color reduction & removal
SEMINAR

JUNE 17, 1998

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S E M I N A R

AGENDA

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North Carolina's Department of Environment and Natural Resources' Division of Water Quality

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Emerging Technologies for Color Removal
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Use of Real Time Dyeing Technology and Other P2 Techniques for Reducing Color in the Effluent
Dr. Warren Jasper and Dr. Brent Smith, North Carolina State University College of Textiles

Discussion and Closing Remarks

Seminar Announced - Reducing/Removing Color from Wastewater

RALEIGH -- A one-day seminar on reducing or removing color from wastewater is scheduled for June 17 at the Adam's Mark Hotel in Charlotte.

Topics include North Carolina state government's perspective on wastewater color reduction, current color removal practices by North Carolina textile operations and municipalities, future trends in color removal technologies, and in-plant techniques for color reduction.

Textile companies discussing their efforts in color reduction include Cone Mills Corp., Flynt Fabrics & Finishing Inc., and Americal Corp.

The seminar is being sponsored by the North Carolina Division of Pollution Prevention and Environmental Assistance, the North Carolina Division of Water Quality, Duke Power Company, the South Carolina Center for Waste Minimization, and the Georgia Pollution Prevention Assistance Division.

Registration is $40 before June 10 or $70 at the registration desk. Please contact John Burke at (336) 249-1480 for more information.

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Date Posted: May 21, 1998

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Introduction

JOHN BURKE
NORTH CAROLINA
DIVISION OF POLLUTION PREVENTION AND ENVIRONMENTAL ASSISTANCE

Color is widely considered solely an aesthetic pollutant although there are studies currently evaluating aquatic toxicity, photo toxicity, and metal bioavailability for specific dye classes. As a result, there has been little regulation of this pollutant. Although its environmental impact may be considered lower than many other pollutants, color is much more readily identifiable by the average citizen.

This issue puts many in the textile dyeing industry and dyestuff manufacturing industry in a somewhat awkward situation. The industry is not mandated to reduce color in the effluent, and doing so typically means significant capital investment in non-process oriented equipment and chemicals. By doing nothing, the industry leaves the potential for bad publicity for reducing the quality of one of North Carolina's greatest assets.

It is the aesthetic issue that makes this pollutant so difficult to regulate. Unlike many other pollutants that have water quality action levels based on testing data, the amount of color that is problematic depends on the perception of the observer. Furthermore, the environment of the stream effects that perception. For instance, a reddish colored effluent entering a fast-moving clear stream surrounded by forest in the western part of the state will be perceived differently from that same effluent entering a slow-moving murky river in the heart of an industrial park in the eastern part of the state.

While the future of color regulation at the state and national level is undetermined, the issue currently is being addressed at a local level. There are a number of industries in North Carolina and other states that are reducing color in the effluent due to local public pressure as well as a desire to "do the right thing." In light of the above example, handling the problem at a local level makes sense. The amount of color a discharger will need to reduce to eliminate its impact on the aesthetics of the receiving waters depends on the background color of the receiving water, the size of the receiving water, and other characteristics.

See back of page.

The following case studies represent textile companies and municipal wastewater treatment works in North Carolina that currently are reducing effluent color with various technologies. These case studies discuss various pressures for reducing color, costs, and benefits of color reduction and removal, and various technologies successful in color removal. Additionally, there is a paper and presentation slides of new technologies and pollution prevention techniques for reducing effluent color.

The purpose of the "Color Reduction and Removal Seminar" is to increase the awareness of the color issue and increase the sharing of information concerning color reduction technology. It is important for industry representatives to stay abreast of the new technological advances that can reduce environmental impacts as well as potentially improve operating efficiency. Many technologies currently in development provide the potential for a "win-win" situation, where the textile industry can be seen as a environmental steward while also improving the bottom line.

To continue the sharing of information on color reduction successes and failures as well as other environmental issues concerning the textile industry, textile industry representatives are encouraged to become members of the P2-tex listserver managed by the North Carolina State University's College of Textiles. Representatives interested in joining this listserver should e-mail a subscription request to brent_smith@ncsu.edu. By using this medium for technology and information transfer, industry representatives are more apt to select technologies most appropriate for their situation and eliminate unnecessary expenditures.

Speaker Information

Speaker Biographies

John Burke

Mr. Burke is an environmental engineer with the North Carolina Division of Pollution Prevention and Environmental Assistance, where he has worked since 1992 providing technical assistance and technology transfer to North Carolina business and industry. Mr. Burke has provided on-site process and wastewater technical assistance to more than 50 textile industries in the state. Mr. Burke is Co-chairperson of North Carolina American Water Works Association's Industrial Wastewater Committee. Mr. Burke has co-authored a paper with Donald Brown of Sara Lee Knit Products, *Color Removal and Brine Reuse from Reactive Dyebath Wastewaters*, for the 1996 North Carolina AWWA/WEA Conference. He is a member of the WEF and AATCC. He received a bachelor of science in biology from the University of North Carolina - Wilmington in 1990 and a master of environmental engineering degree from North Carolina State University in 1995.

Tom Mullis

Mr. Mullis currently is Director of Facilities Engineering for Flynt Fabrics & Finishing. He also is working on a project to reuse water from a batch dyeing plant. Prior to joining Flynt Fabrics & Finishing, Mr. Mullins developed an extensive background with Burlington Industires, Crompton Knowles Corporation, Spiezman Industries, Walter Kiddie, and General Electic. He serves as a consultant with the Mill Point Consulting Firm. His areas of expertise include environmental compliance, source reduction, decoloring waste water, and water reuse.

Michael E. Ellis

Mr. Ellix currently is Business Manager of Textile Chemicals for Clariant Corporation. He has been working in the chemical manufacturing industry since 1977. He has published more than 12 articles dealing with industrial chemical use and operations. Mr. Ellis is a member of the AATCC, TAPPI, and the AIC. He serves as chairperson of the TAPPI High Yield Brightening Subcommittee and member of the TAPPI Chemical Methods Committee. He was a recipient of the RW Barton Award for Excellence in Service to the Pulp and Paper Industry and an American Cancer Society Research Grant.

Bob Cundiff

Mr. Cundiff has more than 25 years in the environmental field. He worked eight years for an environmental engineering firm in the midwest before joining Hoechst in 1979. From 1979 to 1994, Mr. Cundiff was responsible for the environmental, safety, and health areas at the production facility in Mount Holly, North Carolina. This facility manufactures 300 products including dyes, resins, textile auxiliaries, and other specialty chemicals. In his current position as Environmental Specialist with Dystar L.P., Mr. Cundiff provides environmental support to Dystar's customers. With his background in chemical engineering, Bob's efforts are focused on minimizing environmental problems through source reduction, product substitution, and cost effective treatment alternatives.

Jeff Golliher

Mr. Golliher has 14 years' experience in textile dyeing and finishing. Mr. Golliher currently works as Superintendent of Dyeing & Waste Water Manager for Americal Corporation.

Leonard Stogner

Mr. Stogner is President of Environmental Wastewater Services and Vice President of Rayco Utilities Inc. both in Concord, North Carolina. Mr. Stogner formerly worked with Bisanco International in Columbia, South Carolina. Mr. Stogner has designed and installed industrial pretreatment and treatment systems in Canada, New Jersey, New York, Virgina, North Carolina, South Carolina, and Georgia. He has developed and received a patent for a method of removing color while reducing toxicity in textile effluent. Mr. Stogner has several certifications including NC Grade IV, SC grade B, and Hazardous Materials Technician. He has an undergraduate degree from Clemson and an engineering graduate degree from Duke University.

Arthur Toompas

With Cone Mills Corporation since 1969, Mr. Toompas presently serves as the Corporate Environmental Engineer. Mr. Toompas served as past chairman of the North Carolina Textile Manufactures Association's Environmental Committee and Preservation Committee, past president of North Carolina's Air Pollution Control Association, and past chairman of the Institute of Textile Technology's Environmental Committee. Mr. Toompas serves as honors chairman for the American Association of Textile Chemist and Colorist's Environmental Committee. He is a member of the ATMI, WEF, AICE, and AWMA. He has a bachelor of science degree in chemical engineering from North Carolina State University.

Jeff Wells

Mr. Wells has published several articles including "Color Removal in Textile Mills Effluent Using Cloth – Media Filtration Technology," WEASC and "A Case Study Regarding Dye Recovery in a Textile Plant," AATCC. Mr. Wells is a member of the NSPE, ASCE, WEF, Tau Beta Pi, Chi Epsilon, and Phi Kappa Phi. He has a bachelor of science degree in Civil Engineering from North Carolina State University in 1993. He graduated Magna Cum Laude of his class. He also has a master of science degree in Civil Engineering from the University of North Carolina - Charlotte in 1998.

Charles Van Zandt

Mr. Van Zandt is Assistant Water Reclamation Division Superintendent and Industrial Pretreatment Coordinator for the City of Eden. He has been involved in color concerns since the late 1980s. Mr. Van Zandt has certifications in NC Grade IV, NC Class I, and Land Application/Residuals Officer. He has presented papers on color removal at the North Carolina Pretreatment Coordinator's Workshop and for the Association of American Textile Chemist and Colorist Conference.

Mike Bahorsky

Mike Bahorsky, ERM, has a strong commitment to researching and applying cost-effective solutions to complex textile water quality problems. His experience spans more than 30 years and includes field participation in the development of effluent guidelines for the Environmental Protection Agency, developing pollution prevention strategies for the industry, developing and applying improved treatment appproaches such as natural treatment methods, SBR's, and anaerobic methods of color removal. He has worked on and provided engineering solutions to a number of toxicity related problems, and conducted numerous E/H/S compliance evaluations. He has degrees in environmental science, chemistry, and a master's degree in health science.

Dr. Warren Jasper

Dr. Warren Jasper is an Associate Professor in Textile Engineering at North Carolina State University. He received his bachelor of science and master of science degreess from MIT and his doctorate in aeronautics and astronautics from Stanford University. Since joining the faculty in 1991, Dr. Jasper's main interests have been in applying real-time network-based control theory to textiles. Some of his applications include real-time batch dyeing control, neural-network color recipe formulation, and fabric defect detection in woven fabrics. He currently works with ATMI in designing and implementing a communications protocol/database standard for spinning.

Dr. Brent Smith

Dr. Brent Smith is a Professor in Textile Chemistry at North Carolina State University. He received his bachelor of science degree in chemistry at North Carolina State University and his doctorate in Chemical Physics from the University of Florida. Recognized as aninternational expert in pollution prevention, Dr. Smith has worked in more than 75 major industrial on-site projects throughout the world. He is author of the book "Best Management Practices for Pollution Prevention in the Textile Industry," published by the United States Environmental Protection Agency. In addition to pollution prevention, Dr. Smith is knowledgeable in wet processing practices, as well as dry side science and technology.

Case Studies

COLOR REDUCTION & REMOVAL

Flynt Fabris & Finishers, Inc.

Americal Corporation

Cone Mills

City of Eden
Wastewater Treatment Plant

Flynt Fabrics & Finishers, Inc.

