108		89.2		3319	40
	50		.110		89.0		3346	40
	60		.157		84.0		3817	32
	70		.199		80.0		4056	27
3	10	1.00	.005		99.5	5628	2185	61
	20		.099		90.0		2573	54
	30		.100		90.0		2948	47
	40		.107		89.3		3096	44
	50		.111		89.0		3220	42
	60		.158		84.0		3972	29
	70		.200		80.0		4176	26

TABLE 5. SELLERS REACTIVE DYE WASTE

Effluent		Color Absorbance			
Cycle	Bed Volume	Influent	Effluent	Wave-length	% Removed
1	5	4.80	.13	340	97
	10		.17		97
	15		.53		89
	30		.99		80
2	5	4.80	.15	340	97
	10		.18		96
	15		.98		80
	30		1.00		79
3	5	4.80	.16	340	97
	10		.19		92
	15		.73		84
	30		.99		80

Capital and Operating Costs--Adsorbent Resin Process

Hosiery Waste Plant Color Removal (20,000 gal/day, 2 shift)

A. Capital Cost (installed)

Equipment, tanks, pumps, columns, etc.	$63,000
300 gal/day Simple Methanol Stripping Still	10,000
Engineering & Field Supervision	7,500
60 cu. ft. Adsorbent Resin (for 2 columns)	6,000
Total Capital	$86,500

B. Operating Costs/Yr.

1,800 gal Methanol make-up at 98% recovery	$ 900
Resin Amortization (5 yr. life)	1,200
Electricity and supplies	500
Repairs (3% of Equipment Capital $71,000)	2,130
Steam at $2/1000 lbs. for 300 gal/day MeOH	700
Labor, 1/5 man per two shifts	4,000
Operating cost/year., total	$ 9,430/yr.

At 300 day/year operation cost--
$/1000 gal = $9430 x 1000 gal/(20,000 gals x 300) = $1.57/1000 gals
Capital costs amortized as operating costs/1000 gals = $1.90
Total annualized operating costs = $3.47/1000 gals

Assumptions:

(1) Stripping of MeOH done during the two shifts, but automatic adsorption run around the clock.

(2) Savings realized by reuse and recycle of water and some surfactants and polythethylene softener will balance off other miscellaneous costs as taxes, etc.

(3) Concentrated oily dye methanol stripped waste will be dripped into oil furnace and burned as fuel.

(4) Small amounts of acid dyes when used with Disperse dyes in some plants would be handled by the same single resin such as XAD-7.

(5) Capital costs amortized over ten years at an annual interest rate of 10%.

Capital and Operating Costs--Ozonation Process

Hosiery Waste Plant Color Removal (20,000 gal/day, 2 shift)

A. Capital Costs

60#/day Ozone Plant (Air Feed)	$25,000
Auxiliaries (Air driers, Compressors, pumps, etc.)	12,000
Piping and installation for ozone	10,000
Treatment contactor, tanks, controls, installation	8,000
Total Capital	$55,000

B. Operating Costs/Yr.

800 KW hrs/day (Electricity O_3 & Auxiliaries at 3¢/KW x 300 days	$ 7,200
Cooling Water at 70°F at 0.8 g/min/# O_3	1,200
Repairs (3% of Capital Equipment)	1,650
Labor, 1/10 man per two shifts	2,000
Operating Costs/yr. total	$12,050

Cost in $/1000 gals = 12,050 x 1000/20,000 x 300 = $2.00/1000 gals
Capital costs amortized as operating costs = $1.21
Total annualized operating costs = $3.21/1000 gals

Assumptions:

(1) The ozone dosage to reduce color to acceptable limits was estimated to be 35 mg O_3/liter of waste. This is a modest assumption in that O_3 dosages run from 5.0 mg to 1000 mg/liter as shown in the ozone cost studies in the appendix sections of this report.

(2) Capital cost amortized over ten years at an annual interest rate of 10%.

A comparision of the two processes, O_3 vs. Resin Adsorbent, shows that the operating cost estimates are fairly close to each other and a demonstration plant for each on the same dye waste could decide which may be better. At first appearances, the ozone approach is more simple and direct, but a build-up of the decolorized ozidized dyes and surfactants by ozonation would certainly occur. For instance, it is well known that Disperse dyes are sold as mixture of the dye at about 40% and a dispersion agent as lignin sulfonate 60%. It is also known that lignin sulfonate is fairly readily attacked by ozone. Thus, a portion of the effluent would have to be discarded to avoid a build-up of organic compounds in the recycle system. On the other hand, by the adsorbent process, as long as the colored dyes are removed, any additives such as surfactants, wetting and dispersion agents would be left unchanged and usable. This would be an extra saving. Thus, in the make up for each new dye formula only part of the additives would have to be added.

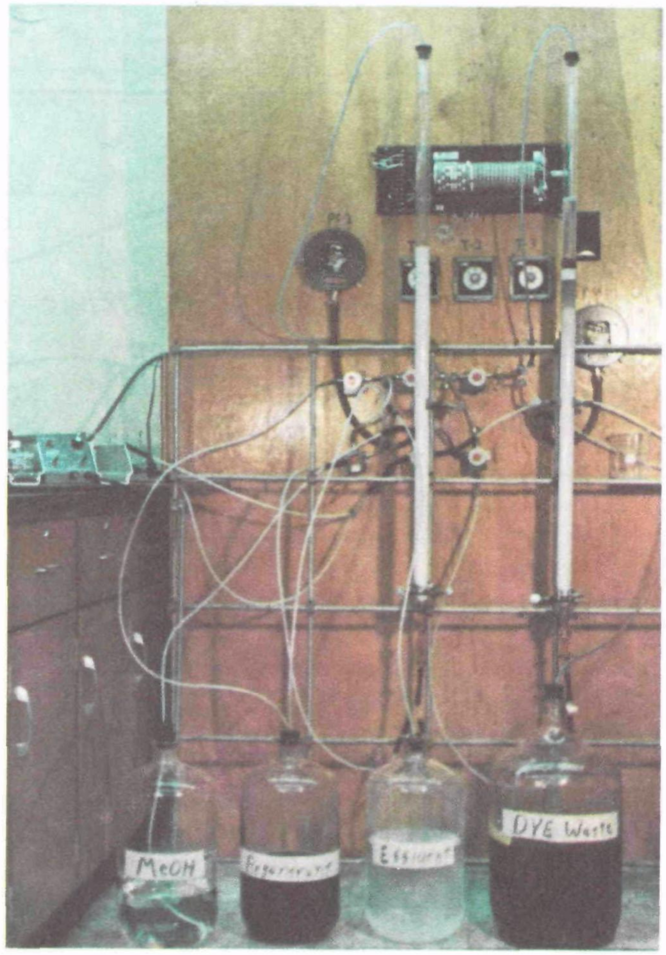


Figure 1. The automatic bench scale pilot unit.

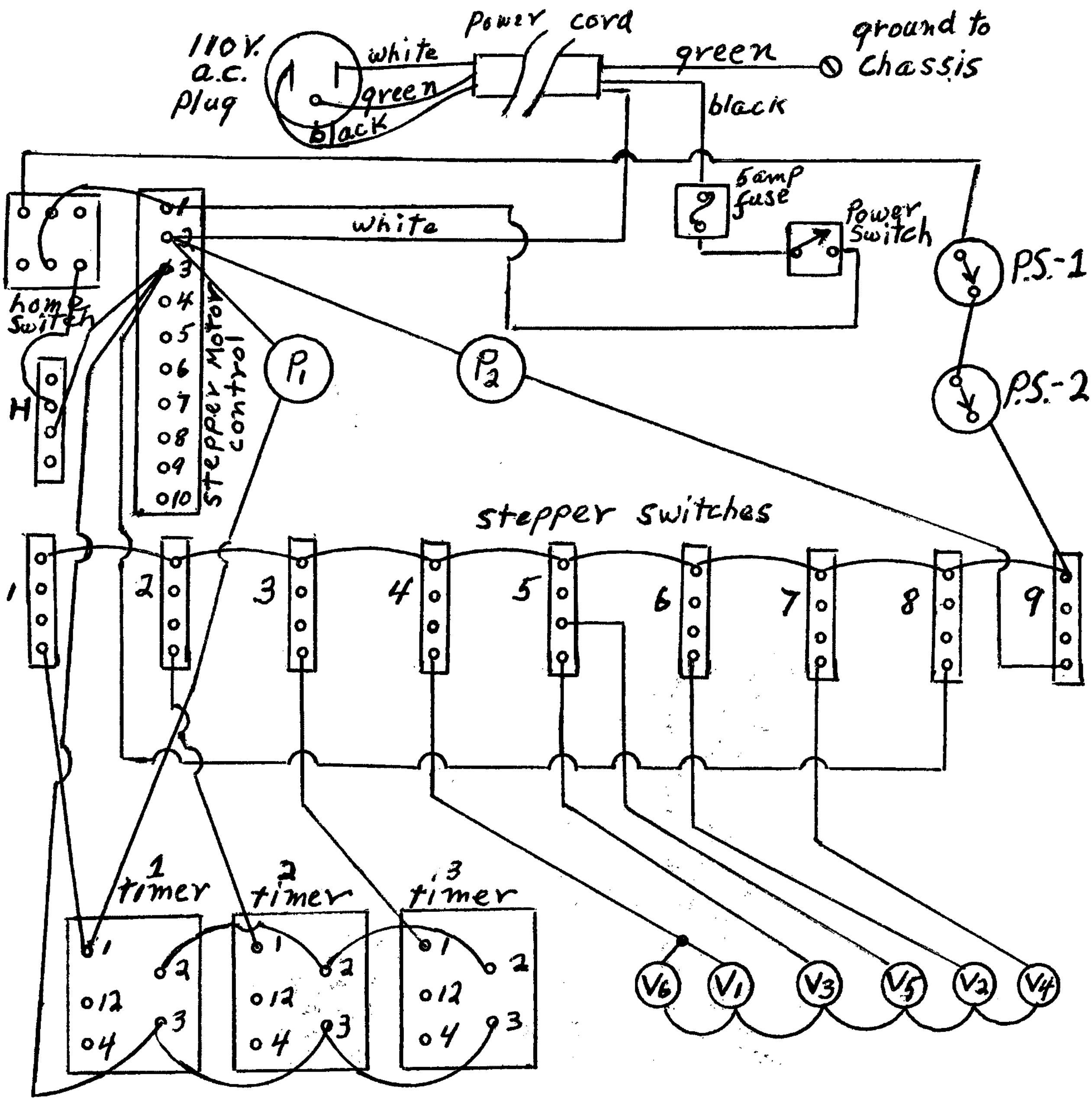


Figure 2. Pictorial wiring diagram.

