Dyeing of Cotton Fabric with Reactive Dyes Using Ozonated, Spent Dyebath Water

ABSTRACT

A dyebath reuse study using reactive dyes was completed. Dyings were done with blue, red and yellow dyes and a dye mixture containing equal amounts of each of the three dyes. The spent dyebath water from these four dyeings was mixed, filtered and ozonated. The four shades were dyed again in baths containing 90% ozonated water and 10% fresh tap water. Only 10% of the amount of salt used in the original dyeing was required for the dyeings in recycled water since the salt in the 90% recycled water was still present. The experiment was repeated through five reuse cycles. Color reproducibility of dyeings done in the recycled water was excellent, closely matching the color attained using fresh tap water as the dyeing medium. The pH of the spent dyebath water decreased upon ozonation. Although the pH decrease was about the same in each new cycle, the amounts of caustic soda needed to adjust back to the original dyebath pH value increased with each cycle. This shows that ozonation of spent dyebath water produces substances which tend to buffer the solution.

KEY TERMS

Dyebath Reuse
Effluent
Ozonation
Spectrophotometer
Wastewater

Textile manufacturing plants are required to remove color from effluents. Traditional treatment methods such as extended aeration remove only part of the color from dyehouse wastewater. Additional treatments that may be used to remove color after traditional biological treatment include chemical coagulation, adsorption on carbon and oxidative decolorization with ozone or chlorine. These tertiary treatments are expensive when applied to the total volume of wastewater from a dyeing and finishing plant.

Color removal at the point source in the plant instead of after the color has been diluted by waste streams from other wet processes is another approach to color pollution abatement. Decolorization of spent dyebath water immediately after draining the dye machine has several possible benefits. First, the cost of an advanced technology such as ozonation or hydrogen peroxide may be economical when applied to a small volume of colored water although it is too costly for mixed wastewater treatment. Furthermore, treatment for color removal at the dye machine gives the plant the option of reusing the chemicals such as salt, water and energy. Alternatively, the plant may discharge the decolorized water into the plant's waste treatment facility.

Several laboratory studies and industrial demonstrations of dyebath reuse are reported in the literature. In one approach to dyebath reuse, the dyebath was analyzed spectrophotometrically at the end of the dye cycle and the required amounts of dyes and chemicals were added to reconstitute the dyebath for reuse. The method was applicable only if the residual dye in the bath was not changed by the dyeing process. Cook and co-workers used this method in pilot plant scale studies on dyebath reuse with disperse dyes. Subsequent plant trials on dyebath reuse in dyeing nylon 6 and nylon 66 pantyhose with acid dyes showed savings in energy, water, dyes and chemicals. A recent study at the University of Rhode Island showed that spent direct dyebaths can be analyzed spectrophotometrically and reconstituted for subsequent direct dyeing on cotton. Another approach to dyebath reuse is to remove residual coloring matter prior to reuse so that the color does not interfere with subsequent dyeings.

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The method may be applicable to any class of dyes provided sufficient color is removed so that the residual color does not interfere with subsequent dyeings. Burkinshaw reported that the residual dyes in spent reactive dyebaths interfere with subsequent dyeings even though the dyes were hydrolyzed during the dyeing process. Research at Auburn University indicated that use of chlorine and ozone were effective in decolorizing dyebath water for reuse in dyeing. Chlorination was effective in removing direct, acid and reactive dyes, while it was less effective for disperse dyes. Chlorination was concluded to be inefficient in decolorizing disperse dyes because of low solubility and particulate state of disperse dyes in water. Ozone decolorized all classes of dyes in the study. The reaction of insoluble disperse dyes with ozone was much slower than that of soluble dyes such as acids, direct and reactive dyes.

Residual coloring matter can also be removed from spent dyebath water using membranes. A recent paper described the use of nanofiltration and reverse osmosis to concentrate the dye in spent reactive dyebaths and rinse waters. The salt contained in the permeate from nanofiltration can be recycled in dyeing. The hydrolyzed reactive dyes in the concentrate still require disposal.

Many studies have been published concerning the removal of color from textile wastewater. Russell Corp. studied chlorination for color removal after biological treatment (aeration) of wastewater. The studies showed that 150-250 ppm chloride was required at pH 7.0 to 9.7 to decolorize wastewater from 1000 ADMI units to below 300 units. Only 50 to 150 ppm was required when the wastewater was in the pH range of 5.0 to 7.0. This study also

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showed that 5 to 15 minutes contact time was required for decolorizing wastewater with chlorine.