CASE STUDY

company profile and history

Flynt Fabrics and Finishers, Inc., manufactures and markets knit fabrics for children's wear, active wear, and fabric for print markets. The textile company has six facilities state-wide employing 450 people. Flynt Fabrics established a dye operation facility in Hillsborough, North Carolina, in 1987, which manufactures approximately 200,000 pounds per week of polyester and cotton circular knit and open width goods. The facility currently bleaches 40% and dyes 60% of incoming fabrics. These fabrics are wet processed in two or more of the following baths: scour, bleach, dye, and finish. The facility operates a pad bleaching and countercurrent rinsing station and Scholl Bleachstar system for fabric bleaching, and fully automated low liquor ratio jet dyeing machines. Finishing agents can be added in jet machines or padded on before drying.

The Hillsborough facility discharges approximately 500,000 gallons of process wastewater per day to a publicly owned treatment works (POTW), which subsequently is discharged into the Eno River. The textile processor contributes approximately 50% of the influent load to the POTW. The presence of dyes caused the true color in the facility's effluent to average 3,000 ADMI. The facility faced public pressure to reduce color in its effluent soon after start-up. Flynt has responded by looking at several options for color reduction and has developed the capacity to greatly reduce its wastewater color properties.

color reduction and removal

The majority of the process wastewater from Flynt's Hillsborough facility is dilute bleach and rinse waters, constituting up to 75% of the flow. Conversely, the problematic color arises from a relatively small volume of dyebath discharges. The discharge from dyebaths ranged in true color from 5,000 to 20,000 ADMI. The most problematic class of dyes used by Flynt are reactive dyes. The reactive dyes are supplied by Dystar L.P., formerly a unit of Hoechst Celanese Corporation. Some of the workhorse reactive dyes have a fixation percent as low as 65%. Thus, 35% of the dye is entering the sewer.

Flynt historically has treated its wastewater in a 250,000 gallon aeration basin using a 40 hp surface aerator. (See Figure 1, Section B.) The facility pH adjusts the effluent before entering the system, and after about 12 hours of retention time the wastewater is discharged to the sewer.

Soon after the City of Hillsborough approached Flynt with the color problem, the facility began researching technologies and techniques to eliminate color in the effluent. While investing in end-of-pipe treatment technologies, Flynt implemented in-plant techniques and technologies to reduce color in the effluent and improve treatability. These include:

1. Substituting lower fixation reactive dyes with higher fixation dyes.
2. Modified dye formulations to improve fixation.
3. Investing in fully automated dye equipment to improve shade repeatability and optimize dye usage.
4. Investing in countercurrent rinse and pad bleach machinery to reduce hydraulic load on future treatment system.

After reducing color from the source, Flynt evaluated a number of technologies and chemistries to reduce color in its effluent. Flynt worked closely with the Dyes & Paper Chemicals Group and Dyes Group of Hoescht Celanese Corporation (HCC). The Specialty and Paper Chemicals Group was purchased by Clariant Corporation in July 1997. The patented technology being disussed here, a new color reduction system, marketed as COLOR-ACT®, resides in the Textile Chemicals Group of Clariant.

COLOR-ACT 5319F is a product containing a reducing agent, sodium hydrosulfite. This product effectively breaks the double bonds in the dye structure that refelect color for many dyestuffs. Flynt selected this product because of its low aquatic toxicity.

Through a series of pilot studies and on-site evaluations, Flynt and the chemical suppliers developed an efficient color removal system (see Figure 1, Section A). The system consists of a dissolving unit, which puts the COLOR-ACT 5319F into aqueous solution. The dosage of COLOR-ACT 5319F is automatically ratio controlled based on on-line input from a spectrophotometer. The spectrophotometer analyzes color in the mill effluent before discharge into the aeration basin. The ability to dose the decoloring product based on the level of color discharged helps control chemical costs. The optimum operating parameters for the reducing agent are a pH from 9-12 and temperature from 100^{O} to 120^{O}F.

Flynt regularly maintains a true color level in the effluent leaving the aeration basin of 100 ADMI.

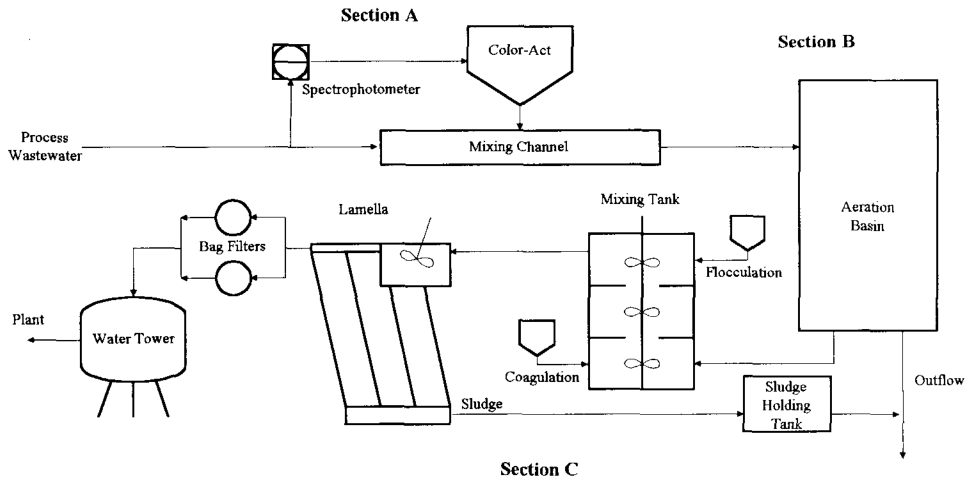

Figure 1: Flynt Fabric's Process Flow Diagram of Wastewater Treatment

Color Reduction and Removal - Economics (treating 500,000 gallons per day)

Total Estimated Capital Costs $112,000
(Includes: Dissolver, online spectrophotometer, and control unit = $15,000)

Total Estimated Operating Costs $112,50O/yr
(Includes: COLOR-ACT 5319F @ 500 lbs./day 300 days/year)

Wastewater Reuse

While there is no payback solely on this type of color treatment scenario, Flynt realized that after color was eliminated there was very little reason not to extend treatment and facilitate wastewaterreuse. With this new perspective, the facility invested in a physical-chemical system to remove the remaining solids and supply the dyehouse with recycled water (see Figure 1 Section C). A vertical coagulant and flocculant three-stage stir tank (lamella) holding basin and bag filter capable of processing 1,000 gallons per minute (gpm) was installed to treat the portion of the decolorized wastewater. The treated water is held in an on-site water tower, which is plumbed into the tap water line coming into the dyehouse. The facility uses a flocculation promoter, COLOR-ACT 5313 and a coagulant, COLOR-ACT 5314, both sup plied by Clariant. The coagulant is dosed in the range of 150 parts per million (ppm) and the flocculant in the range of 5 ppm. Flynt expects the treatment to enable the facility to recover 60% of its wastewater for reuse.

Wastewater Reuse Economics (treating >300,000 gpd)

Total Estimated Capital Costs **$400,000**
(Includes: Mixing Tank, Lamella Clarifier, Holding Basin, Bag Filter, and Pumps and Piping)

Total Estimated Operating Costs **$126,000/yr**
(Includes: Chemicals, Maintenance, Labor at $1.40/1,000 gallons. Sludge is handled by the city.)

Total Estimated Operating Savings **$270,000/yr**
(Savings from water reuse: At $3.00/1,000 gallons (water/sewer))

company contact

Tom Mullis, Director, Facilities Engineering, Flynt Fabrics & Finishing
(919) 732-1600
Bob Cundiff, Environmental Specialist, Dystar L.P.
(704) 395-6697
Michael Ellis, Business Manager, Clariant Corporation
(704) 395-6697

notes

Americal Corporation

CASE STUDY

company profile and history

Americal Corp. manufactures and markets knit nylon hosiery. The textile company has four facilities that employs 1,300 people and grosses an estimated $75 million in sales annually. Americal established a dye operation facility at Henderson in 1968, which manufactures approximately 150,000 dozen pair of nylon and blended nylon hosiery per week. The facility currently dyes all hosiery that is processed. These fabrics are wet processed in two or more scour, dye, or finish baths. The facility operates paddle batch and pressure dyeing equipment.

The Henderson facility discharges an average of 150,000 gallons per day of process wastewater to a publicly owned treatment works (POTW), which subsequently is discharged to the Nut Bush Creek. The textile processor contributes approximately 6% of the influent load to the POTW. Due to an ongoing aquatic toxicity problem with the POTW's effluent, Americal installed an advanced wastewater treatment system to significantly reduce pollutant loading to the POTW. Soon after the start-up of the system, the local POTW began reducing pollutant limits and requesting color reduction in the facilities effluent. The presence of dyes caused the textile facility's effluent to average 500 via platinum cobalt colorimeter.

color reduction and removal

Although color reduction was not an existing goal when Americal purchased the wastewater treatment equipment, the facility found it could significantly reduce color in the effluent with the same chemistry used to remove other regulated pollutants. Historically, Americal has treated its wastewater in a 300,000 gallon aeration basin using two 40 hp surface aerators. *(See Figure 1, Section A.)* Roughly 140,000 gallons of process wastewater enter the lagoon daily.

To reduce pollutant loading, the facility invested in a number of technologies and equipment. Figure 1, Section B depicts the treatment system installed by Americal. This system is not a package unit but a composite of new and used equipment. Wastewater leaving the lagoon enters a collection tank, which also collects recirculated effluent from the dissolved air flotation system and filter press. Approximately 30,000 gallons per day is recirculated.

The mixed effluent is pumped to the head of a four-stage mixing tank. Each stage holds 5,000 gallons and is equiped with four coarse bubble diffusers. In the first stage, the oxidation reduction potential (ORP) is monitored and potassium permanganate is added to maintain an ORP of about 1,200. Dosage ranges between 150-200 ppm of 20% potassium permanganate. Effluent is gravity fed to next stage where ORP is monitored and maintained about 750. In the second stage, the pH is adjusted to 2.5 using a blend of ferrous sulfate and sulfuric acid, dosage is roughly 20 gallons/hr. A coagulating agent, blended aluminum chlorohydrate, and polyamine also is added at approximately 200 ppm (400 ppm during dark shade season). Effluent is gravity fed to the third stage where the pH is monitored and adjusted to 9.5 using a blend of lime and caustic slurry. Approximately 4.5 gallons per hour of this blend is added. The effluent enters a final aeration stage and is then gravity fed to the head of the DAF system.

The influent to the DAF is supersaturated with air using a venturi tube and 1 hp compressor and approximately nine gallons per hour of a 0.5% anionic polymer is added. The dissolved air filtration (DAF) system is rated at approximately 120,000 gallons per day, but is running at higher rates. Treated effluent is discharged to the sewer.

Sludge exits the DAF and enters one of two 13,000 gallon aerated cement block pits. Approximately 12,000 gallons of 3% sludge is generated weekly from these pits and pumped to a filter press. The filter press is equipped with a sludge thickening station where thickening agents are added daily. The press typically generates a sludge with 18% solids and is disposed of at a local landfill. About 80 tons of sludge is disposed of monthly.