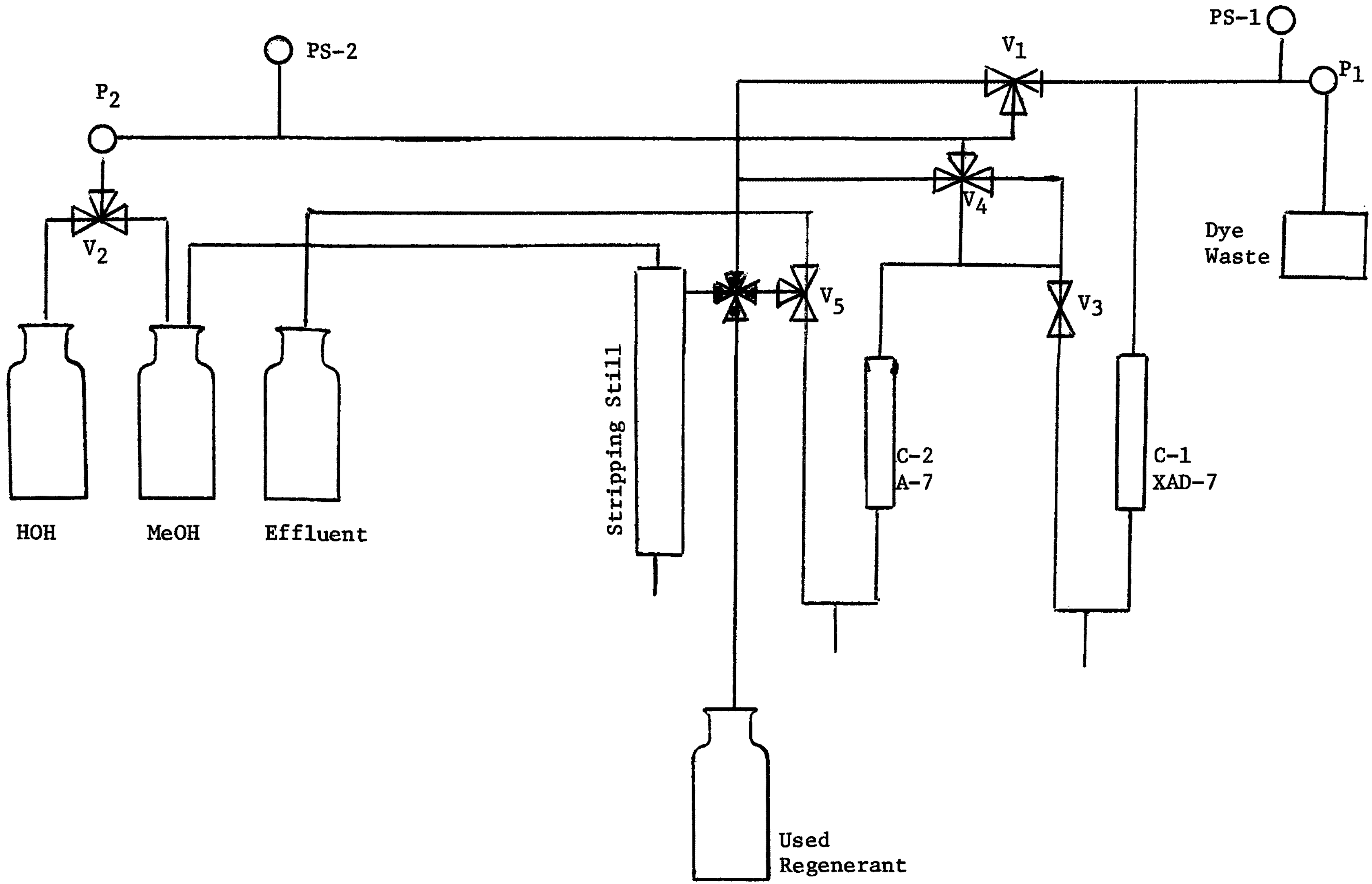


Figure 3. Sketch of bench scale pilot unit, each column containing a different resin in series.

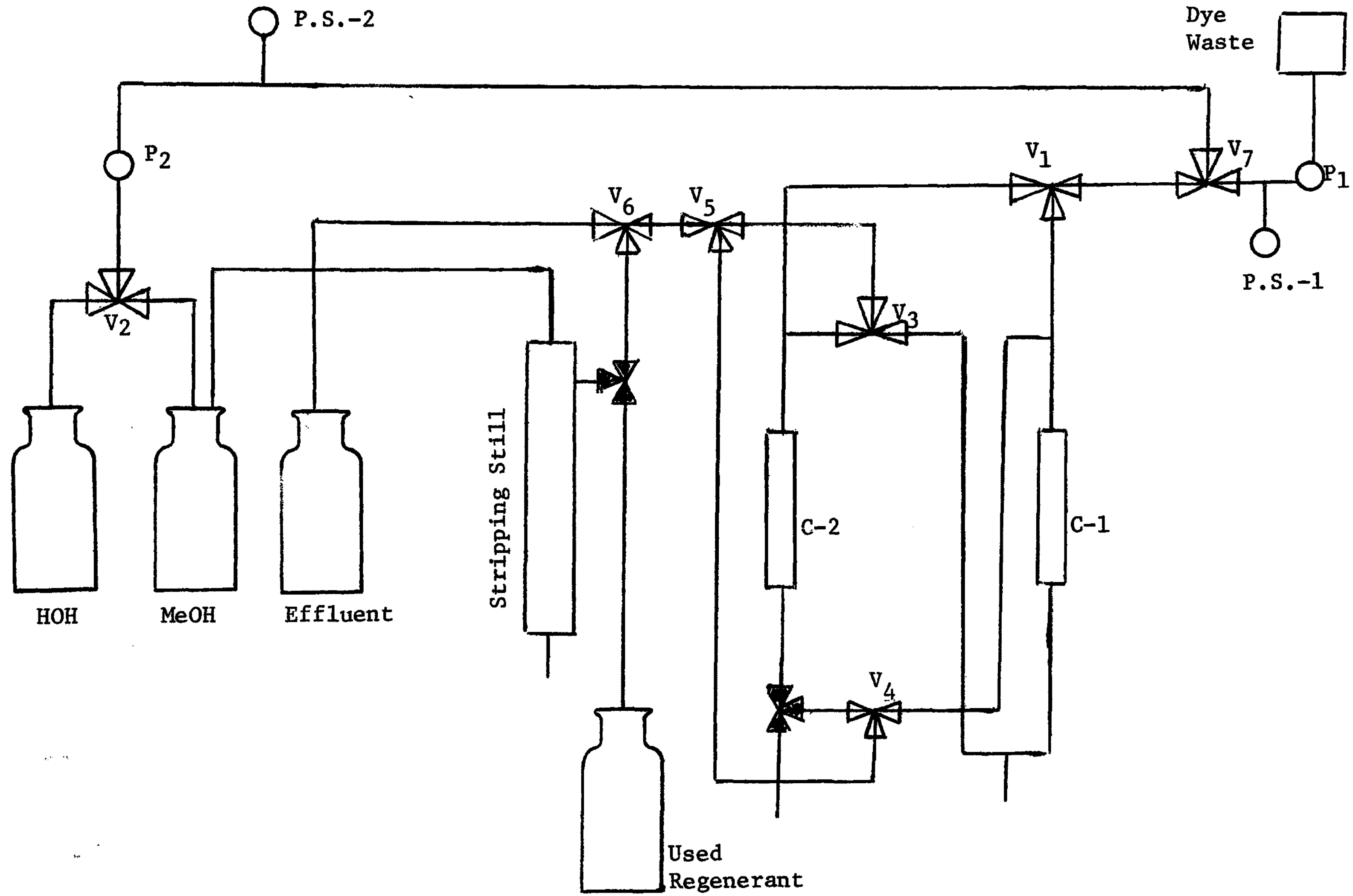


Figure 4. Sketch of bench scale pilot unit, each column containing same adsorbent resin.

