TITLE: Biological Renovation and Reuse of Spent Reactive Dyebaths

Project Number: G96-2

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Project Goal: To evaluate the feasibility of using an anaerobic bioreactor system for the color removal and reuse of spent reactive dyebaths

ABSTRACT

The objective of this project is to biologically renovate reactive dyebaths and reuse the high-salt containing mixture in the dyeing process. An anaerobic, fixed-film bioreactor to achieve reducing conditions leading to the azo bond cleavage of reactive dyes will be developed. This approach will accomplish two goals: (a) destruction of the dye azo bond and therefore elimination of the color from the plant effluent; and (b) reuse of the renovated process water and salts which in turn will lead to wastewater volume reduction and water as well as salt conservation. The results of the proposed study will demonstrate the effectiveness and applicability of anaerobic biological processes as a low-cost decolorization and reuse technology for spent reactive dyebaths. Nine commercial reactive dyes have been chosen and represent the range of chemical structures in reactive dyes. The following tasks will be completed during the first project year: a) Development of anaerobic, suspended-growth stock cultures to be used in subsequent batch experiments; b) Batch anaerobic toxicity tests using a wide range of dye concentrations; and c) Batch experiments to determine the kinetics of color removal by the stock anaerobic cultures.

INTRODUCTION

The single most pressing environmental problem facing the textile industry is related to reactive dyes. The increased use of cotton has led to substantial growth in the usage of reactive dyes. As a result, the management of the spent reactive dyebaths has become a challenging and

pressing problem. The textile industry is confronted with the problem of color removal and effluent salt content reduction. As regulations becoming ever more stringent, the need for more technically and economically efficient means of both color and salt reduction from the plant effluent grows more acute. At the present time, there are no economically attractive means to achieve the reduction of these two parameters.

The key question addressed by this project is whether an effective (both technically and economically) means can be found to reuse spent reactive dyebaths. In addition to the dye, these streams have very high salt and heavy metal concentrations. Existing physical/chemical technologies for color removal are very expensive and commercially unattractive. Although it is extremely difficult to oxidize reactive dyes, their reduction can be achieved relatively easily. Microbial anaerobic processes are capable of producing and maintaining low oxidation-reduction potential conditions. Under such conditions, the dye azo bond undergoes cleavage, therefore permanently destroying color (Brown and Laboureur, 1983a; Chung and Stevens, 1993). Fast oxidation of aromatic amines produced as a result of dye reduction is expected based on literature data on the fate of these compounds in oxic environments (Brown and Laboureur, 1983b; Brown and Hamburger, 1987; Pagga and Brown, 1986; Shaul *et al.*, 1991).

OVERALL RESEARCH APPROACH

Anaerobic, batch and fixed-film bioreactors will be used in this study. All anaerobic tests will be performed at 23 and 35°C and selected experiments conducted at a higher temperature. The following reactive dyes have been chosen: Black 5; Red 2 and 120; Blue 4, 7, and 19; Yellow 3, 15, and 17. These dyes were selected as representative of the range of chemical structures in reactive dyes.

This study will be conducted in three phases. In Phase I, anaerobic, methanogenic processes will be tested for their efficacy in color removal. The suitability of other organic constituents of the spent reactive dyebaths (e.g., sequestering agents) as potential carbon source(s) for these processes will be assessed and glucose will also be used either as the primary

or auxiliary carbon source. Batch anaerobic toxicity tests as well as assays for the evaluation of the kinetics of color removal will be performed with the selected dyes. In Phase II, the effect of high salt concentration on the anaerobic processes and the acceptability of the renovated water for reuse in the dyeing baths will be assessed. The effect of salts will be tested in batch assays at varying salt levels as well as by gradually increasing the salt concentration of the bioreactors influent. In the event of very low degree of decolorization products destruction under anaerobic conditions, continuous reuse of the renovated spent dyebaths will lead to a build-up of these substances, requiring periodic disposal. In order to test the biodegradability as well as toxicity potential of these products, aerobic assays simulating the activated sludge process will also be conducted. During Phase III, the effect of heavy metals (e.g., Cu) on the anaerobic processes with regard to decolorization of metallo-dyes [e.g., phthalocyamine monochlorotriazinyl (Blue 7)] and the suitability of the treated spent dyebath for reuse will be investigated. In summary, two end-points will be used for the assessment of the spent dyebath decolorization and reuse: stability of the anaerobic bioreactors and suitability of the renovated solution for reuse.