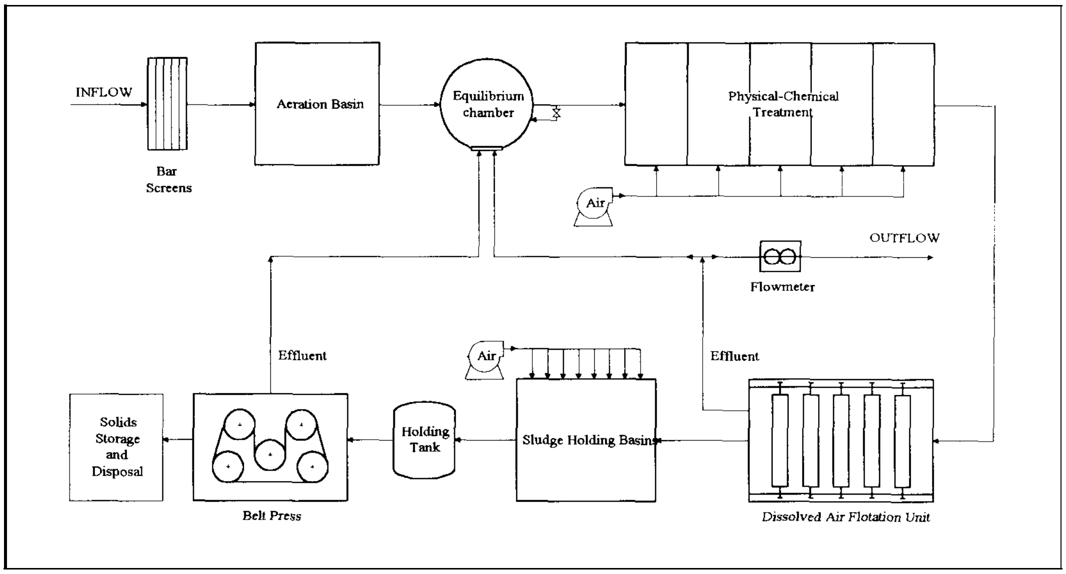

Figure 1: Flow Diagram of Americal's Wastewater Treatment System

Economics: (Based on 150,000 gallons per day, 300 days per year)

Total Estimated Capital Costs $285,000
(Includes: Chemical dosing chambers, DAF, piping = $175,000, Building Structures (Press, Chemical) = $50,000, Filterpress = $60,000)

Total Estimated Operating Costs $101,250 to $135,000
(Includes: Chemicals = $1.50 - 2.00/1,000 gallons, Maintenance, Sludge, Electricity, Water, Etc. = $0.75 - l.00/l000 gallons)

The final effluent is near colorless with an estimated ADMI of less than 50. At this level and being only 6% of the POTWs influent, there is little color problem at the POTW generated by Americal. The facility currently is installing a second DAF system to increase the system's capacity.

Jeff Golliher, superintendent of dyeing and wastewater management, (919) 431-3063

notes

Cone Mills

CASE STUDY

company profile and history

Cone Mills manufactures and markets denim fabrics. The textile company employees 6,200 people at its 10 facilities company-wide and grosses an estimated $750 million in sales annually. Cone Mills established a vertical denim processing operation in Greensboro in the early 1900s that manufactures approximately one million yards of denim per week. It also has several facilities in Cliffside that also manufacture about one million yards of denim per week.

The Greensboro facility dyes 100% of denim fabrics. Woven fabrics are processed in a number of continuous wet processes that may include scouring, desizing, mercerizing, sulfur dyeing, indigo dyeing, and finishing. This facility operates a number of dyeing ranges including five long ranges, a raw stock range, and an over dye range. These processes generate approximately 1,250,000 gallons per day of wastewater that subsequently is discharged into Buffalo Creek following treatment.

Dyeing operations at the Cliffside facilities also dye 100% of denim fabrics. Wet processes used at these facilities include slashing, sulfur dyeing, indigo dyeing, and finishing. The dying ranges include two long ranges, as well as a beam and package dye house. These facilities directly discharge approximately 900,000 gallons per day of wastewater into the Second Broad River after treatment.

Two decades ago, Cone Mills started taking the initiative to reduce the color in its effluent from both of its plants. Since then it has developed very effective systems of color removal. It approaches effluent color reduction by investing in both dye recovery and dye removal technologies.

CASE 1: GREENSBORO

The Greensboro facility's wastewater discharge averages 3,000 ADMI before treatment due to the presence of indigo and sulfur dyes. Because indigo and sulfur dyes form much larger compounds than other dyestuffs, a portion of these dyes can be recovered with the use of ultrafiltration equipment. In 1976, the Greensboro facility invested in an ultrafiltration system capable of processing 100 gpm of wastewater and filtering to particle sizes of 50,000 molecular weight. The system is capable of recovering an average of 100,000 pounds of dyestuff annually. The system utilizes a number of shaker screen systems to remove suspended solids, 400 mesh size and larger. As opposed to end-of-pipe color treatment technologies, the system provides a payback by reducing the amount of dyestuffs purchased. The approximate cost of a system capable of processing 100 gpm in today's dollars is $1.5 million.

Despite using ultrafiltration, the Greensboro facility still had significant amounts of dyestuff entering an activated sludge treatment system that was not designed to remove color. (Section A of Figure 1 provides a schematic of the treatment system before color removal technologies were introduced.) Only an estimated 50% of the color was being removed by the activated sludge basin and subsequent clarifiers. Cone Mills then decided to add a physical/chemical treatment system using coagulants and flocculants to remove the remaining color, shown in Section B of Figure 1. Basically, the coagulant, a polyamine, is introduced at the beginning of the mixing basin averaging 30 parts per million (ppm). The flocculant, an anionic powder, is added in the second portion of the basin, averaging 4 ppm. After the polymer addition, the flocculated material enters one of three 250,000 gallon upflow clarifiers. Approximately 30,000 gallons of biosolid sludge at 1.5% is generated daily. This sludge is mixed with other wasted sludge and stored in an aerobic digesting pond for land application. The overflow from the clarifier runs through a weir basin for color sampling before entering a polishing pond. The Greensboro facility now averages less than 100 ADMI with effluent discharged to the Buffalo Creek.

Economics (treating 1,250,000 gpd):

Total Estimated Capital Costs **$895,000**
(Includes: chemical mixing and feed systems = $20,000, mixing basin = $75,000,
3 clarifiers = $800,000)

Total Estimated Operating Costs **$250,000/year**
(Includes: chemicals = $200,000/year, labor = $30,000/year, maintenance and energy = $20,000/year)
(Does not include: byproduct land application, which is mixed with aeration basin solids, $30/1,000 gallons)

The Cone Mills, Greensboro, facility currently is investigating the use of anaerobic or anoxic organisms for the efficient and cost-effective removal of color from its wastewater.

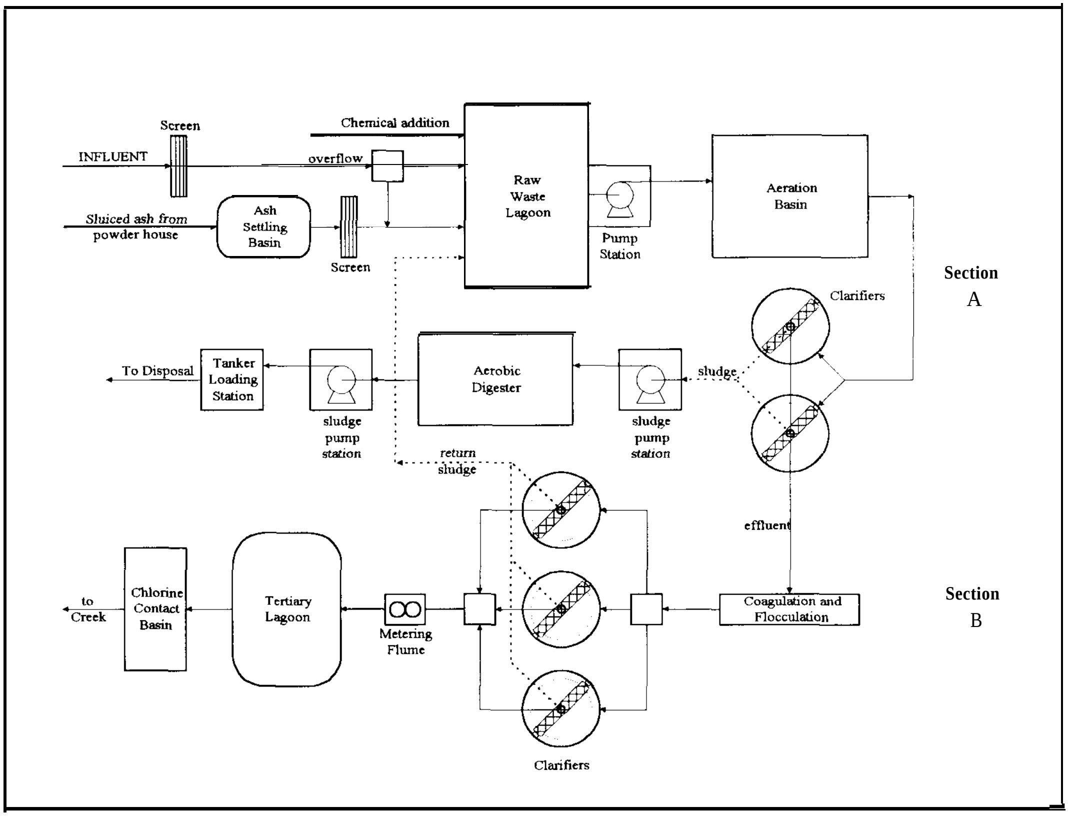

Figure 1: Cone Mills (Greensboro) Wastewater Treatment Facilities

CASE 2: Cliffside, Dye Recovery and Color Removal

Cone Mills invested in dye recovery also at the Cliffside facility starting in the mid 1970s. Ultrafiltration was used to recover indigo dyes from the rinse water of the dye ranges. The ultrafiltration system initially installed was capable of processing 50 gallons per minute (gpm) of rinse water and filtering it down to 10^{-6} microns. Two years ago Cone Mills installed an improved ultrafiltration unit, capable of filtering 80-100 gpm, with efficiency characterized by 40% COD removal and 99% indigo dye recovery.

Cone Mills also constructed a WWTP at the Cliffside facility in the mid 1970s for the treatment of the final effluent before discharge. The system first constructed consisted simply of aeration and clarification, along with disinfection/dechlorination, resulting in an effluent with a color averaging 1,500 ADMI. Cone Mills wanted to achieve a greater color reduction in its effluent and added a physical/chemical color removal system in 1995, shown in Figure 2. In this system, a poly quad polymer, is added at 30-35 ppm to achieve coagulation and flocculation of the particulate matter in the wastewater, including the dye molecules responsible for the color. The stream is then passed through one of the three six-disk AquaDisk filters, which separate the solids fraction from the liquid to concentrate the color into the solids. The solids, in the form of color sludge, then are pumped to a biosolids holding tank to be land applied or are pumped back to the aeration basin for further treatment. Approximately 150,000 gallons of 1% sludge is generated daily by the color removal system. The final effluent has an average color of less than 100 ADMI by the time it is discharged.