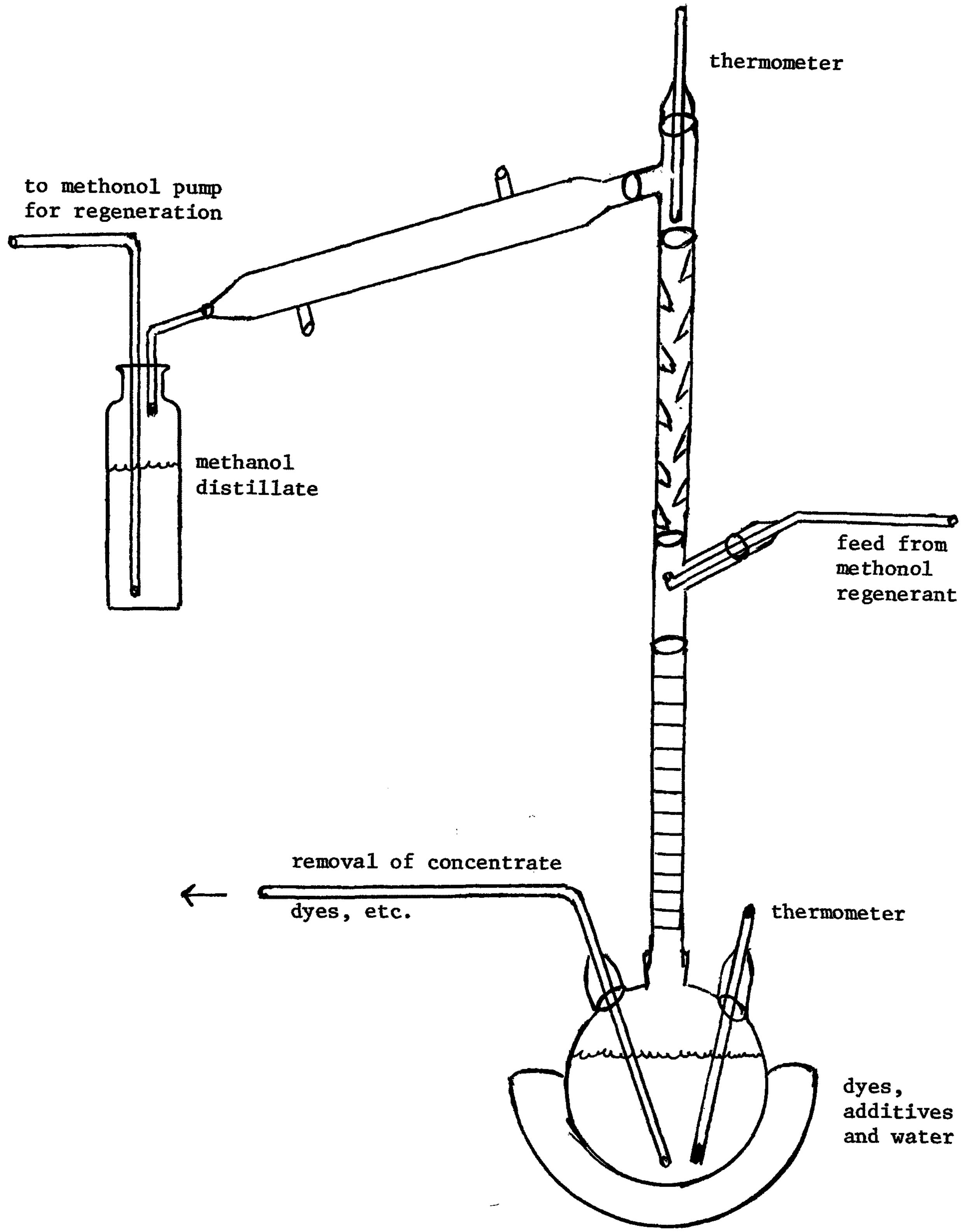
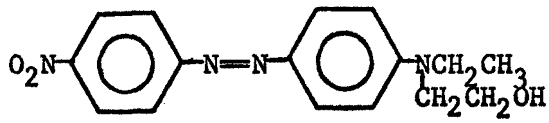
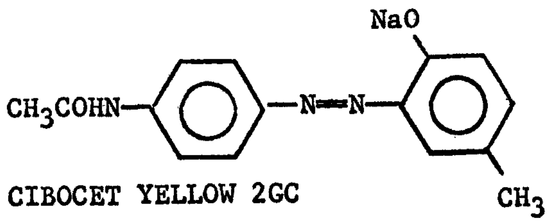


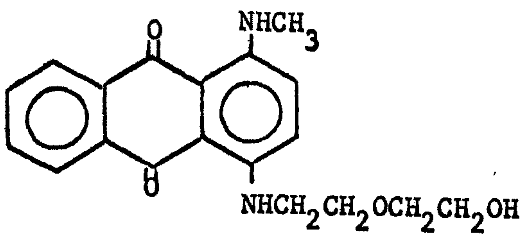
Figure 5. Semi-continuous stripping still.



TERASIL-SCARLET B

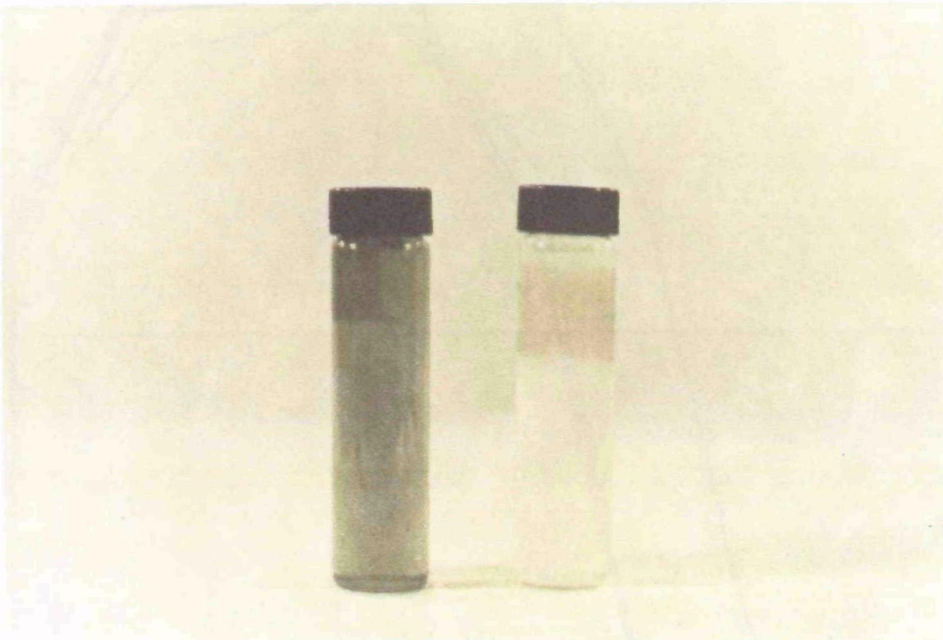


CIBOCET YELLOW 2GC



CIBOCET BLUE BN

Figure 6. Main colors, Glen Raven disperse dyes.



Influent Effluent

Figure 7. Hanes disperse dye wast, color photo showing complete removal of color after 120 BV, same resin.

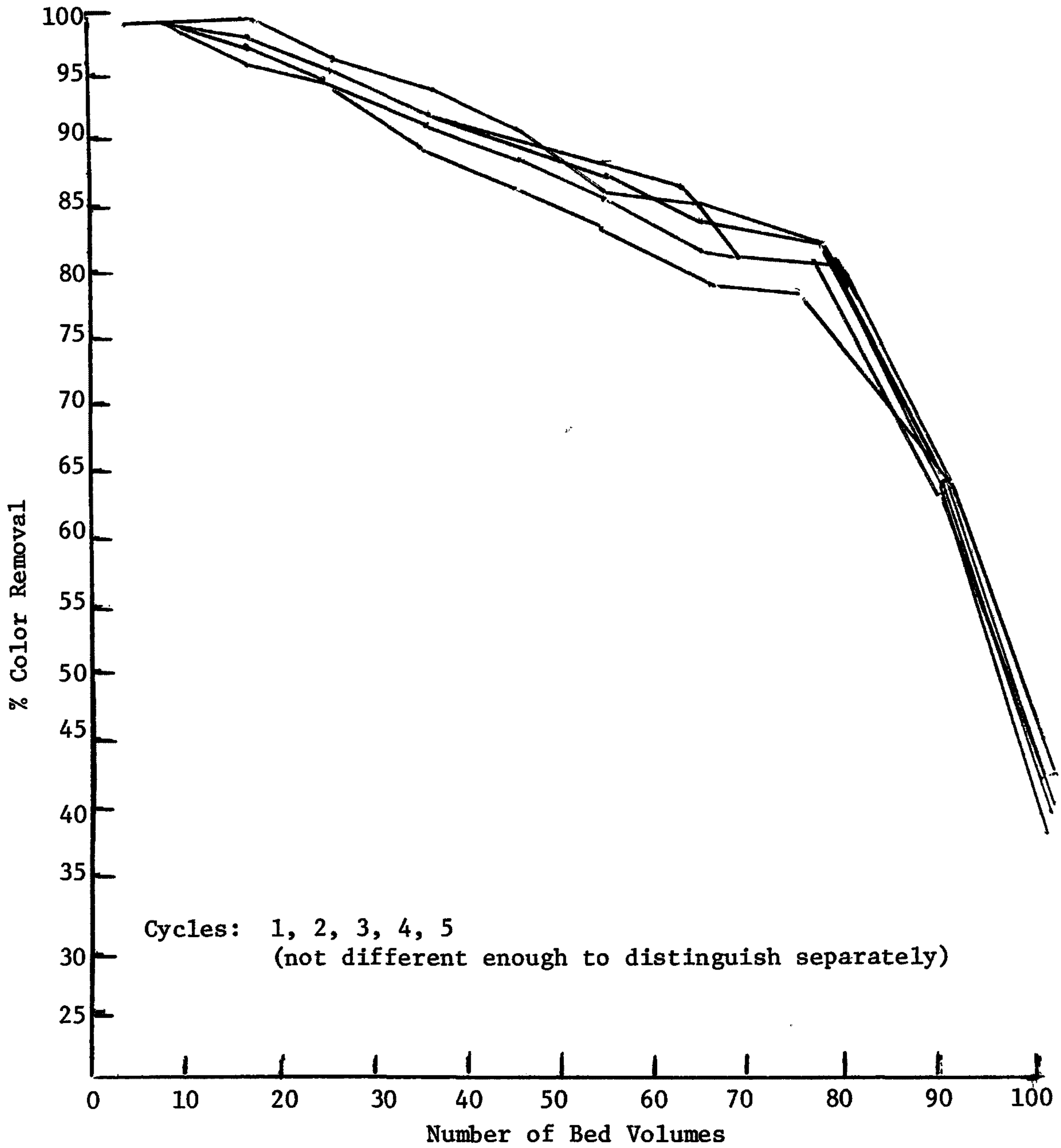


Figure 8. Hanes disperse dye waste, % color removal vs. bed volumes treated.