FIRST YEAR RESEARCH

The following tasks will be completed during the first project year:

Task 1: Development of anaerobic, suspended-growth stock cultures to be used in subsequent batch experiments.

Task 2: Batch anaerobic toxicity tests using a wide range of dye concentrations.

Task 3: Batch experiments to determine the kinetics of color removal by the stock anaerobic cultures.

The remaining of this report outlines activities under way as well as future activities during the first project year.

Selection and Characterization of Dyes

Table 1 summarizes the dyes selected for this study and their manufacturers. All dyes are of commercial quality. Spectrophotometric scanning of dilute dye solutions has been performed to identify absorption maxima for each dye. Detection and quantification of the dyes will be achieved by high performance liquid chromatography. Since commercial dyes contain other admixtures, dye purification will be achieved by adsorption of aqueous dye solutions to a synthetic resin followed by dye extraction with solvent. Efforts are under way to optimize this purification technique. Based on the results of the purification step, the purity of each dye will be assessed. However, for all biological tests, the commercial dyes without any purification will be used.

Table 1. Selected reactive dyes

Color Index	Commercial Name	Supplier
Black 5	Remazol Black B	DyStar LP
Red 2	Procion Red MX-5B	BASF Corp.
Red 120	Procion Red HE-3B	BASF Corp.
Blue 4	Procion Blue MX-R	BASF Corp.
Blue 7	Cibacron Turquoise G-E	Ciba-Geigy Corp.
Blue 19	Remazol Brilliant Blue R	DyStar LP
Yellow 3	Cibacron Yellow R	Ciba-Geigy Corp.
Yellow 15	Remazol Yellow GR 110	DyStar LP
Yellow 17	Conazol Golden Yellow G	General Colors & Industries

Anaerobic Stock Cultures

An anaerobic, methanogenic culture enriched from estuarine sediments and used in our laboratory for dechlorination studies will be used in order to assess the specificity (or lack of) of

the culture for the cleavage of the dye azo bonds. This culture is fed with glucose as the main carbon and electron source and is maintained at 23°C. In addition, another anaerobic suspended culture is under development with inoculum obtained from a mesophilic, municipal anaerobic digester. This culture is fed with a mixture of organic compounds (dextrin and peptone), maintained at 35°C and batch-fed once a day with a retention time of 20 days. Both cultures will serve as stock for subsequent batch experiments.

Anaerobic Toxicity Assay

A batch assay is underway using the dechlorinating stock culture maintained at 23°C to evaluate any potential toxicity of the selected dyes to the anaerobic microorganisms as well as to determine the anaerobic biodegradability of these dyes. Two concentration levels of each dye are used, 100 and 1000 mg/L, and two sets of serum bottles have been prepared with and without glucose addition, respectively. Biodegradation of the selected dyes under anaerobic, methanogenic conditions will be assessed by the production of methane either in the absence of glucose or in the presence of glucose as excess gas produced over and above that in the glucose-amended controls. A similar batch assay will also be performed with the methanogenic culture maintained at 35°C when this culture has reached steady state.

Kinetics of Color Removal

Batch experiments will be performed to determine the kinetics of color removal for each dye under methanogenic conditions by using the above described stock, anaerobic cultures. Parameters to be evaluated include: initial dye concentration, biomass concentration, temperature (23 versus 35°C), addition of a degradable carbon source (glucose versus a mixture of organic compounds used as a feed to the mesophilic stock culture). Because of analytical difficulties, each of the reactive dyes will be tested separately using a high performance liquid chromatography technique.

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