Economics (treating 900,000 gallons per day (gpd)):

Total Estimated Capital Costs $1,500,000

(Includes: Chemical Mixing and Feeding Systems, Mixing Basins, AquaDisk Filters, and Biosolids holding tank)

Total Estimated Operating Costs $60,000/year

(Includes: Chemicals $50,000/year, Maintenance and Energy = $10,000/year)

(Does not include byproduct land application, which is mixed with aeration basin solids, $30/1,000 gallons)

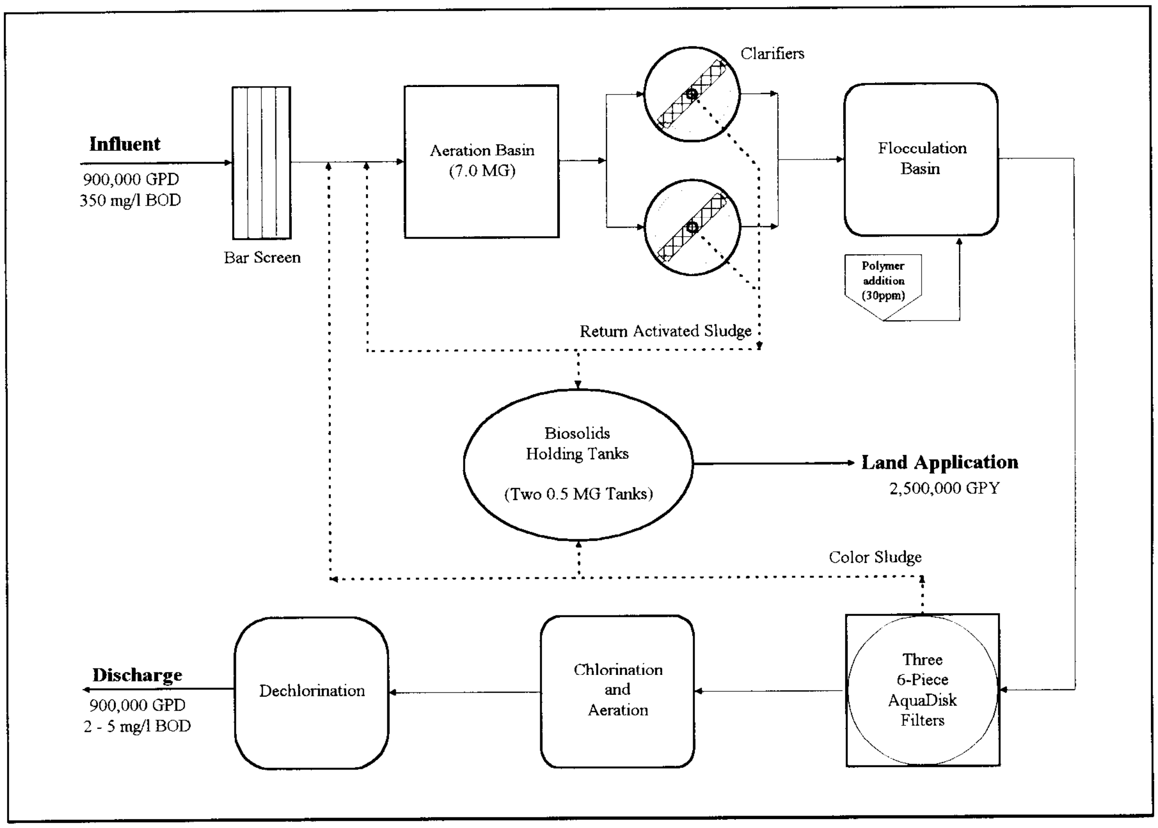

Figure 2: Cone Mills (Cliffside) Process Flow Diagram

company contact

Arthur Toompas, corporate environmental engineer, (910) 379-6226

notes

City of Eden

Wastewater Treatment Plant

CASE STUDY

company profile and history

The city of Eden, located on the Virginia and North Carolina border, lies along the confluence of Smith and Dan Rivers. The Mebane Bridge wastewater treatment plant (WWTP) discharges into Dan River, which flows back into Virginia after passing through Eden. The WWTP treats a 13.5 million gallons per day (MGD) flow consisting of 60% industrial and 40% domestic wastewater. During the years there have been several large textile industries in the area, both in Eden and upstream of the city, that have contributed colored wastewater to the river. In the late 1980s, residents of towns downstream of Eden started to complain about the color in the river coming from Eden's WWTP. Thus, the Mebane Bridge WWTP was required to monitor for color at the influent, effluent, upstream on the Smith River, and upstream and downstream on Dan River.

The city of Eden was given numerical limits of 300 ADMI units as part of its NPDES permit for wastewater discharge into Dan River. Because Eden is currently the home of four large textile manufacturers (two fleecewear mills, a blanket finishing mill and a carpet manufacturer, all which discharge colored wastewater to the WWTP), the city required all these color producing industries to conduct studies for removal options. Finally, a decision was made that the most cost-effective solution would be for the city to incorporate color removal at the plant. This decision was made because the city was preparing for a plant expansion and thus could include this into the total costs and also because the plant's biomass could remove up to 25% of the color. The city could then charge back the cost for color removal to the industries. Eden thus started exploring different options in removal to tackle the combined colored waste stream at the WWTP.

color reduction and removal

City officials looked into several technologies for color removal, as well as other similar cases that would be useful for comparison. The city of Martinsville, Virginia, had undergone a similar color requirement a decade earlier and had looked into several technologies such as carbon absorption, ozonation, chlorination, and chemical precipitation (polymers). It found the estimated capital cost for removal by carbon adsorption would be about $6 million, oxidation by ozonation $5 million, removal by chlorination $1 million, and removal by chemical precipitation $100,000. Because the city's WWTP is very similar in operation and characteristics to the one in Martinsville, Eden's city engineers decided to use chemical precipitation (polymers) because of the low capital costs, as well as the lower operating costs when compared to other technologies.

The color of the wastewater influent ranges from 500 to 10,000 ADMI units, with an average value of 2,000. Color removal by chemical precipitation begins with polymer addition at the outflow of the aeration basins. This takes advantage of the fact that 25-30% of the color is already removed by the activated sludge biomass in the two 7.0 MG aeration chambers. A flocculant polymer, a cationic polyamine, is stored on-site and continuously is injected directly into the aerated wastestream at 30 ppm 24 hours a day. The precipitate then is collected by clarifiers along with the other suspended matter. This colored sludge then is pumped to a sludge-holding and digestion tank. The sludge is stored in two 2MG holding lagoons for land application. It is estimated that 1,000,000 pounds of polymer is used each year for the removal of color in Eden's wastestream. The color of the effluent after treatment at the WWTP is less than 100 ADMI units.

The arrangement the city of Eden has with the industrial dischargers is the costs of purchasing polymers and the operations (one operator, maintenance of feed equipment, etc.) of the removal process are incurred by industrial users that discharge colored wastewater. Each industry monitors the color in its own waste stream, and is billed a percentage of the total monthly cost of color removal at the WWTP. This percentage is based on the amount of excess color units over the surcharge limit times their total monthly flow. Color units are based on ADMI color discharged above 300 and the volume of water used. The total monthly costs for color removal range from $40,000 to $60,000 per facility.

Currently, there are currently three industries discharging color wastewater to the Mebane Bridge WWTP. They have been working together with the WWTP under this arrangement for the past decade in a concerted effort to reduce the amount of color pollution received by Dan River.

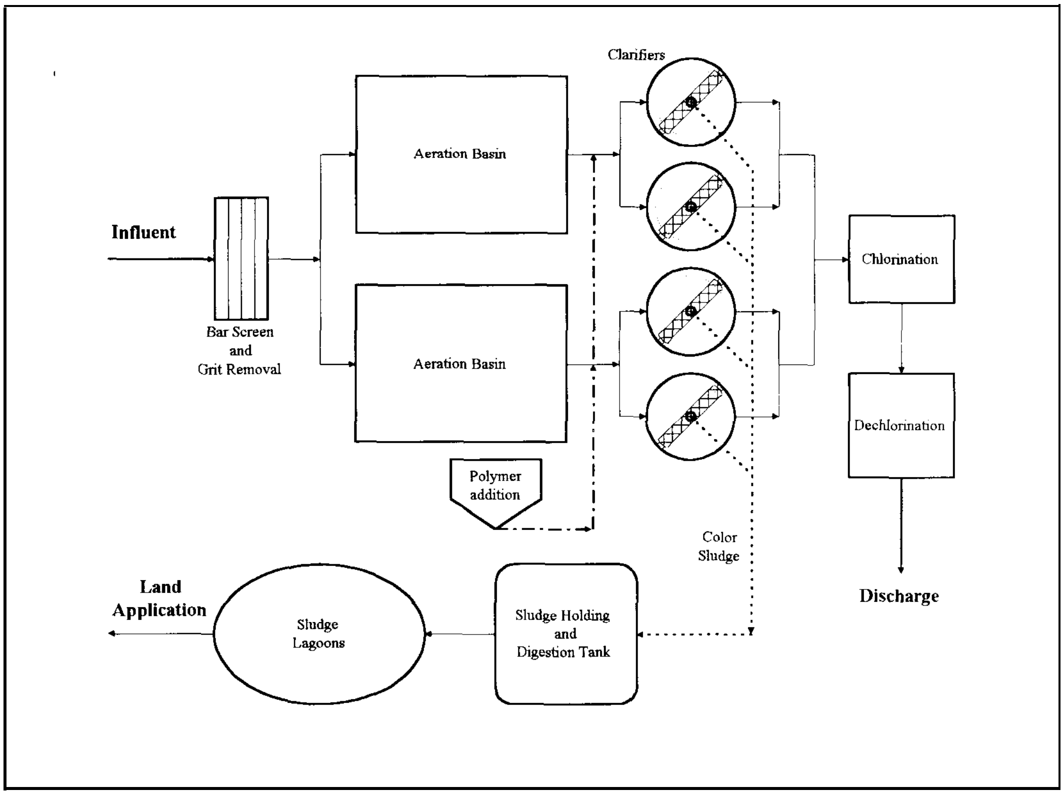

Figure 1: Process Flow Diagram of Mebane Bridge Wastewater Treatment Plant

Economics (treating 13,500,000 gallons per day (gpd)):

Total Estimated Capital Costs	$ 100,000
(Includes: Polymer addition system = $100,000)	

Total Estimated Operating Costs	$ 651,000/year
(Includes: polymer = $650,000/year maintenance = $ l,000/year)	
(Does not include sludge handling costs. Solids are mixed with aeration basin solids.)	

Charles Van Zandt, assistant water reclamation division superintendent and industrial pretreatment coordinator, (910) 379-6226

notes

Additional Case Studies

COLOR REDUCTION & REMOVAL

Belmont Dyers, Inc.

Sara Lee Knit Products

Sara Lee Knit Products

CASE STUDY

company profile and history

Sara Lee Knit Products (SKLP) manufactures and markets knit fabrics for a variety of apparel markets. SLKP is owned by Sara Lee Corporation, which employees 141,000 people worldwide and gross an estimated $20 billion in sales annually. The products manufactured by SKLP are wet processed at its "textile" plants by either a dyeing or bleaching operation. SLKP engineering wanted to conduct production scaled processes to investigate color removal options to reduce color discharges. A facility was chosen that was easily suited for the installation and operation of the new process and representative of the production and design of the majority of other facilities.

The majority of the process wastewater from Sara Lee's textile facilities are dilute rinse waters, constituting up to 90% of the flow. Conversely, the problematic color arises from a relatively small volume of dyebath discharges. The discharge from dyebaths ranged in true color from 70,000 to 5,000 ADMI. Sara Lee uses mainly reactive dyes for dyeing cotton. The most problematic dyes are the darker shade reactive dyes. Sara Lee identified that those discharges with the strongest color also contained the majority of sodium chloride, another problematic pollutant. The company selected ultrafiltration/ nanofiltration as a technology that could remove the color and other suspended solids and leave the sodium chloride and water for reuse in the dyeing process. The treatment system is shown in Figure 1.