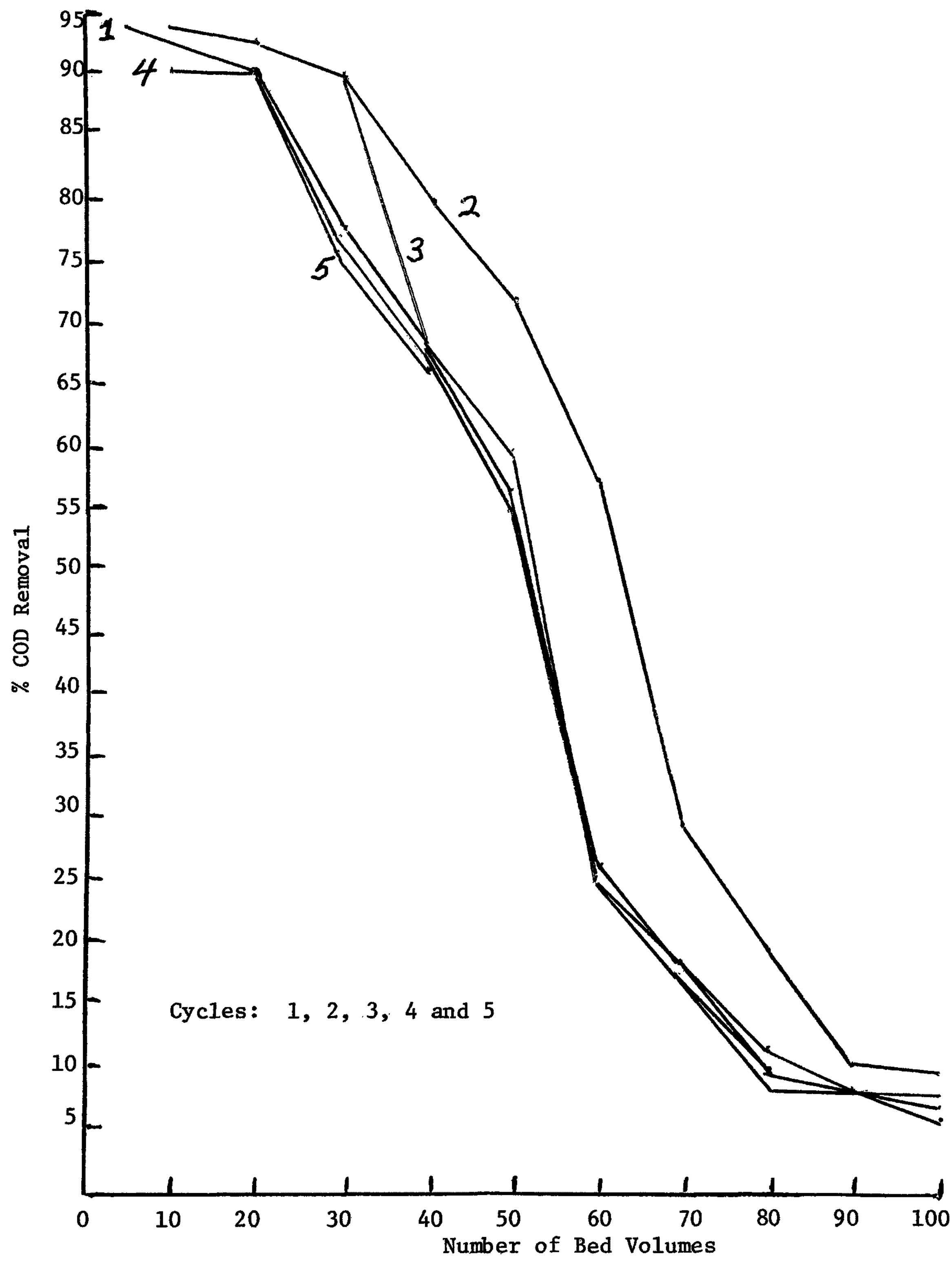


Figure 9. Hanes disperse dye waste, % COD removal vs. bed volumes treated.

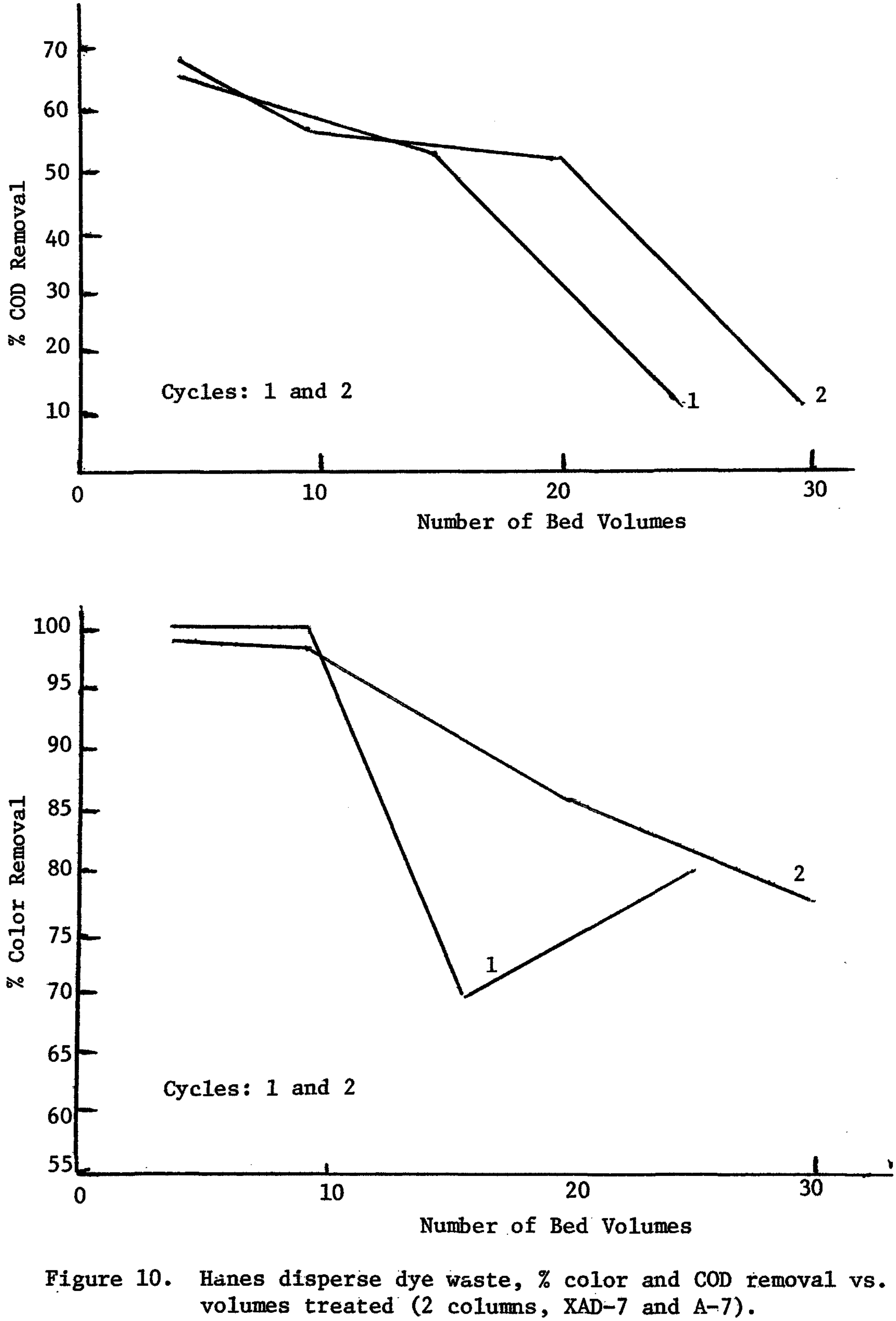
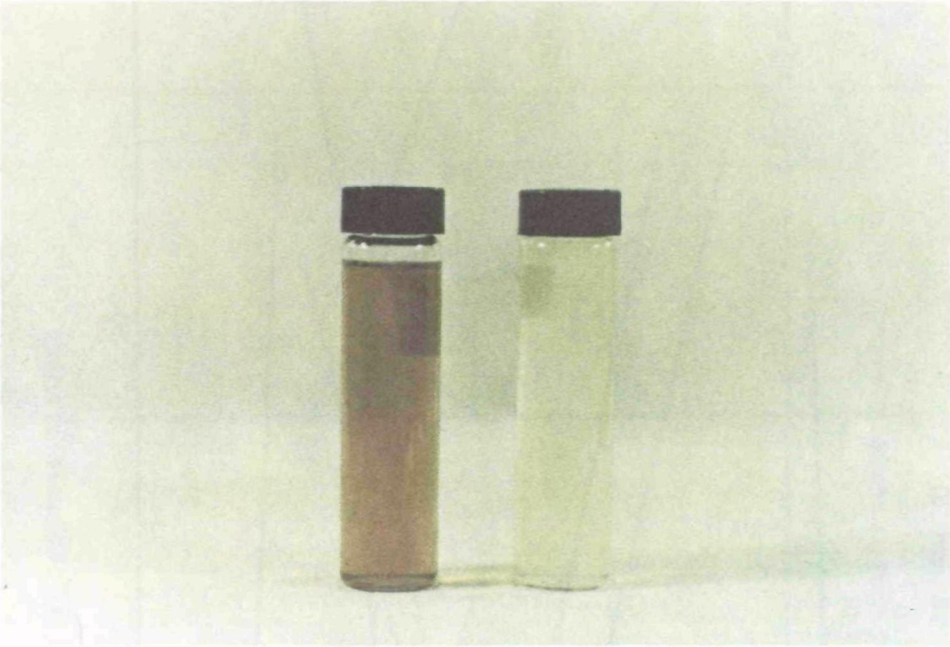


Figure 10. Hanes disperse dye waste, % color and COD removal vs. bed volumes treated (2 columns, XAD-7 and A-7).



