

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

C02-GT09

Competency: Chemistry

Color Destruction in Mill Effluent via Biomimetic Methods

Project Team:

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Objective:

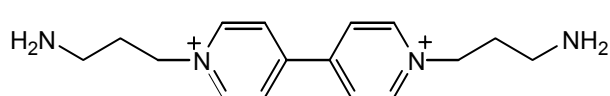
Our objective is to attach biomimetic catalysts to the surfaces of nanofiber based filtration media to decolor residual dyes in dyehouse effluent using low energy and low cost materials.

During the three years of this project, the team plans to:

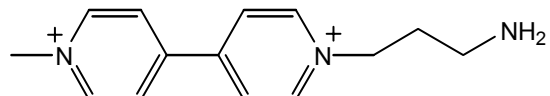
- Attach reactive oxygen producing agents to the surface of nanofibers.
- Determine and optimize the effectiveness of the destruction of residual dyes in the effluent by these agents.
- Determine the mechanisms of the reactions and their dependencies on pH, local environment, polymer chain mobility, ...
- Determine the effect of these materials on the bacteria in wastewater treatment facilities.

Progress Statement:

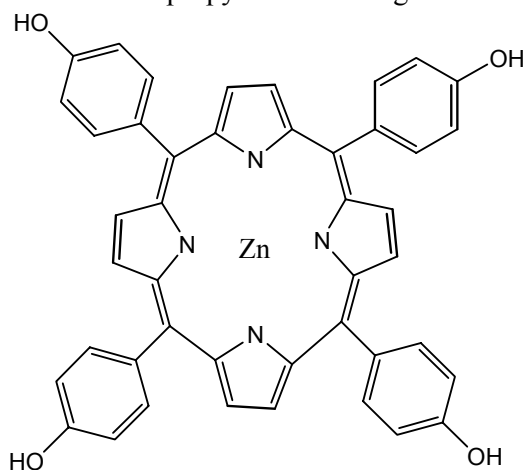
Several porphyrins and viologens have been synthesized. Specifically, methyl propylamino viologen, dipropylamino viologen, zinc tetrahydroxyphenylporphyrin, and zinc tetracarboxyphenylporphyrin have been synthesized and characterized.



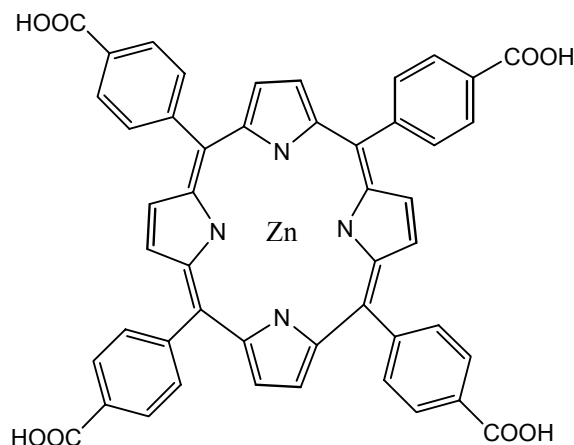
Dipropylamino Viologen



Methyl Propylamino Viologen



Zinc Tetraphenylhydroxy Porphyrin



Zinc Tetraphenylcarboxy Porphyrin

In addition, we have grafted poly(acrylic acid), PAA, to the surface of nylon-6,6 to facilitate attachment of the porphyrins and viologens and are in the process of attaching them. We have also grafted protoporphyrin IX to the surface of nylon-6,6 using PAA as a coupling agent. We have developed a new coupling process to improve the uniformity of the coupling reaction to facilitate testing.

X-ray photoelectron spectroscopy, XPS, has shown that 60% of the surface of the fibers is covered with the desired porphyrin molecule. We are attempting to increase the coverage to increase the amount of the active moiety. In addition, these samples are in the process of being tested for their effectiveness in destroying dyes in simulated mill effluent.

Next Year's Goals:

The effectiveness of the porphyrin and viologen derivatives in destroying dyes in mill effluent will be tested. The amount of singlet oxygen produced during illumination will be measured. The durability of these agents will be determined. New porphyrins and viologens will be synthesized to enhance their durability *and* maximize the amount of singlet oxygen produced. In addition, we will measure the toxicity of both the initial mill effluent and the treated effluent on several bacteria to determine if this treatment improves or worsens the environmental impact of the effluent.

Approach:

Modified natural porphyrins, synthetic porphyrins, synthetic metalloporphyrin, and related materials (e.g. phthalocyanines) based catalysts will be grafted to poly(acrylic acid) or other polymers to form nanofactories. The nanofactories will be optimized to destroy several target dyes. These nanofactories will be sited on the surface of nylon, cotton, and polyester via biochemical techniques and reactive dye chemistries. This will eliminate the need to remove the catalysts from the products or effluent. Nanofibers will be used when possible to get the largest surface areas and hence the maximum number of reactive sites. The concentration of catalyst and types of catalyst will be varied. The local pH will be adjusted via conversion of the remaining acid groups to neutral species or amines. The mobility of the PAA chain will be varied by lightly cross-linking it. The molecular weight of the PAA will also be varied as well as the solvent under which the chemistry will take place. The use of no additional solvents will also be explored. Thus at least eight different variables will be explored to determine how they affect performance. Chemometrics will be used to unravel this complex problem.

In particular, our initial efforts will be to synthesize manganese 5-(4-carbomethoxyphenyl)-10,15,20-tris-(2,6-dichlorophenyl)porphyrin and analogs. These porphyrins as well as protoporphyrin IX and its metallo-derivatives will be grafted to poly(acrylic acid) via the techniques developed in NTC project C98-A17 and subsequently attached to nylon nanofibers (from eSpin). Azo- and other dye solutions will be flowed through these fabrics in the presence of H₂O₂. The rate of decolorization will be followed spectrophotometrically. Stojiljkovic will test whether any byproducts of these factories cause an increase in mutagenicity and toxicity. The reaction conditions, rates, and catalyst lifetimes will be determined.

Subsequently, Stojiljkovic (expertise: use of porphyrins and metalloporphyrins in microbiology) will explore the use of porphyrins and metalloporphyrins to simulate biological reactions to construct chemicals of interest to the textile enterprise. Michielsen (expertise: polymer physics, fiber physics, surface modification of polymers) will explore means of coupling the nanofactories to fiber surfaces. It is anticipated that nylon, PET, cotton and even PP will be suitable substrate candidates. He will determine the effectiveness of the grafted porphyrin-based catalysts and determine the effect of grafting on the kinetics, yield and lifetimes. He will define the relevant polymer physics of the graft porphyrin-containing polymer, including the polymer chain mobility, the polymer molecular weight, and its solubility in the reaction mixture. He will also study the effects of changing the local pH, the cross-link density, the fiber substrate, and the immersion solvent. He will also study the effects of other substituents on the effectiveness of the porphyrin-based catalysts. He will also use chemometrics to unravel the complex interplay between the many variables.

It is believed that by combining the means used by microbes to construct and destroy chemicals with modern chemical techniques and polymer physics, new techniques can be developed to destroy residual chemicals used by the textile enterprise. The proposed research will result in environmentally benign, efficient destruction of colored species in an energy efficient means.

Outreach to Industry:

The investigators will work with eSpin to design fiber substrates that are optimal for these applications and with Synar Technologies Inc. to develop the porphyrin derivatives. The results will be presented at ACS, APS, Fiber Society and other professional meetings and will be published widely.

New Resources Required:

None