Sara Lee installed an ultrafiltration/nanofiltration system capable of handling 7.5 gpm of the 350 gpm wastewater generated from wet processing operations at this location (economic summary is based on an 80 gpm system). This small system is effective in reducing total color of the effluent by treating those discharges with the most color and salt. Like other Sara Lee facilities, this location has a dual effluent piping system that allows selected dyebath discharges to be collected separately from the majority of dilute wastewater. The soleniod valves splitting these discharges are controlled by the dyebath computer. The facility has programmed the computers to discharge selected high color and salt discharges to a separate holding tank for treatment.

The collected wastewater is pumped to a 2,600 gallon tank that circulates wastewater through the tubular ultrafiltration membrane. The permeate is pumped to a 2,600 gallon nanofiltration holding tank, and the filtrate returns to the ultrafiltration holding tank. The ultrafilter removes suspended solids, leaving dissolved solids and color in the permeate. The permeate is pumped from the nanofiltration holding tank to the nanofilter. The permeate from the nanofilter, a clean effluent with sodium chloride, is pumped to a holding tank for reuse in the dyeing process. Approximately 95% of the influent is returned as clean brine water for dyeing reuse. The filtrate is pumped back to the holding tank.

Solids collected in the holding tanks are pumped to a phys/chem treatment system for removal. Approximately 5% of incoming wastewater is pumped to this system. Ferrous sulfate and cationic polymer are added to precipitate solids and a small amount of anionic polymer subsequently is added to enhance flocing. The floc settles in a clarification/sludge thickening tank. Solids are collected from the tank and pumped through a plate and frame filter press. Clean water is decanted from the settling tank and discharged to the sewer.

Economics (Based on treatment of 120,000 gallons per day (gpd) with facility using low salt reactive dyes. A facility using high salt reactive dyes could see increased savings from brine recovery. See Figure 1.)

Total Estimated Capital Costs **$ 580,000**
(Include: Ultra/nanofiltration system = $ 500,000, phys/chem system = $ 80,000, and ancillary equip.)
(Does not include: dual effluent piping system)

Total Estimated Operating Costs **$139,000 / year**
(Includes: Maintenance $15,000 / year, Labor = $70,000, Energy = $15,000, Sludge = $4,725)

Total Estimated Operating Savings **$ 350,000 / year**
(Includes: Brine recovery = $245,000 / year, water recovery = $ 100,000 / year)
Additional savings of **$500,000 / year** are applicable for a facility removing color from total effluent with polymer treatment or paying the local POTW to remove color.

By installing an 80 gallons per minute (gpm) system for a facility discharging around 0.5 MGD, Sara Lee

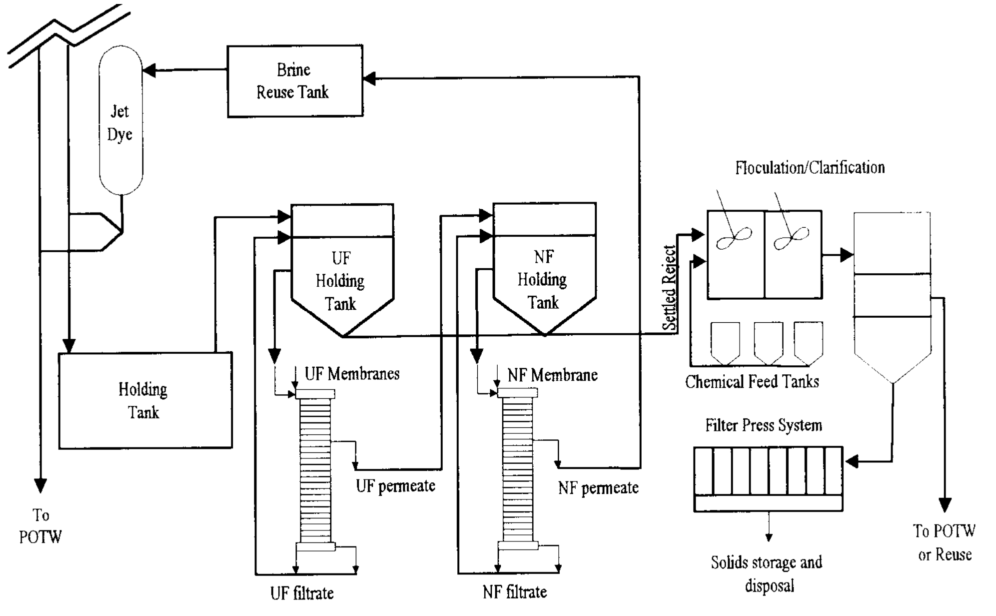

Figure 1: Process Flow Diagram

Total Estimated Capital Costs $ 580,000
(Include: Ultra/nanofiltration system = $ 500,000, phys/chem system = $ 80,000, and ancillary equip.)
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Additional savings of $500,000 / year are applicable for a facility removing color from total effluent with polymer treatment or paying the local POTW to remove color.

By installing an 80 gallons per minute (gpm) system for a facility discharging around 0.5 MGD, Sara Lee estimates that effluent discharges can be reduced to below 200-300 ADMI.

company contact

Donald Brown, senior facilities engineer, (910) 519-5610)

Belmont Dyers, Inc.

CASE STUDY

company profile and history

Belmont Dyers is a package dyeing plant located in Belmont, N.C. The facility was purchased by Meridian Industries, which grosses approximately $320 million in sales annually. Belmont employees 160 people and processes approximately 280,000 lbs. per week of cotton yarns in custom colors for end products such as blankets. The facility currently bleaches 5% and dyes 95% of incoming yarn.

Belmont's facility discharges between 350,000 and 400,000 gallons per day (gpd) of process wastewater to a publicly owned treatment works (POTW), which subsequently is discharged into the Catawba River. The facility is approximately 10% of the influent load to the POTW. Belmont recently expected an increase in production, which would have caused its water demands to rise between 650,000 and 750,00 gpd. This created some challenges for the company with regards to the availability of water as well as the disposal of the wastewater. After discussions with city officials, a decision was made that a limit of 300,000 gpd would be set for the availability of water supplied to the company, as well as the limit for the amount of wastewater allowed for discharge to the POTW. In order to provide process water for the expected increase in production, Belmont decided to recycle their effluent using state-of-the-art treatment.

color reduction and removal

To recycle the effluent, Belmont needed a treatment system to remove a majority of pollutant in the wastewater. It was determined that the color concentration in process wastewater average 2900 ADMI units. The major dyetypes used in the facility are reactive and direct. The level of color and levels of TSS, BOD, metals, and pH all would need to be treated significantly to allow for water reuse. The POTW itself had a requirement for the color of the effluent to be only 200 ADMI units.

Several test studies were conducted, and it was determined that electrochemical precipitation would be the preferred method for treatment of the effluent, see Figure 1. Prior to treatment, a 200,000 gallon influent tank collects wastewater to equalize the flow to the electrochemical treatment. This influent tank requires agitation to prevent the dyes from stratifying inside the tank.

The electrochemical treatment consists of six "F" size electrochemical cells containing iron plates that generate ferrous iron ions when amperage is applied to the cells. Five cells are on-line simultaneously, while the sixth is a standby. The ferrous ions, which dissolve from the anode, combine with hydroxide ions generated at the cathode to produce an iron hydroxide precipitate. The iron hydroxide reacts with the dye particles to form a co-precipitated hydroxide matrix. Because there is iron hydroxide sludge buildup on the individual electrodes, an acid wash of 15% sulfuric acid is performed daily on each cell for approximately 30 minutes. The iron plates themselves are recycled for scrap iron once they are spent.

After electrochemical treatment, the pH is adjusted to 9.5. The iron hydroxide becomes insoluble, then the absorbed substances are removed flocculation and precipitation. At the time of this study, the separation process was also facilitated by the addition of 20 parts per million (ppm) of coagulant and 7 ppm floculant from BETZ Chemical, W22, and W14 respectfully. The effluent flows through a lamella to clarify the solids from the liquid. The solids are collected at the bottom and pumped to a holding tank, then into a filter press system. This 50-cubic-foot plate and frame filter produces a sludge with 30% solids. The filtrate from this press runs into the influent tank.

The supernatant from the lamella is held in a wastewater tank for recycling. The recycled water is polished through a two-stage multi-media filter system and a reverse osmosis unit designed to handle 175 gpm.

The whole system is controlled automatically by programmable logic controller (PLC) and a touch screen user interface. Operators are able to monitor and maintain the system for the treatment to run at optimal conditions. Belmont started reusing wastewater without reverse osmosis treatment. While this was successful, the facility invested in reverse osmosis to assure a continuous supply of quality water for all wet processing.

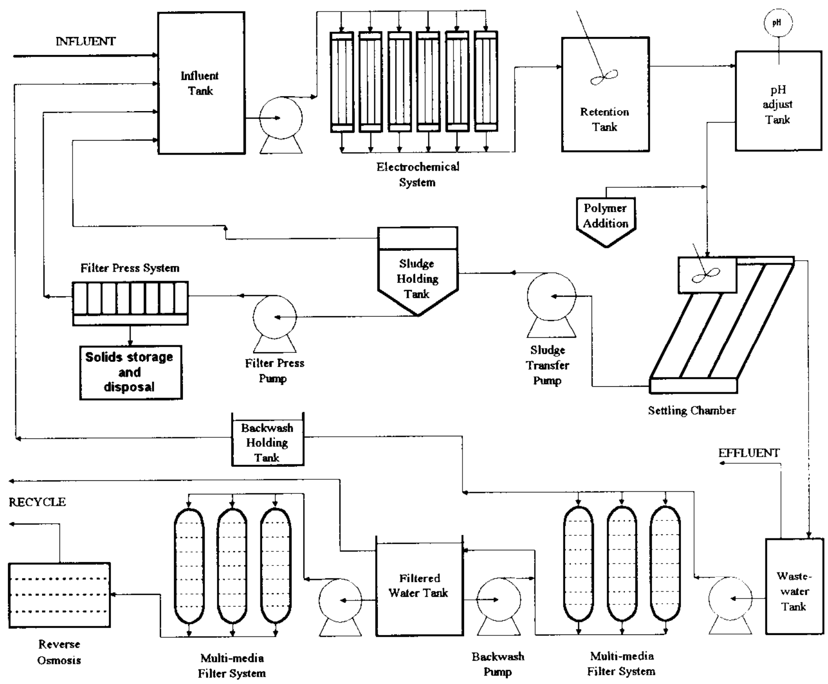

Figure 1: **Process Flow Diagram**

Belmont has been able to achieve a 99% color reduction in their effluent down to less than 25 ADMI. Additionally, the facility is able to recover up to 70% of its wastewater for reuse in its process.

Economics (treating 500,000 gpd):

Total Estimated Capital Costs $ 4.5 million
(Includes: Electrochemical/Phys/Chem/Dewatering/Multimedia filters/RO/Ancillary Equipment)

Total Estimated Operating Costs $ 1.2 million/year
(Costs are estimated at $7.5/1000 gallons and 325 operating days)
(Savings from water recycle not included: recovering 70% at $3/1,000 gallons (water/sewer fees) equals $ 350,000/year savings)

Because of the relatively high operating costs, Belmont currently is investigating alternative treatment technologies that may reduce the costs of the current system. This research includes the use of an inorganic polymer that may eliminate the use of the electrochemical technology.

Bob Setliss, <title>, (800) 438-2165

Presentations

COLOR REDUCTION & REMOVAL

Dr. Mike Bahorsky
Environmental Resource Management, Inc.

Dr. Warren Jasper and Dr. Brent Smith
North Carolina State University
College of Textiles

Emerging Technologies for Color Removal

PRESENTATION

Dr. Mike Bahorsky
Environmental Resource Management, Inc.