Influent   Effluent

Figure 11. Glen Raven disperse dye waste, color photo of color removal.

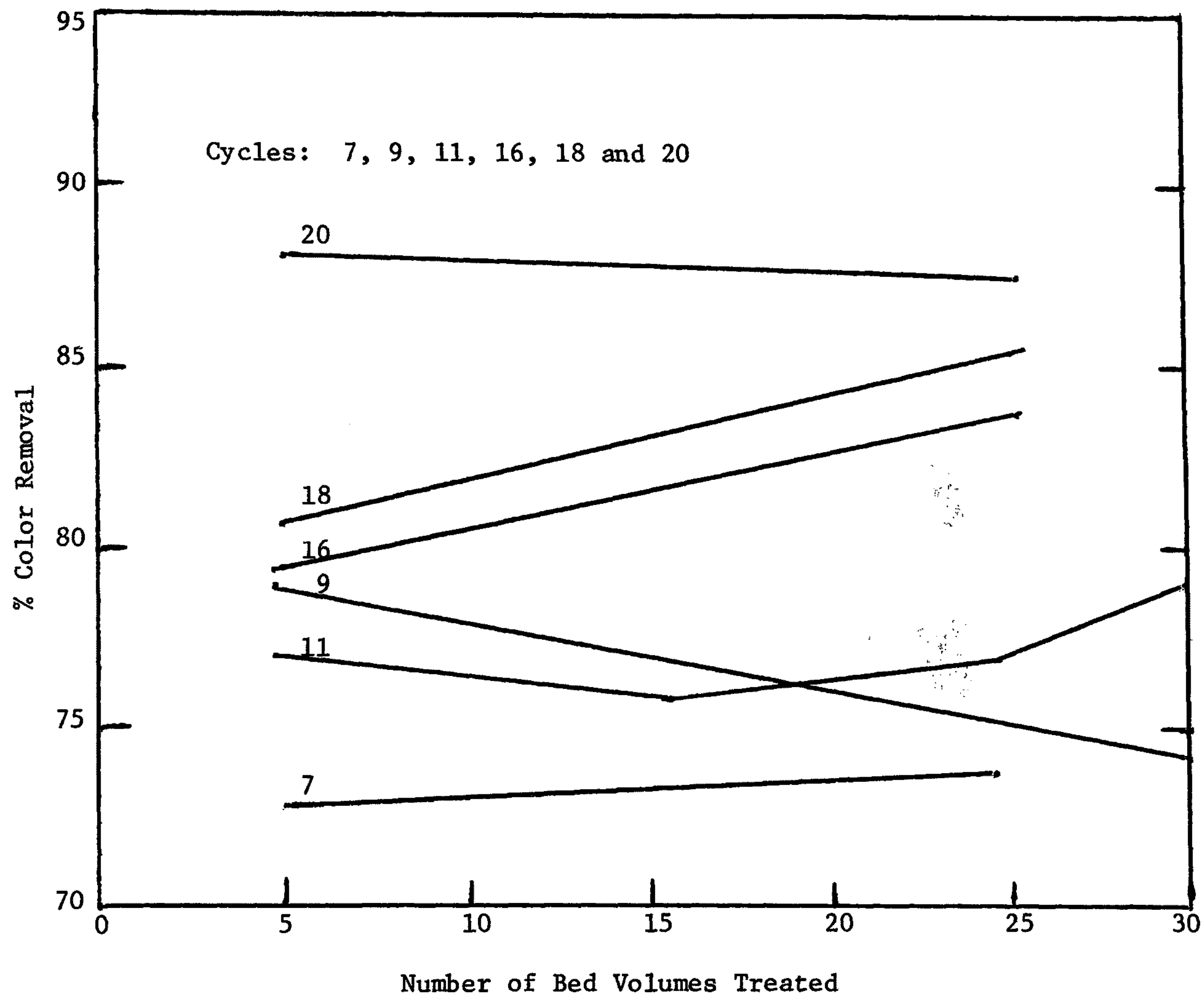


Figure 12. Glen Raven Disperse dye waste, % color removal vs. bed volumes treated.

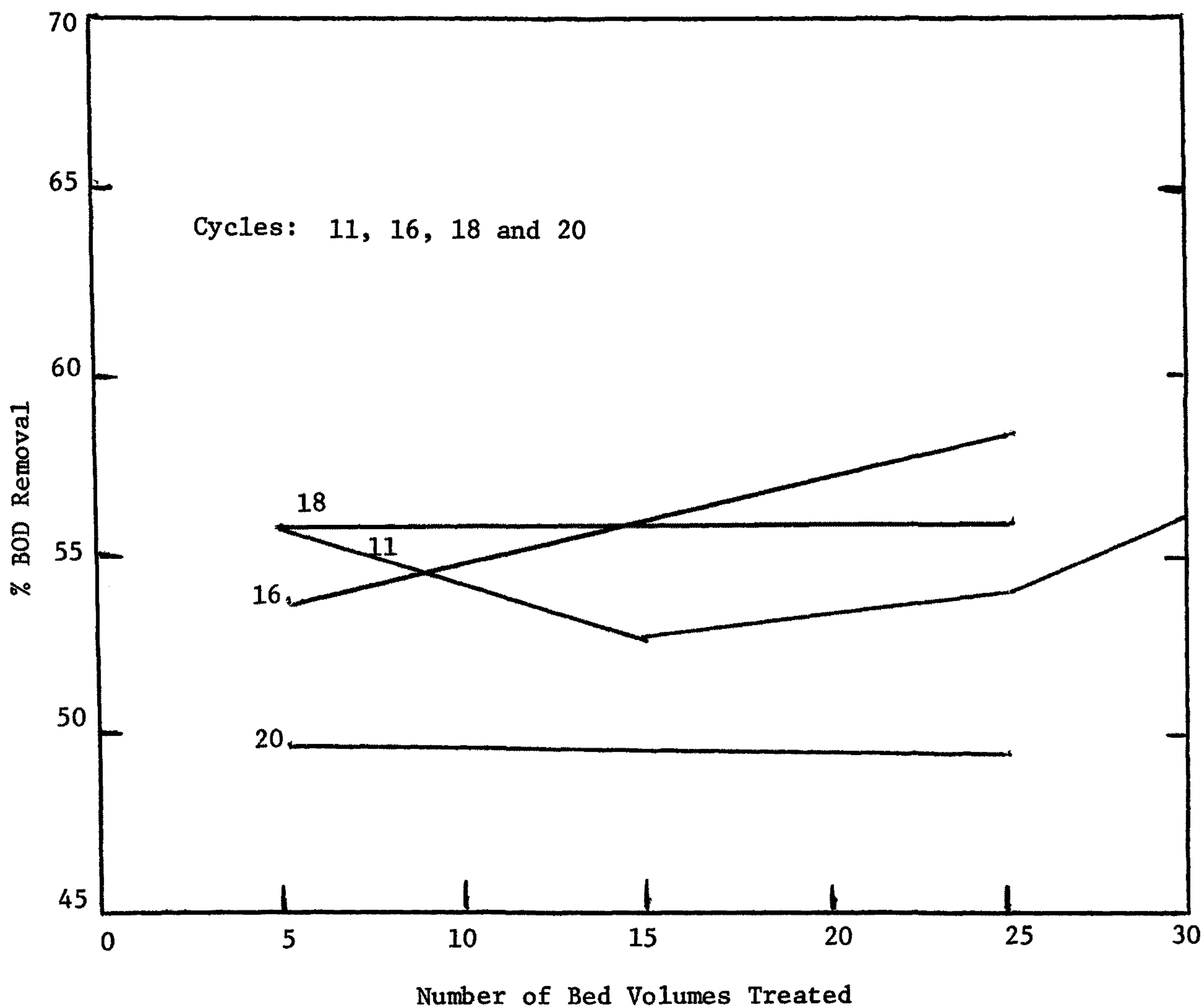


Figure 13. Glen Raven Disperse dye waste,' % BOD removal vs. bed volume treated.