Snider and Porter used ozone to decolorize acid, direct, basic and disperse dyes. The direct, acid and basic dyes at 0.1% concentration in water decolorized in 15 to 30 minutes treatment time with 270 to 540 mg/L ozone applied. The disperse dyes decolorized very slowly and required very large doses of ozone. Horning studied chlorine and ozone for removal of color from textile wastewater. Carriere reviewed ozonation of biologically-treated waste from carpet mills and found that ozone at low dosage rates was effective in decolorizing the wastewater. Beszedits reported on ozonation for color removal from biologically-treated waste and reported that the method was effective for waste-containing reactive dyes but not for sulfur and naphthol dyes. Gregor reported that addition of hydrogen peroxide to wastewater enhanced color removal by ozone. Fenton's Reagent, which is believed to function by a mechanism similar to ozone, has also been recently studied for color removal from textile wastewater. Removal of disperse dyes was reported to be enhanced by Fenton's Reagent. A laboratory study of dyeing with spent dyebath water renovated by ozonation was performed. The object was to better understand the feasibility of and variables involved in dyebath reuse based on ozonation.

**Experimental Procedure**

**Dyeing**

The three vinyl sulfone reactive dyes shown in Table I and their mixtures in equal parts were used for this study. A 100% cotton bleached fabric was used. Dyeings were done on 15-gram samples at a 30:1 liquor-to-fiber ratio in an Ahiba Mathis Texomat laboratory dyeing machine. The formulation contained the following:

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>C.I. Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remazol BR</td>
<td>Reactive Blue 19</td>
<td>![Chemical Structure]</td>
</tr>
<tr>
<td>Blue R Special</td>
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<tr>
<td>Remazol Brilliant</td>
<td>Reactive Red 21</td>
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<tr>
<td>Red BB</td>
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</tr>
<tr>
<td>Remazol Golden</td>
<td>Reactive Yellow 17</td>
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<tr>
<td>Yellow G</td>
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The "all-in" dyeing method was used. That is, all ingredients were added to the bath before the fabric was added. Fabric was entered in the dyebath and agitated for five minutes at room temperature. Then the temperature was raised to 160°F and held for 30 minutes.

At the end of the dyeing, the dyebath water was collected and saved. The dyed fabric samples were rinsed with tap water and washed for ten minutes at 160°F in a solution containing 1% of acetic acid. The fabrics were rinsed again with tap water and air dried.

The four different colors of spent dyebath water were combined and filtered through Whatman No. 2 filter paper. The filtered water was ozonated for 15 minutes. The ozonated water was divided into four equal parts from which new dyebaths were made by adding amounts of dye equivalent to that used in the original dyeings. About 10% fresh water was added to make up for water lost by evaporation and in the fabric. Caustic soda was added to raise the pH back to the level in the original dyebath, and salt was added to adjust the conductivity back to that of the original dyebath. These dyebath solutions were then used to dye another set of four samples. The reuse process was repeated through a total of five reuse cycles.

**Ozonation**

A Welsbach T-816 Ozonator was used. It produced 4.32 g/hr of ozone at approximately 2% concentration in oxygen feed gas and a flow rate of two liters per minute. The operating conditions of the ozonator were 110 volts AC, 200 watts and 8 psig oxygen pressure. Ozone was passed through a fritted glass diffuser into spent dyebath water in a glass tower approximately 25 cm tall. The excess ozone gas was passed through a gas wash bottle containing potassium iodide solution to trap the ozone. Ozone consumption was measured by thiosulfate titration of the iodine liberated from the potassium iodide solution. About 99% of the color was removed by ozonation to prepare the spent dyebath for reuse.

**Color, pH, Conductivity**

**Measurement and Pictures**

Color was measured with a Bausch & Lomb Color Scan II spectrophotometer. Color coordinates and color differences were calculated by Milton Roy QCS software using illuminant D6500 and 10 degree standard observer. A Fisher Accumet Model 915 pH meter was used. Conductivity was measured with YSI Model 35 conductivity meter. Photomicrographs were made with Meiji Techno Co. LTD MEII EMZ-TR microscope, Javelin MOS solid state camera JE 3362 and Hitachi VY 150A color video printer.