Emerging Technologies for Color Removal

MIKE BAHORSKY, Environmental Resources Management (ERM)
1998 Color Reduction and Removal Seminar, June 17, 1998, Charlotte, North Carolina
North Carolina Division of Pollution Prevention and Environmental Assistance

Introduction

A practical and cost-effective method to eliminate textile wastewater dye color has been sought for more than 25 years. Among the vast array of available options which exist, there is no compelling, simple, cost-effective, or universally acceptable methodology which presents itself (EPRI 1996, Keary 1994, Cooper 1993, Bahorsky, 1992, Halliday 1986). From the commercially available color removal possibilities, there are six distinct groups of methods: biotreatment, coagulation, adsorption, membranes, electrolysis and oxidation.

However, when color removal is considered, usually there are important secondary considerations that go beyond simply removing color. These considerations include: sludge production and handling cost requirements, the level of operational skill required, the operational and maintenance attention needed, the long-term system reliability, and the total system costs. In view of such complexity, the following state-of-the-art review critically discusses technology from the six primary groups of color removal methods with the purpose of visualizing promising directions for the future.

Review of Contemporary Methods of Color Removal

Conventional aerobic biological processes used in the textile industry generally are unsuccessful in significant dyestuff removal beyond the adsorbing capacity of the biomass. One reason for this is that dyes are designed to be bio-resistant. This problem is reflected in the long retention times of textile extended-aeration systems, which generally operate at two to three days detention. This is also the reason why municipal treatment systems at eight to 12 hours detention are much less successful at color removal. However, research data is increasingly being gathered that indicate certain dyes are susceptible to anoxic/anaerobic decolorization. An anaerobic decolorization step followed by an aerobic step may represent a significant advancement in biological treatment and decolorization in the future. Nevertheless, because of the typical time lag for such innovation, it is unlikely that any full-scale applications will emerge in the near future. An advantage of biological treatment over Physical-Chemical (P-C) treatment methods, such as coagulation systems, carbon adsorption, and membrane systems, is that more than 70% of the organic material present as measured by the COD test may be converted to biosolids. In the P-C methods, organic material is directly separated from the main stream and requires further treatment.

Coagulation is one of the oldest practiced methods of wastewater treatment. However, the application of coagulants often is practiced as more of an art than a defined science. Perhaps this is why there are so many varying degrees of success in the removal of color. Coagulation may be accomplished by organic coagulants or organic polymers, and both have been successful in color removal.

Organic polymers usually are favored, although more costly, because they tend to produce less sludge than their inorganic counterparts (EPRI 1996). However, Hall and Mirenda (1991) pointed out that excessive polymer use may be toxic to bioassay test organisms Electrochemical methods, which employ degrading iron and/or aluminum electrodes, have been evaluated on different dye classes and have performed well for disperse, direct, and acid dyes (Tincher 1989). Reactive dyes, however, tend to be difficult for electrochemical treatment processes. An attractive advantage of electrochemical methods is that the entire package of chemistry and separation equipment may be acquired. However, the question exists as to whether or not a direct chemical approach would be less costly and less problematic for long-term. This emphasizes the fact that there is no generally acknowledged coagulation technology system available as a reference. This is likely to be because the coagulation chemistry usually is approached individually, as are separation equipment selection and filtration equipment selection. Some efforts have been made, however, to define optimal chemistry, expected sludge production, ideal settling equipment and design specifics, and optimum filtration methodology (EPRI 1996, and Bahorsky 1994).

Carbon is the most commonly applied of the various types of adsorption processes available. Activated carbon may be applied in the granular form and housed in contact columns, or in the powder form. Powdered activated carbon (PAC) is generally applied directly to an activated sludge system. A number of full-scale granular carbon applications were attempted on dye wastewater discharges during the 1970s (Velvet Textile, Blacksburg, Va.; Crompton and Knowles, Reading, Pa.; and a Pennsylvania carpet mill, Hollytex), and bench scale tested during the mid-1970s, Best Available Technology Economically Available (BATEA) EPA/ATMI, industry project.

There are no recent reports of operating facilities. The major problem with carbon is that while bench tests may show excellent treatment performance, full-scale operation is fraught with severe problems, such as clogging and biofouling (Churchley 1993). Today there are some PACT systems in operation, such as at Vernon, Conn. Because of the variability of dye house discharges and the fact that insoluble dyes, such as disperse, sulfur, vat, and pigment dyes, are not removed by carbon adsorption, carbon is best preceded by a filter and used in conjunction with a coagulation step. Reife (1996) provided an excellent review about the carbon adsorption of dyes. Reife concluded that, in general, carbon adsorption of dyes is neither very efficient nor economical. Halliday (1986) also described carbon test results involving various dyes and gave special focus to the operational problems of carbon systems.

Membrane techniques offer the appeal of recovering and reusing chemicals and dyes, and producing reusable water. There have been successes in the use of full-scale ultrafiltration systems to recover and reuse polyvinyl alcohol size (PVA), indigo dye, and to purify sodium hydroxide (caustic). Brown (1997) reported on a successful pilot system capable of removing dye color and returning a brine solution for reuse. A double-trough ditch system was said to be necessary in Brown's salt recovering system in order to isolate recoverable salt discharges. Dr. Jeff Porter of Clemson University (1975) has provided numerous forums on membrane methods during the years. He has conducted extensive research for his evaluations of membrane techniques.

In general, it can be said that membrane systems are costly, operation and maintenance intensive, and will generate a concentrated dye stream requiring additional treatment, if the dye recovered cannot be reused.

Buckley (1992) reviewed membrane processes in general and applications for dye wastewater treatment. A state-of-the-art membrane system would include an isolated waste stream, a pretreatment system likely to involve a coagulation process and adequate filtration capability, followed by one or more membrane systems. The type of membrane system selected would be far less important than the reliability of the pretreatment system used to protect the membranes from clogging and fouling. Cost and complexity are, therefore, the main factors limiting the appeal of membrane technology.

Electrolysis methods, such as the brine cell, have been evaluated on dye wastewaters with varying degrees of success. These tests have been carried out in the pilot-scale, but no full-scale application has been demonstrated. Methods that produce chlorine, such as the brine cell, also may generate undesirable chloramines. A 1991 dye wastewater test, involving 20 minutes detention time at 970 mg/l COD, produced 2,577 mg/l of chloroform and trace amounts of chloromethane, bromodichloromethane, and 1,1,1-trichloroethane.

In respect to oxidation methods, it has been said that modern dyes are resistant to mild oxidation conditions, such as those that exist in biological treatment systems. Suitable color removal, therefore, must be accomplished by more powerful oxidizing methods, such as chlorine, ozone, Fenton's reagent (peroxide and ferrous sulfate), UV/peroxide, UV/ozone, or other oxidizing techniques or combinations. Chlorine methods have proven to be good dye oxidizing methods, and can be applied by very simple techniques at low capital and operating costs. However, the potential of chlorine forming undesirable compounds with nitrogen-containing components of the wastewater, as described in the previous section, has limited the acceptability of this method. Fenton's reagent and UV-assisted peroxide techniques also have been evaluated. The limited penetration of UV light into dye solutions in the case of UV/peroxide methods, the cost of the Fenton's reagent approach, and the process complexity in general have limited the development of these methods and, therefore, the general appeal. Oxidation processes, like carbon and electrolysis methods, also tend to be more successful on soluble dyes than insoluble types.

Oxidation using ozone gas has been one of the most commonly evaluated methods for dye color removal during the past 30 years. Warren Perkins, University of Ga., has provided a number of classic studies using ozone methods to renovate and reuse dye wastewater since the early 1970s. Working against the widespread application of ozone techniques is the fact that modern dyes are designed, among other things, to be ozone resistant. This fact and the high cost of ozone system technology have inhibited significant applications of the technology. The following section describes previous ozone research, full-scale experiences, and ozone cost examples.

A review in Smith's Asian Textile Journal (1974) described a 0.87 MGD dyehouse in Kanebo, Japan, which successfully applied ozone and activated carbon for color, BOD and TSS removal. The article stated that extremely high decolorization, effective organic removals, and no sludges were produced in a simple and stable operation. Costs were quoted at $0.34/1000 gallon in 1974 dollars.

In a 1977 industry/EPA pilot study (BATEA Project), where advanced treatment methods were evaluated at 19 textile facilities, only one facility was determined to be feasible for ozone treatment, and this was in combination with filtration and carbon. Perkins (1979) described the renovation of dyebath water by chlorination and ozonation from studies conducted in the late 1970s. Ginocchio (1984) evaluated four methods of color removal for a municipality and concluded that ozone was helpful but could be made more effective and economical by the addition of a chemical coagulation system before the ozone. Various components that interfered with the ozone process also were described. Halliday (1986) reviewed ozone studies in the early 1980s that included Dalton, Ga., carpet mill effluents. Ozone dosages of 45 mg/l were said to produce 90% color removals and 40% COD removals. A particularly important finding was that when total suspended solids were reduced, the ozone dosage could be reduced to 26.5 mg/l.

In more recent reviews, Langley and Leist (1994) discussed how ozone dramatically improved the biodegradability of textile mill wastestreams. Authors described ozone theory, recent technology developments, and equipment costs. Costs were focused on a Georgia POTW where a five-week study was conducted. Namboodri, Perkins, and Walsh (1994) revisited the idea of decolorizing dyes with chlorine and ozone in the 1990s. Sixteen dyes were tested, and the required decolorization dosages and treatment performance were described. Matsui (1996) of Gifu University, Japan, a long-term ozone researcher in the decolorization area, provided an excellent review of the ozone treatment of dye wastewater. In addition to illustrating the reaction products of ozonated dye solutions, Matsui discussed the toxicity of ozone and ozone degradation by-products. Eckenfelder (1988) and Tozer (1994) evaluated various methods of treating dyehouse discharges and concluded oxidation was the best method for removing color and toxicity from wastewaters. The methods compared included coagulation and activated carbon. Tozer found that an ozone dose of 17 mg/l enabled meeting discharge requirements for direct dye wastewaters. Furthermore, Ceriodaphnia and fathead minnow bioassay tests showed that ozonation did not adversely affect effluent toxicity. Rearick (1997) discussed a project involving oxidation, coagulation, and membrane technology to remove dye color and recover salts. Fenton's reagent costs and flocculation costs to accomplish decolorization ranged from $3.45 to $7.40/1000 gallon. The difference in costs is a reflection of the wastewater variability.

In 1996, an Electric Power Research Institute (EPRI) report produced by Hydroscience compared some primary decolorization methods in terms of construction costs and major operating component costs at 2.0 MGD Flows, Table I. From Table I the cost of a 2.0 MGD ozone system is seen to be $3.02 million.

In 1997 Perkins described a United States municipal facility that installed an ozone system for about $2.5 million in capital costs for a 4.5 MGD design flow. The facility was using about $1 million per year in coagulants to remove color. Annual operating costs were estimated to be $200,000 (liquid oxygen, electric power, maintenance, etc.). The design provided for 45 mg/l ozone. No costs were provided for prefilters or other ozone system components. A report by Churchley (1993) provided complete costs for a 10 MGD ozone system installed in the U.K. for textile color removal. The cost of $8.2 million U.S., included equalization, sand filters, ozone equipment, and pumping. Churchley found that while treatability studies had shown 8-to-13 mg/l ozone would be required to achieve acceptable U.K. color standards, as much as 45 mg/l ozone were actually needed in full-scale operation. It would be expected that without a filter these costs could be significantly higher.