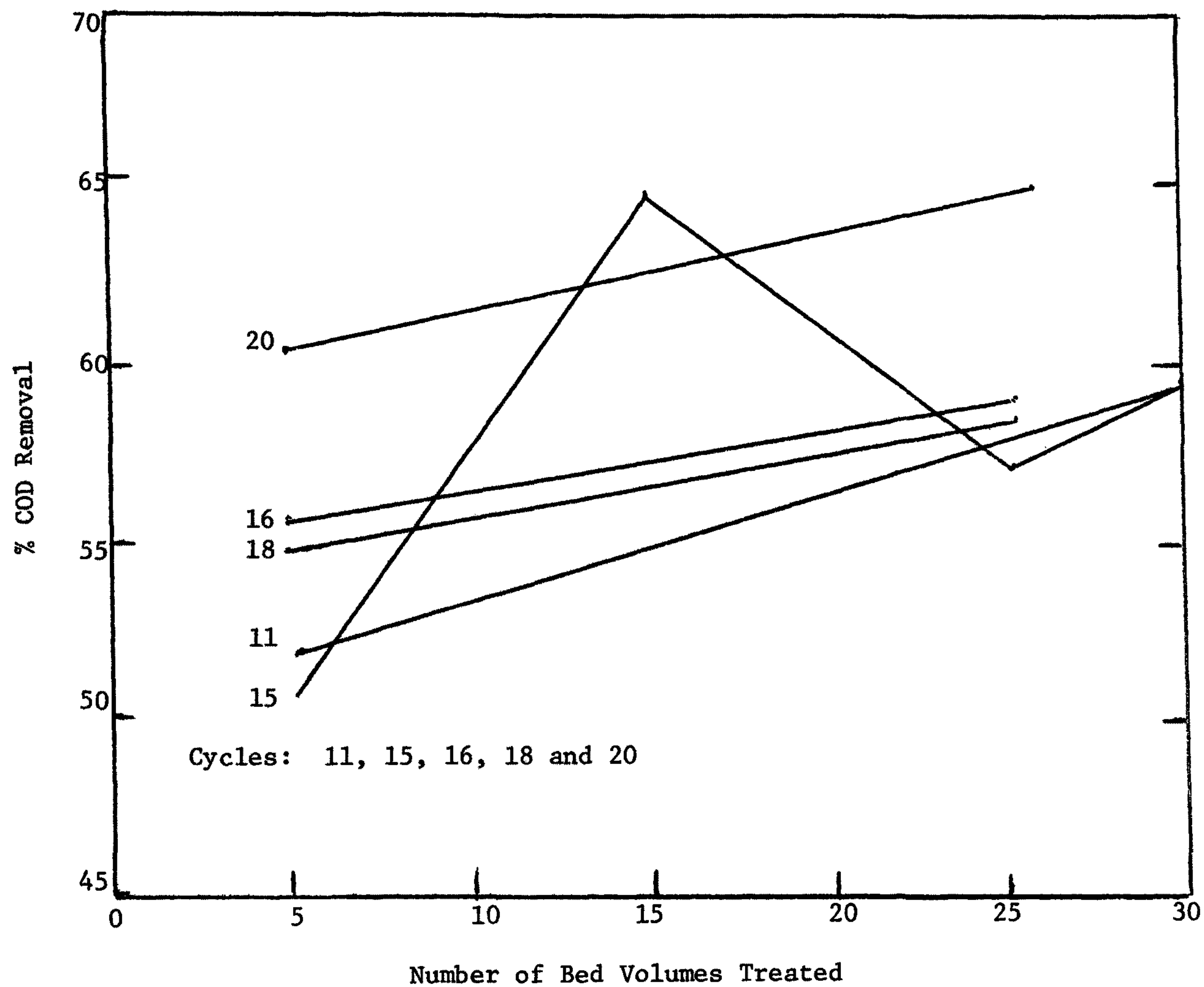
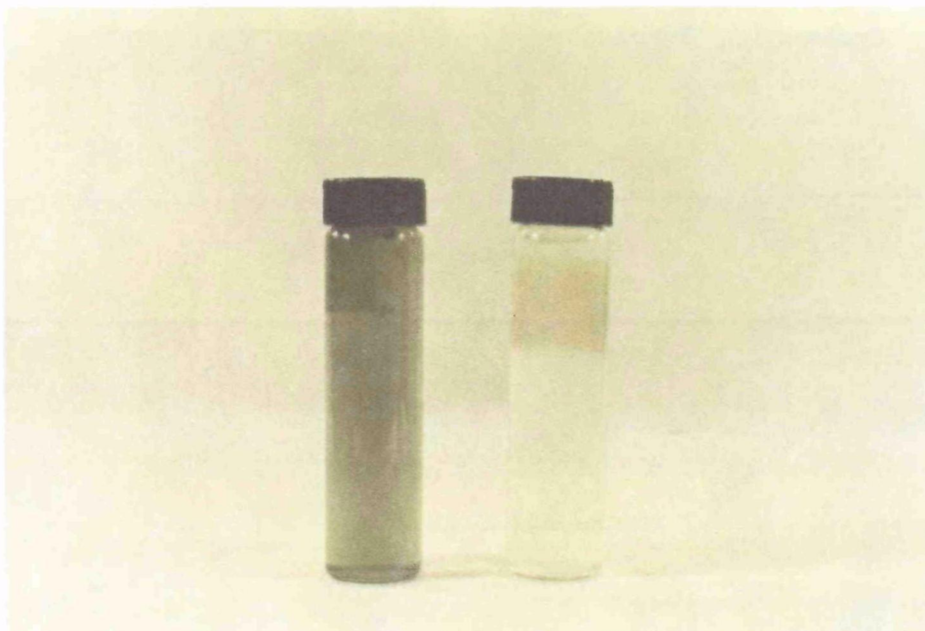
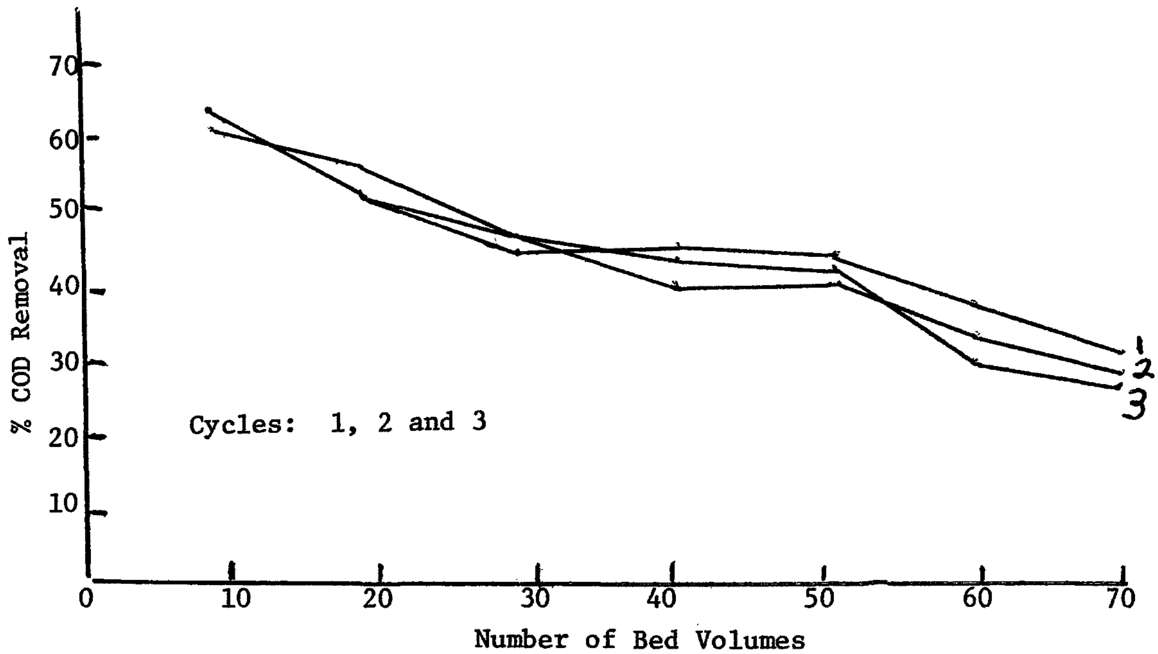


Figure 14. Glen Raven Disperse dye waste, % COD removal vs. bed volumes treated.



Influent Effluent

Figure 15. Hanes acid dye waste, color photo of color removal.