**Results and Discussion**

**Dyeing Results**

The color differences in L*, a*, b* color space between samples dyed using tap water and samples dyed using ozonated spent dyebath water are shown in Table II.

All L* values for the yellow, red and blue colors were slightly negative when compared to the standards dyed in tap water. However, the differences were so small that the colors were not visibly different. The greatest color differences were in the red samples which averaged 0.93 color difference units from the standard for the five recycles. These differences were not visually distinguishable. Spectrophotometric reflectance curves for these red samples were almost superimposable.

**Effect of Ozonation on pH and Conductivity**

Table III shows pH values of the spent dyebath before and after ozone treatment. An interesting observation is that the pH fell nearly the same amount after each ozone treatment, but the amount of caustic soda needed to adjust pH to that of the original dyebath pH of 10.95 increased with each recycle. Fig. 1 graphically shows this trend in alkali required to adjust the pH. The effect of ozonation on pH suggests formation of acidic dye decomposition products. Since the spent dyebath was decolorized only to the colorless point, oxidizable organic fragments remain in the bath after
ozonation. Some of these fragments are further oxidized in subsequent cycles and buffer the solution. Table IV shows conductivity values of the spent dyebaths before and after ozonation. Ozonation did not measurably affect conductivity of the solution. Although ozonation produces soluble dye decomposition, the number of new ions formed is insufficient to change the conductivity of the highly conductive dye formulations used in this project. Since ozonation did not affect the conductivity much, salt addition was needed to adjust the conductivity before the water was recycled in dyeing. The amount of salt added in each subsequent dye cycle was just that proportion needed to adjust the conductivity of the added fresh makeup tap water.

Decolorization of Spent Dyebath Water by Ozonation

Fig. 2 shows a decolorization rate isotherm for a 1100 mL sample of spent dyebath containing all three of the dyes. The initial dyebath contained 2% on weight of fabric of each of the three dyes or a total dye concentration of 0.67 g/L (as dye product). Assuming 70% fixation and 30% hydrolysis in dyeing, the residual dye concentration in the spent dyebath water was about 0.20 g/L before ozonation. About 93% of the color was eliminated in the first five minutes of ozonation. While 15 minutes of treatment with ozone was required for 99% color removal. The amount of ozone consumed as 50% efficiency of ozone utilization was 160 mg/L in 5 minutes and 480 mg/L in 15 minutes.

Blank Dyebath Dyeing

Blank "dyeings" were done with ozonated spent dyebath water in the Ahiba Mathis dyeing machine exactly as the actual dyeings in recycled water but without dye. The blank dyeings decreased the lightness of the bleached fabrics about 0.50 lightness \((L^*)\) units. This difference in fabric brightness of the bleached and blank dyed samples could not be detected visually. These lightness \((L^*)\) results of the blank dyeings are consistent with those reported in Table III for dyeings in recycled water with the blue, red and yellow colors.

Effect of Filtration of the Spent Dyebath

Preliminary recycle experiments gave poor brightness in the yellow and red shades. This decrease in brightness was traced to the presence of small undisolved particles in the dyebath after dyeing. Therefore, a filtration step was included in the recycle procedure. After each dyeing cycle the spent dyebath water was filtered through Whatman No. 2 filter paper. The filtration step solved the problem of dulling of the shade in ozonated water.

Conclusions

Excellent color reproducibility was
Ozonation lowered the pH value of spent dyebath water and the amount of caustic soda needed to adjusted pH to the original value for reuse in dyeing increased with each cycle. This phenomenon implied that buffer-like substances formed because of ozonation.

Acknowledgements
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References

How's Your Laboratory Detergent Supply?

AATCC Detergent 124—Used for testing smoothness appearance, dimensional changes in home laundering and soil release. 50 lb. container $115 plus shipping & handling. Order No. 8351

AATCC Detergent WOB—Without optical brightener, used in testing colorfastness to washing. 20 lb. bucket $65 plus shipping & handling. Order No. 8352

AATCC Detergent 171—Used for AATCC TM 171 — simulated floor cleaning by hot water extraction method. 20 lb. bucket $65 plus shipping & handling. Order No. 8722

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