In summary, a recurrent characteristic of the advanced treatment methodologies described in this section is their tendency to periodically reappear under the guise of new innovations. In the 1970s these technologies were generally known as physical-chemical techniques. In full-scale industrial applications they did not live up to expectations of performance more often than not, they were expensive in capital and operating costs, and they usually required a very sophisticated operator. In the case of biological treatment, the conversion was one of organic pollutant to a biosolid by-product. In the case of coagulation, activated carbon, and membrane filtration, the conversion was from the main stream aqueous media to a more concentrated stream, or a media transfer. This meant other steps were needed for complete treatment. Oxidation or electrolysis methods converted some organic to CO_2 and water vapor, but not entirely. In the 1980s, these same methods reappeared to be known as Advanced Wastewater Treatment (AWT) technologies. The results however were the same. In the 1990s, the methods reappeared again as Zero Discharge Technology, Hazardous Waste Treatment Technology, or High Tech solutions. It is highly recommendable therefore that those seriously considering the use of these methods refer to system designers having long-term experience with the performance, problems, and reliability of these methods. A primary reason for returning to the methods of the past is often unfortunately the problem with any innovative or radically improved method, and that is lack of familiarity. While everyone seeks the "breakthrough," few potential users, consultants, or regulators are willing to accept the window-of-risk and the developmental work necessary to properly implement an innovation. Clearly the basis for this reluctance is mainly the cost generally involved. In recognition of these impediments, the following section reviews emerging concepts that have had some developmental history and show strong promise of effective textile dye color treatment, demonstrate preliminary reliability, and suggest cost-effectiveness.

Emerging Technology

It has been described how biological treatment systems have been relatively unsuccessful in removing refractory textile dyestuffs. The reason for this poor performance is that textile treatment facilities and operational strategies have not been developed to full potential or optimized for difficult-to-degrade textile components. This means that treatment systems built in the 1960s to 1970s generally have not been significantly improved since they were built. The main improvements in biological systems which have occurred have been in the recognition that trickling filters, aerated lagoons, and high-rate activated sludge systems are not competitive with extended aeration systems in refractory pollutant removals. The primary direction of activated sludge improvements for textile wastewater treatment has been in enlarging aeration basin sizes in respect to detention time in an effort to enable better color removal.

These designs have been based mainly on empirical conceptualizations. In terms of operational improvements, textile operators have not attained the level of operational skill potentially available essentially because training mainly is in municipal methodologies. Early surveys (Bahorsky 1990) disclosed that extended aeration treatment systems could be defined as having anywhere from 12 hours hydraulic detention time to 20 days. Power levels varied from 9 HP/MG (horsepower/million gallons volume) to 353 HP/MG. Operationally, biosolid levels in the aeration basin were seen to vary from 500 MLSS (mixed liquor suspended solids, a biosolids concentration measurement) to more than 10,000 MLSS. Today this landscape is relatively unchanged from the 1960s. There also is no commonly acknowledged reference text available describing optimum design and operational conditions for biological color removal, or for textile treatment system designs in general. In summary of this historical review, it can be said that there is considerable potential within conventional biological systems to improve color removals in the textile industry. Therefore, in the most cost-effective approach to improved color removal, consideration should be given to ensuring that the basic site-specific biological system is first optimized before considering add-ons. Once the basic system is optimized in performance, one of the more attractive add-ons emerging is the concept of anoxic or anaerobic pre-treatment.

Evidence is accumulating worldwide (Bow 1994, Terzis 1997, Fontenot 1998, Bahorsky 1996) that supports the idea of reductive dye decolorization mediated by facultative/anaerobic bacteria. Of the vast array of color removal options (see earlier list) few possess the simplicity, and cost-effective promise of an anaerobic pre-treatment step prior to an abbreviated aerobic polishing step. The ultimate objective of an anaerobic step is to facilitate the aerobic step by decolorizing dye molecules and, thereby reducing the need for extended air systems with large basins and high power levels. Weber (1991) was one of the first to describe the anaerobic decolorization of disperse dyes in stream sediments, and preliminary indications are that reactive dyes are also highly susceptible to the reductive anaerobic decolorization process.

The finding that dye decolorization occurs under anaerobic soil conditions was observed during natural system treatment of textile acid dye wastewater in 1980 while conducting a pilot treatment system evaluation of the overland flow land treatment mode (Bahorsky and Deemer 1990). Table II illustrates pilot-scale bioassay data on overland flow effluents taken during the application of 100% mill wastewater. The raw wastewater acute and chronic toxicity tests, and the two effluent tests, were taken before the hillside fully “matured” in its optimal treatment capability. It is of interest to note that the natural system treated run off showed a stimulatory effect of the treated effluent relative to the number of Ceriodaphnia off-spring which were produced. Table III shows COD removals from the pilot-scale tests. At CODs averaging 2172 mg/l, the natural system produced 86% removal of the raw textile wastewater. The full-scale overland flow system, built as a polishing step after an aerated lagoon, and located in Gordonsville, Va., has now been operating satisfactorily in terms of color removal for over ten years.

This system is remarkable for a number of other important reasons. First the treatment system is located on a zero flow 7Q10 stream. This is a stream that essentially dries up in the summer time. Therefore, the discharge limitations imposed were very strict at 5mg/L BOD and TSS. The original aerated lagoon system also never met bioassay test requirements and discharged excessively high color. After the overland flow treatment was constructed, dye color and toxicity were never a problem. This was true for the toxicity testing even at 100% effluent using both Ceriodaphnia dubia and fathead minnows. Table IV lists the treatment mechanisms found in natural systems for textile pollutants. The potential for natural system polishing steps when applicable is evident in this example. Reed (1991) discussed the potential of natural systems for polishing effluents to the point of producing potable water.

A third emerging technology is a catalyzed ozone process that significantly improves the conventional method of ozone treatment. The following discussion describes how two color removal methods are combined to produce a synergistic color removal effect. Eckenfelder (1988) demonstrated how activated carbon could remove certain dye color by adsorption, significantly improve toxicity test results, and improve metal removal, Table V. He also showed how ozone could be used for improving organic removals and toxicity test results, Table VI. In a study of the catalyzed process (Eco Purification Systems, Inc.), tests were conducted in glass columns containing a carbon catalyst and compared to ozone effects without the catalyst, or "plain" ozone. A simplified schematic of the treatment system is shown in Figure 1. Before applying the ozone, the carbon was partially saturated with dye and organic chemicals. Wastewater and ozone were then fed up-flow through the catalyst bed. The plain ozone control was run without the carbon catalyst in place. Raw waste feeds and ozone dosages were monitored continuously.

The dyes selected for the evaluation are shown in Table VII. These dyes were selected for their volume of use in the industry and their molecular structure characteristics.

In the catalyzed process, organics, metals, and ozone are attracted to the carbon. The organics are adsorbed to the carbon and the ozone is chemisorbed to the carbon surface. Vigorous reactions occur that have been demonstrated not to involve OH- radicals. The oxidized by-products are desorbed from the carbon, such as CO2 and H2O, and the carbon is regenerated in place. The ability to regenerate carbon in place is a major operational cost benefit not available in the conventional carbon application mode. Table VIII demonstrates how the catalyzed ozone system performs compared to the conventional method of ozone treatment, or plain ozone.

It can be seen that in each case involving the soluble dyes that the catalyzed ozone process produces significantly better color, COD, and TOC removals than the conventional or plain ozone method. The Basic dye was removed more efficiently than the rest of the dyes, and only required a retention time of 30 minutes compared to the other dyes that generally required 60 minutes retention. It should be noted that the ozone concentration required and the detention time needed will be a function of the dye concentration. In this case the raw waste mixtures were virgin chemicals and dyes. After a biological treatment system, it would be important to know whether or not the organic molecules were "softened" by the biological treatment. Biological oxidation would likely improve the adsorption characteristics and the ozone oxidation requirements. In evaluating the sulfur dye, treatability was closer to the conventional ozone process. This is because insoluble dyes are poorly adsorbed into carbon. Without appreciable adsorption into the carbon, the synergistic effect does not manifest itself.

In the case of sulfur dyes, the amount of ozone needed for removal down to trace amounts of color is twice to three times that needed for the most difficult soluble dye. The COD however is removed without difficulty, similar to the soluble dye tests. Comparative results show that the catalyzed process (84% COD removal) continues to have an advantage over the conventional ozone (60%) method in COD removals.

Conclusions and Recommendations

In conclusion, it can be said that there are many methods available for textile color removal. The primary questions in terms of practicality, however, have to do with the system designer's long-term familiarity with textile color problems, costs, long-term performance, system reliability, and the magnitude of the problems that develop in operation and maintenance. Emerging innovative systems were discussed, and the features that demonstrated their promise were examined against the current state-of-the-art. The methods included a biological pretreatment step, a biological polishing step, and an oxidation step that could be used in-plant or at the end of the pipe. It was recommended that a rational approach to seeking a cost-effective application of any emerging method of interest should involve a site-specific preliminary bench test for feasibility, an appropriate pilot study to ensure the long-term performance reliability and to establish realistic scale-up costs. Anything less than these two critical steps could compromise the anticipated treatment performance and the cost-estimating accuracy.

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notes

TABLE 1

COMPARATIVE COSTS FOR DECOLORATION METHODS AT 2.0 MGD FLOW

Technology	Construction Costs (x $1000)	Major Operating Cost Component ($/year)	Construction Costs ($/GPD)
Ozone	3,020	460	1.51
Carbon	890	5,000	0.45
Coagulation	585	1,060	0.29
Equalization/Chlorination	985	1,500	0.49
Chlorination	325	740	0.05

Ref: Electric Power Research Institute Study, 1993.

TABLE 2

RESULTS OF CERIODAPHNIA AFFINIS 7-DAY REPRODUCTIVE POTENTIAL TEST

Test Concentration	Percent Survival	Young per Female		Young per Surviving Female	
		Total	x (+S.D.)	Total	x (+ S.D.)
Raw Mill Wastewater					
Control	100	127	12.7 (6.1)	127	12.7 (6.1)
0.3%	80	65	6.5 (4.7)	62	7.8 (4.4)
1%	100	22	2.2 (1.8)	22	2.2 (1.8)
3%	80	0		0	0
10%	0	0		0	0
30%	0	0		0	0
Overland Treated Run-Off					
Test 1 1%	80	98	9.8 (8.5)	95	11.9 (8.3)
3%	90	151	15.1 (6.2)	151	16.8 (3.4)
10%	100	232	23.2 (5.8)	232	23.2 (5.8)
30%	100	231	23.1 (3.0)	231	23.1 (3.0)
100	50	38	3.8 (3.1)	26	5.2 (2.7)
Test 2 1%	90	159	15.9 (6.5)	159	17.7 (3.5)
3%	90	177	17.7 (5.8)	152	16.9 (5.5)
10%	100	243	24.3 (4.0)	243	24.3 (4.0)
30%	80	254	25.4 (6.3)	198	24.8 (6.8)
100%	80	97	9.7 (9.9)	97	12.1 (9.7)

TABLE 3

OVERLAND FLOW COD REMOVAL AT LOADINGS AROUND 2000 MG/L

Data	Feb. 7	Feb. 22	Mar. 2	Mar. 22	Apr. 25	Average
Raw COD, mg/l	2364	2260	1910	1867	2460	2172
Treated COD, mg/l	390	280	297	323	220	302
Percent Removal						86

TABLE 4

NATURAL SYSTEM TREATMENT MECHANISMS

Constituents	Treatment Mechanisms
Organics	Aerobic and anaerobic stabilizations
Suspended solids	Precipitation, filtration, biodegradation
Metals	Adsorption, ion exchange, plant up-take
Nitrogen	Volatilization, mineralization, nitrification, denitrification
Color	Adsorption, anaerobic reduction, aerobic oxidation, UV

TABLE 5

DOSAGES OF POWDERED ACTIVATED CARBON FOR THE REMOVAL OF ORGANIC CARBON, COLOR, AND HEAVY METALS

	Wastewater Composition (mg/l)							
	BOD	**TOC**	**TSS**	**Color**	**Cu**	**Cr**	**Ni**	**Bioassay LC_{50}***
Influent	320	245	70	5,365	0.41	0.09	0.52	
Biotreatment	3	81	50	3,830	0.36	0.06	0.35	11
+50 mg/lPAC	4	68	41	2,900	0.30	0.05	0.31	25
+100mg/lPAC	3	53	36	1,650	0.18	0.04	0.27	33
+250mg/lPAC	2	29	34	323	0.07	0.02	0.24	>75
+500mg/lPAC	2	17	40	125	0.04	0.02	0.23	>87

* Percentage of wastewater in which 50 percent of aquatic organisms survive for 48 hours.