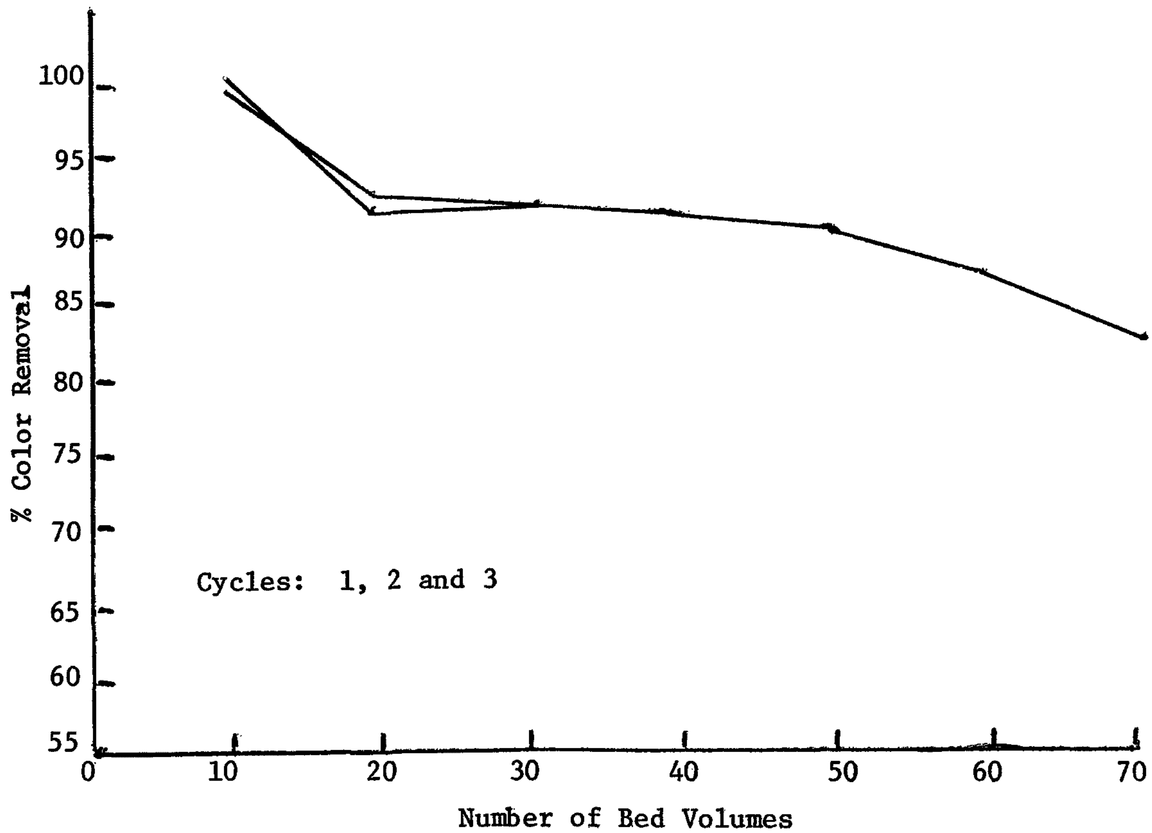
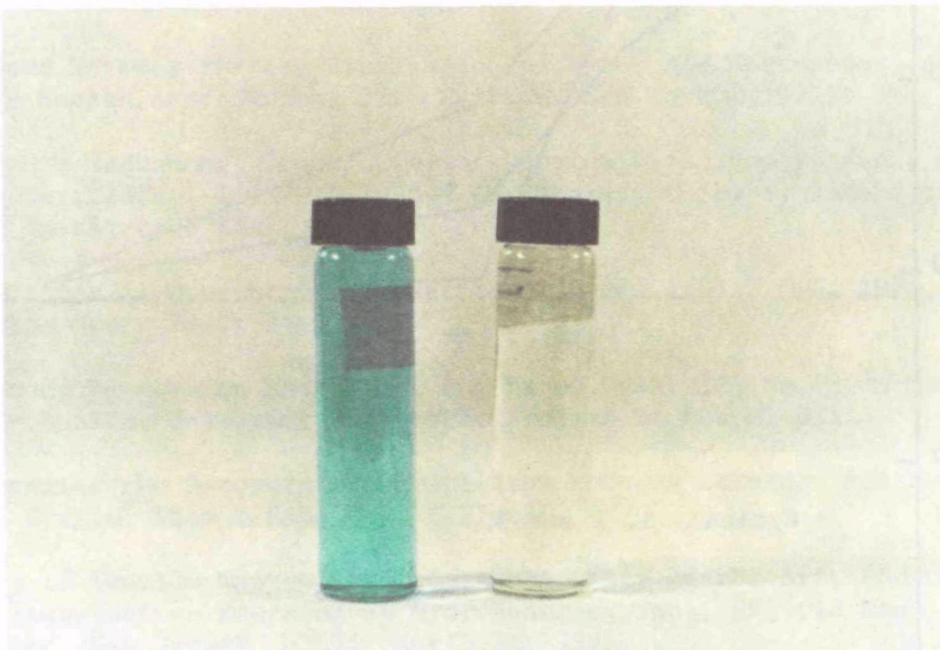


Figure 16. Hanes acid dye waste, % color & COD removal vs. bed volumes treated.



Influent Effluent

Figure 17. Sellers reactive dye waste, color photo of color removal.

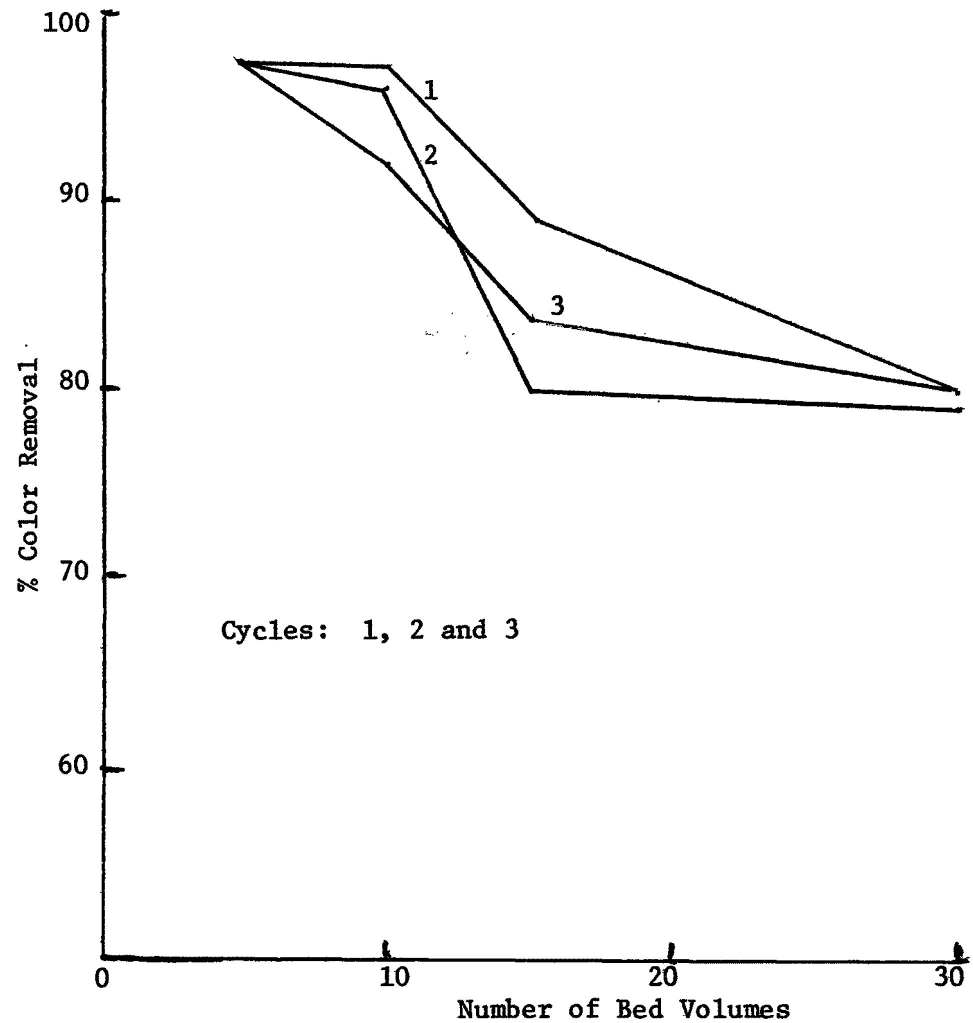


Figure 18. Sellers reactive dye waste, % color removal vs. bed volumes treated.

SECTION VI

REFERENCES

1. Proposed Criteria for Water Quality, Vol. 1, Report No. EPA-R-3-73-003. U. S. Environmental Protection Agency.

2. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 13th Edition, New York, (1971).

3. Abstracts Workshop: Ozone/Chlorine Dioxide Oxidation Products of Organic Materials. 11/17-19/1976. Cincinnati, Ohio, by International Ozone Institute & EPA.

4. Carcinogens in U. S. Drinking Waters, OZONews 1(3): 1-4, 1974, International Ozone Institute.

5. Dye Study Focuses on Treatment, ESE Notes, Vol. 12, No. 2, School of Public Health, University of North Carolina at Chapel Hill.

6. Process for the Recovery of Phenol from Aqueous Streams, Acetone Regeneration System, Rhom & Haas Co., Bulletin, 1976.

7. Survey of Textile Wastewater Treatment, State of the Art, Add-On Treatment Processes -- Prepared by Hydroscience, Inc., 363 Old Hook Road, Westwood, New Jersey 07675, April 30, 1976.

TABLE OZ-1

ESTIMATED CAPITAL COST FOR OZONATION OF WASTEWATER

	Capital Cost to Add Approximately 5 mg/l Ozone (Disinfection) (× $1,000)	Capital Cost to Add Approximately 1,000 mg/l Ozone (Decolorization) (× $1,000)
Injector Mixers	10.2	10.2
Reactors and Holding Tanks	101.5	101.5
Oxygen Compressors	11.6	69.6
Dryers	16.0	43.5
Ozone Generators	36.3	1,196.0
Ozone Decomposer	1.5	1.5
Piping	49.3	49.3
Electrical	29.0	43.5
Instrumentation	30.5	30.5
Painting	7.3	11.6
Sitework	14.5	14.5
Equipment Supports & Bldg.	72.5	72.5
Total Materials & Labor	$380.2	$1,644.2
Engineering, Contractor's Oberhead, and Fee	$114.1	$ 493.3
Total Capital Cost	$494.3	$2,137.5

RESIN/POLYMER ADSORPTION SYSTEM

OPERATING COSTS FOR 1 MGD PLANT

	dollars/year
Labor at $15,000/man/year	$ 60,000
Electricity at $0.02/KWH	1,000
Maintenance at 6% fixed capital	60,000
Steam at $2/1,000 pounds	38,000
Methanol at 97% recovery	214,000
Polymer replacement at five-year life	42,000
Total	$415,000

or

$1.15/1,000 gallons

or

$0.009/pound carpet

COSTS BY SUBCATEGORY

	Flow (MGD)	Capital	Operating/ 1,000 gallons	Operating pounds product	Total Annualized Cost* /1,000 gal
Wool Scour	1	$ 1,000,000	$1.91	$0.014	2.35
Wool Finish	2	1,500,000	0.98	0.014	1.21
Dry Process	0.35	530,000	1.43	0.002	2.11
Woven Fabric	2	1,500,000	0.43	0.009	0.76
Knit Fabric	2	1,500,000	0.43	0.009	0.76
Carpet Mills	1	1,000,000	1.15	0.009	1.59
Stock & Yarn	1	1,000,000	0.62	0.014	1.06

*ten years at 10%; includes operating costs.

TABLE CA-1

CARBON ADSORPTION SYSTEM COSTS (2.0 MILLION GALLONS/DAY SYSTEM)

Sub-category	Capital Cost		O & M Cost		Combined Cost	
	$ 1,000	$/1,000 gallons*	$/year	$/1,000 gallons	$/year	$/1,000 gallons
Wool Scouring	1,880	.42	318,408	.44	624,408	0.86
Wool Finishing	1,890	.42	327,712	.45	635,712	0.87
Woven Finishing						
(Simple)	1,800	.40	258,312	.35	551,312	0.75
(Complex)	1,950	.43	370,736	.51	624,736	0.94
Knit Finishing						
(Simple)	1,800	.40	253,190	.35	564,190	0.75
(Complex)	1,880	.42	316,360	.43	622,360	0.85
Carpet Mills						
(Simple)	1,810	.40	266,600	.37	561,600	0.77
(Complex)	1,850	.41	293,056	.40	694,056	0.81
Stock & Yarn Dyeing & Finishing	1,840	.41	284,264	.39	583,264	0.80

*Amortized over ten years at an annual interest rate of 10%.

A typical 1 MGD plant may have the following costs; assuming the concentrate can be reused or disposed. No costs for handling the concentrate are included, mainly because there is a lack of information on practicable methods of disposal other than reuse in manufacturing processes. Costs for pretreatment, which could include chemical coagulation, filtration, and pH adjustment, are also not included.

Operating costs	.50/1,000 gallons
Capital Costs (1 MGD rated capacity)	$1,500,000
Annualized capital cost	.67/1,000 gallons
Total cost, including amortization	$1.17/1,000 gallons

PROCESS SUMMARY SHEET

OZONATION

Effectiveness for Treatment of Pollutant	Powerful oxidant which is effective in destroying organic contaminants.
Parameters	Color, fecal coliforms, COD.
Textile Categories Applicable	Polishing step to remove dyes which are inert to conventional treatment. Also may be used for disinfection.
State of Technological Development	Process is well defined. Application to wastewater treatment has only recently become popular.
Application Data Availability:	
1. Benefit to Effluent	Can achieve zero BOD and coliforms, low suspended solids, high dissolved oxygen, low color and COD.
2. Control capability	Highly trained personnel would be required to operate and maintain equipment.
3. Dependability	No concrete data.
Energy Considerations	Fairly low - 1 to 3 kwh/1,000 gallons
Total costs including capital	$0.31/1,000 gallons for 5 mg/l disinfection: $1.89/1,000 gallons for 1,000 mg/l color, organic destruction.
Secondary/Environmental Factors	Ozone is toxic at high concentrations but is relatively unstable.
Other Considerations	Use of pure oxygen improves generation efficiency but increases cost and energy required. Some consideration should be given to ozone in combination with other AWT systems.

PROCESS SUMMARY SHEET

RESIN/POLYMER ADSORPTION

Effectiveness for Treatment Pollutant	90%-95% for color in waste 40% for BOD effluent 60% for COD streams
Parameters	BOD, COD, and color
Textile Categories that are applicable	Generally for all secondary effluents
State of Technological Development	Research and pilot stage. Only one application on a concentrated inplant dye waste stream, apparently performing well. Require pilot testing to determine applicability and design parameters.
Application Data Availability	
1. Benefit to Effluent	Not defined. May be useful for color.
2. Control Capability	Trained operators required to operate regeneration system.
3. Dependability	Not known.
Energy Considerations	Substantial for solvent regeneration system (4MM BTU/hour for a 1 MGD plant). Incineration of organic residue required.
Capital costs	$1 million for 1 MGD plant
Operating costs	Range 0.43 to 1.91/1,000 gallons treatment.
Total annualized costs	$0.76 to $2.35 per 1,000 gallons.
Secondary/Environmental factors	Spent polymer and removed organics disposal may prove a problem.

PROCESS SUMMARY SHEET

ACTIVATED CARBON ADSORPTION
GRANULAR BEDS

Effectiveness for Treatment of Pollutant	Activated carbon should be highly effective for BOD, COD, and color. While it may also reduce TSS, fecal coliforms and oil and grease, mechanical problems may preclude its use as the technology of choice for these parameters.
Parameters	BOD, COD, color
Textile Categories Applicable	All except dry processing, where it does not appear necessary.
State of Technological Development	Carbon adsorption is a well developed technology which has been in use for many years. New methods for the regeneration of spent activated carbon are still being developed and improved.
Application Data Availability:	
1. Benefit to Effluent	Color removal has been demonstrated in the textile industry. BOD and COD removal have been demonstrated in other industries.
2. Control capability	Carbon adsorption is easily controlled. Regeneration is more difficult to control.
3. Dependability	Adsorption is highly dependable. Regeneration requires a high level of skill to operate, and may be less dependable.
Energy Considerations	Carbon adsorption requires very little energy relative to biological treatment. Carbon regeneration is highly energy consumptive.
Total costs including capital	$0.75-0.94/1,000 gallons
Secondary/Environmental Factors	If carbon is regenerated thermally, controls will be necessary to prevent the discharge of air pollutants.
Other Considerations	More than half of the cost, and almost all of the energy requirements of activated carbon systems are associated with the regeneration of spent carbon. If a more effective means of carbon regeneration were developed, the use of activated carbon would be considerably more attractive.

PROCESS SUMMARY SHEET

REVERSE OSMOSIS

Effectiveness for Treatment of Pollutant	Excellent; product stream will contain zero suspended solids and fecal coliforms, low BOD, COD.
Parameters	Soluble BOD, COD
Textile Categories Applicable	All, with pretreatment of secondary effluent.
State of Technological Development	Numerous reverse osmosis installations on water supply. Process development continuing in area of membranes and suitability to wastewater treatment. Main applications in area of wastewater renovation and reuse with recovery of removed materials.
<u>Application Data Availability</u>:	
1. Benefit to Effluent	Product water should generally be reusable.
2. Control capability	Equipment easily controlled.
3. Dependability	Possible problems with membrane fouling, and membrane life. Modular construction facilitates maintenance.
Energy Considerations	Relatively low - pumping to high 300-500 psi pressure only required, however, hadnling of concentrated brine may require use of high energy process.
Total costs including capital	Variable depending upon design and salinity. Range is $.80 to $2.00 plus/ 1,000 gallons.
Secondary/Environmental Factors	None
Other Considerations	Handling of brine (10% to 30%) of inflow an important factor in feasibility of process. May require costly evaporation distillation/ incineration processes. Pretreatment for removal of suspended solids, pH adjustment, and biological growth control is required.

GLOSSARY

acid dye: a dye which has anionic groups which dissociate to give negatively charged coloured ions and applied from an acid dyebath to dye fibers that have basic groups (polyamides, wool, silk, etc.)

Amberlite XAD-7: a synthetic macroreticular polymeric exchange resin of styrene-divinyl benzene with methacrylic ester groups. Amberlite is the designation for Rhom & Haas Co., Philadelphia, Pennsylvania.

Amberlite XE-275: a weak base anion exchange resin.

biodegradable: the type of substance that can be broken down by microorganisms.

BOD: the amount of dissolved oxygen consumed in five days by biological processes breaking down organic matter in an effluent.

chelate: to form an heterocyclic ring compound which contains the heterocyclic metal in the ring.

COD: a measure of the amount of oxygen required to oxidize organic and oxidizable inorganic compounds in water.

disperse dyes: a class of substantially water-insoluble dyes applied from fine aqueous suspensions for dyeing hydrophobic man-made fibers (nylon, polyester, etc.)

Duolite A-7: an aminated phenol-formaldehyde condensate polymeric weak base anion exchange resin of Diamond Shamrock Co., Redwood City, California.

hyperfiltration: a synonym for Reverse Osmosis. A process used in the general sense of leaving behind large molecules or ions that are dissolved in a wastewater which is forced under pressure through a fine porous membrane. Relatively pure water is forced through leaving behind a concentrated solution containing the molecules or ions.

reactive dye: a dye, which under suitable conditions, is capable of reacting chemically with a fiber to form a covalent dye-fiber linkage.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-136	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Automatic Exchange Resin Pilot Plant for Removal of Textile Dye Wastes		5. REPORT DATE July 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Allison Maggiolo and J. Henry Sayles		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Bennett College Greensboro, North Carolina 27420		10. PROGRAM ELEMENT NO. 1BB610
		11. CONTRACT/GRANT NO. Grant R803455-01
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Grant Final; 4/75-4/77
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer for this report is Max Samfield, Mail Drop 62, 919/541-2547.

16. ABSTRACT The report gives results of an investigation of the use of adsorption resins to remove colored dyes from textile dyeing wastewaters, using an automated bench-scale pilot unit. This could make possible the reuse of the treated wastewaters in subsequent dyeing operations. The scale of operation facilitated accumulation of reliable data on which to base cost estimates for commercial operation. At a wastewater treatment rate of 20,000 gpd by resin adsorption, the amortized operating cost is estimated to be $3.47/1000 gal. An estimated capital investment of $86,000 will be required. These costs are believed competitive to other possible dye waste treatment processes. Use of properly selected adsorption resins was found to be effective for removing dyes from textile wastewaters. The finding is particularly important to the use of dispersed type dyes, which are largely inert to biological waste treatment processes, passing through such treatment relatively unchanged. In addition to the possible reuse of treated wastewater and elimination of possible damage to natural aesthetics, the removal of color substances reduces the tendency toward several other ecological problems in effluent receiving waters. Color substances tend to reduce light penetration and subsequent production of oxygen by photosynthesis, damaging marine life and algae growth. They also chelate metal ions, and some are toxic and suspect carcinogens.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Water Treatment	Pollution Control	13B	
Textile Industry	Adsorption	Resin Adsorption	11E	
Decoloring	Polymers		13H	07D
Dyeing				
Waste Water				
Circulation				

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 63
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)