Ref: Civil Eng. Practice, Spring 1698, Eckenfelder

TABLE 6

RESULTS OF OZONATION TREATMENT OF FINAL PLANT EFFLUENT

Ozone Dosage (mg O_3/l)	48-Hour LC_{50}(%)	TOC (mg/l)
0	5.6	152
100	49	96
300	60	108
600	87	88

Ref: Civil Eng. Practice, Spring 1998, Eckenfelder.

TABLE 7

DYES USED IN CATALYZED OZONE TESTS

Dye Name	Color Index Number	Dye Structure
Direct Yellow 106	40300	Stilbene
Acid Orange 156	26501	Disazo
Reactive Black 5	20505	Disazovinylsulphone
Sulfur Black 1	53185	-

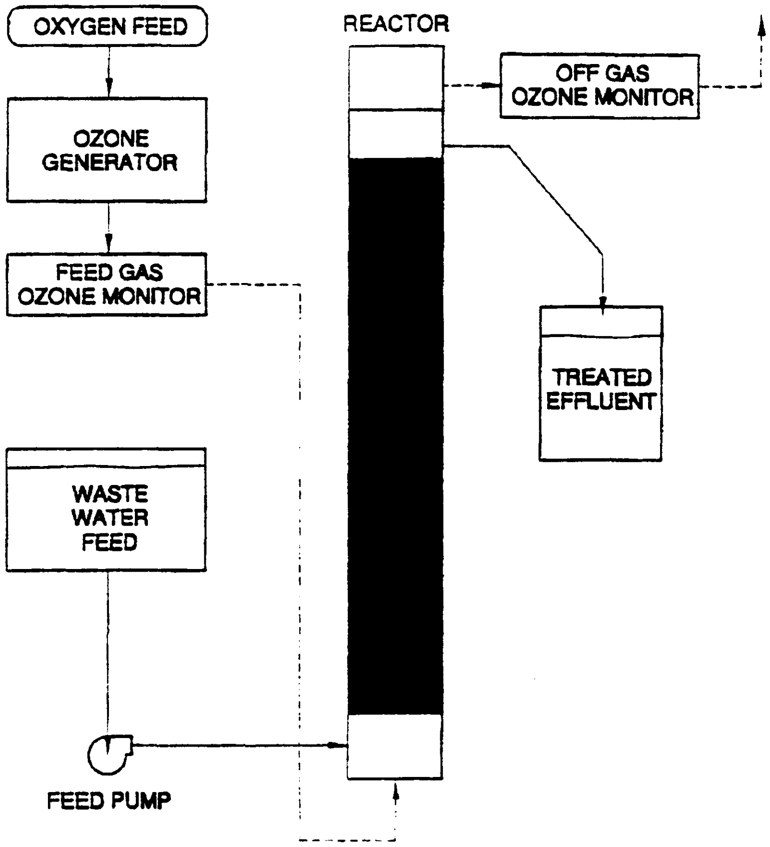

FIGURE 1

OZONE LABORATORY REACTOR

TABLE 8

COMPARATIVE COLOR AND COD REMOVALS - PLAIN vs. CATALYZED OZONE TREATMENT

Condition	Ozone	Raw	Raw	Raw	Treated	Treated		% Removal	
	Dose, mg/l	COD, mg/l	TOC	Color	COD	TOC	Color	COD	Color
Basic Blue									
Cat. Ozone	28	296	98	575	80	30	18	80	97
Plain Ozone	28	208	90	450	152	73	82	27	82
Reactive Black									
Cat. Ozone	100	119	-	2575	7	8	100	94	96
Plain Ozone	146	119	-	2575	106	50	180	11	93
Acid Orange									
Cat. Ozone	180	457	176	6500	136	64	30	70	96
Plain Ozone	190	457	-	6500	380	-	500	17	92
Direct Yellow									
Cat. Ozone	250	610	178	2500	176	69	40	61	98
Plain Ozone	230	740	-	2800	510	-	80	31	97
Sulfur Black									
Cat. Ozone	605	140	39	3925	27	19	160	81	96
Plain Ozone	605	140	38	3925	40	26	12	71	99

Ref: ECO-Purification, 1998.

Color P2 Through Improved Process Control

PRESENTATION

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College of Textiles

Color P2 Through Improved Process Control

Dr. Warren Jasper

Dr. Brent Smith

June 17, 1998

Charlotte, NC

Pollution Prevention

- Looks at processes to avoid wastes
  - Control systems are a key
  - Less expensive than new equipment
  - Improved quality and safety
- **D**ye **A**pplications **R**esearch **G**roup
  - Long term research project on control
  - Many broadly applicable results
    - All results to date are public domain
    - Proven performance

Pollution Prevention

- Applies to four waste types
  - Persistent or difficult to treat
    - Passes through treatment systems
  - Offensive or hazardous
    - Causes great damage if discharged
  - Dispersible
    - Mixes easily with other wastes
  - High volume

Color

- A good pollution prevention target
  - Dispersible
  - Difficult to treat, persistent
  - High volume
  - BUT ... Usually not hazardous
- Three out of four ain't bad!

P2 Methods - Directly Related to Process Monitoring and Control

Process design

Process optimization (individually)

High level of right-first-time performance

Equipment: faults, fouling

Evaluating chemical alternatives

Raw material selection/performance

Pollution Prevention - Methods

Automated bulk dye/chemical systems

Dosing dyes and chemicals

Waste segregation

Avoiding discards & excessive make-up

Waste: audit, detection, quantification

Production scheduling

Facilitates dyebath/waste reuse

Examples of P2 by Better Control

- Flow control on continuous washers
  - Minimum necessary flow
  - How much washing is enough (real-time)
- Dyebath exhaustion control
  - Recipes individually optimized (real-time)
    - How much salt is enough
    - What is the optimum temperature
    - What is the optimum pH
- Accurate mix make-up and dosing

DARG Control Approach

✓ Product (not process) driven

✓ Real-time

✓ Multi-channel

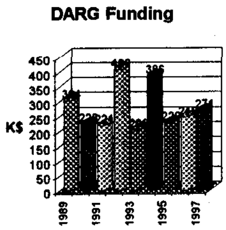
✓ Adaptive
  - Minimizes calibration down time

✓ Advanced methods
  - Neural nets, Fuzzy logic

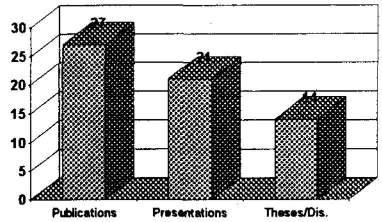
✓ Conforms to public standards

Funding

Total Funding = $2.5M over 9 years

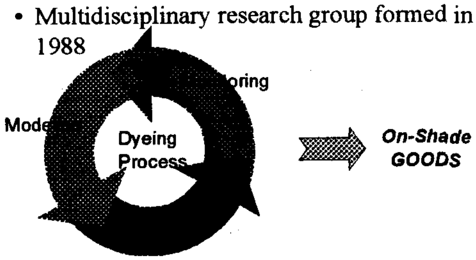


Publications and Presentations



DARG Information

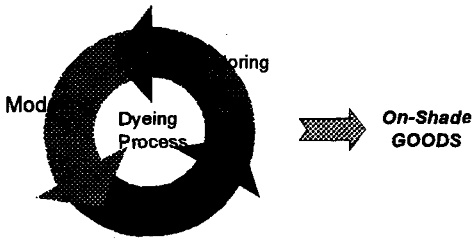
- Multidisciplinary research group formed in 1988



Real-Time Monitoring

- Direct Dyebath Monitoring System
  - Determine Dye Concentration in 3-Dye Mixture in Bath and On Cloth
  - Direct, Acid, Basic, Reactive
  - Dye-Dye Interaction Effects
  - Dye-Salt Interaction Effect
  - Correlation Between Optical and Kinetic Properties
- Flow Injection Analysis
  - Direct, Reactive, Disperse, Indigo
  - HPLC-FIA to Determine Reactive Dye Exhaustion and Hydrolysis
  - Reduce effects of Temperature, pH, Salt, Aggregation on Concentration Measurement

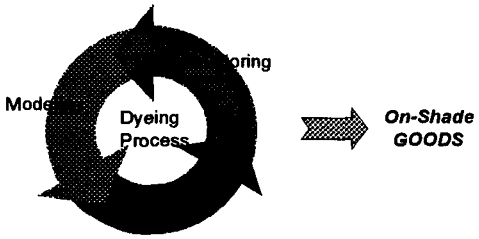
DARG Information



Real-Time Dyebath Modeling

- Parametric
  - Langmuir
  - Diffusion Models
  - Dimensionless Groups
  - System Identification (ARMA)
- Non-Parametric
  - Neural Networks
  - Fuzzy Logic

DARG Information



Real-Time Control

- Fuzzy Logic Control of Single Direct Dye (Rule Based)
- Direct Dyebath Monitoring and Control of Single Direct Dye
- Dosing Control of Two Acid Dyes on Nylon
- Network/Distributive Approach to Real-Time Control
- Neural Network Based **Color** Matching System

Systems Monitored / Controlled

- Acid dyes on Nylon
- Fiber reactive on cotton
  - Exhaustion and fraction hydrolyzed
  - In real-time
- Basic dyes on acrylic
- Direct dyes on cotton
- Disperse on polyester
- Indigo - continuous dyeing

Machines Monitored / Controlled

- Lab
  - Ahiba - Texomat
  - Package dyeing - colormat
  - Continuous padder
- Pilot plant
  - Gaston County Package Machine
  - Gaston County Jet

Project Status

- Monitoring systems available now
  - Lab and pilot plant
  - Portable systems for in-plant use
- Consortium of users is starting up
  - Based on previous research
    - $2.5 million funds, 22 researchers, 9 years
    - All results to date are public domain
  - Five companies are committed
  - $30K per year membership / 3 years

Conclusion

- Multidisciplinary/TEAM approach to
  - Graduate student education/research
  - Generation of new information
  - Solving **Fundamental** dyeing problems
- Close interaction with industry is critical for our continued success