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Degradation of a textile azo dye using biological treatment followed by photo-Fenton oxidation: Evaluation of toxicity and microbial community structure

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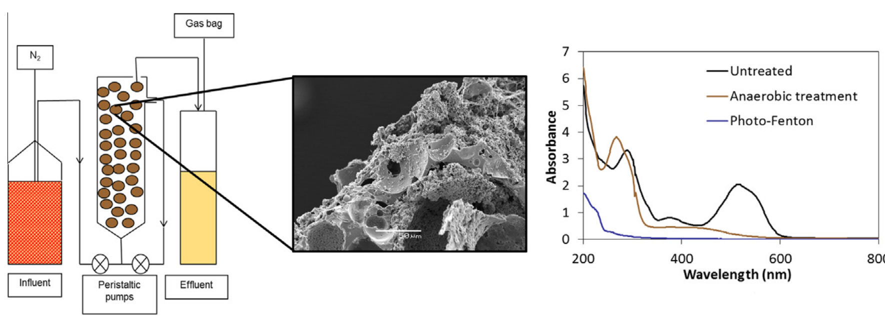
HIGHLIGHTS

- COD and UV absorbance were effectively reduced (>90%).
- The final effluent was non-toxic to *Artemia salina* and Microtox.
- DGGE was used to detect bacteria and eukaryotes in the biological process.
- Algae were detected for the first time in a reactor treating textile effluent.

GRAPHICAL ABSTRACT



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ABSTRACT

Many commercial dye preparations are cocktails of active dyes and various by-products that are recalcitrant to biological degradation and end up in significant amounts in the effluent after the dyeing process. Conventional wastewater treatment processes are not able to degrade such compounds and detoxify the effluent, thus alternative treatments should be developed.

In our work we suggest to use photo-Fenton oxidation as post-treatment after an anaerobic biofilm process, in a way to minimize the reagents needed. This process was used for treatment of synthetic textile wastewater containing the commercial azo dyestuff Remazol Red, starch and sodium chloride. The treated textile effluent had COD lower than 18 mg/l even when using initial Fenton reagents concentration as low as 1 mM ferrous ions and 10 mM hydrogen peroxide. The acute toxicity was higher in the biologically treated than in the untreated effluent. Photo-Fenton oxidation successfully reduced the toxicity and the final effluent was non-toxic to *Artemia salina* and Microtox, with the exception of the effluent containing high concentration of sodium chloride, which was moderately toxic to Microtox. For the first time the presence of algae was detected in a reactor treating textile wastewater using denaturing gradient gel electrophoresis (DGGE); bacteria and fungi were also abundant.

The results of this study suggest that using advanced oxidation after biological treatment is an effective way to degrade the organic compounds and remove toxicity from textile effluents.

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1. Introduction

Textile wastewater is one of the most problematic industrial effluents to treat. The dyes used, mostly azo dyes, are stable to light, washing and most chemical oxidants; moreover, 2–50% [1,2] of the dyestuff end up in the effluent after the dying process. Many commercial preparations are cocktails of active dyes and various by-products that are recalcitrant to biological degradation, therefore the pollution load is even higher. Large amounts of salt, in the order of 5–50 g/l, are used to improve the binding of the dyes to the fabric and use of sizing agents like starch or cellulose is necessary to facilitate the weaving [3]. Thus, the complexity of textile effluents is due to the presence of low or non-biodegradable compounds together with the high salt and organic load.

While traditional biological treatments are effective in reducing COD and BOD, mineralization of the azo dyes and their aromatic derivatives is not always obtained and the treated effluent can remain toxic [4,5]. To improve the effluent quality, addition of physical and/or chemical treatments is necessary.

Several biological processes have been evaluated for treatment of textile effluents. Anaerobic treatment has been shown to be efficient in color removal; moreover, it has lower nutrients requirements than the conventional activated sludge process, which is desirable since textile wastewater is characterized by a low content of nitrogen and phosphorous [3]. To obtain high COD reduction it is crucial to reach high biomass concentration; at the same time, easy separation of the treated effluent from the biomass is preferable. Thus, biofilm and granular reactors are suitable solutions. Mixed microbial communities are preferred when dealing with wastewater as they are more effective in degrading organic compounds and also less sensitive to toxicants compared to pure cultures. Nevertheless, there is high interest in improving our understanding of the biological processes by studying the microbial community and identifying the dominating species. Polymerase Chain Reaction coupled with Denaturing Gradient Gel Electrophoresis (PCR-DGGE) is commonly used to study the diversity and complexity of microbial communities in various types of systems [6,7]. Use of PCR-DGGE allows identification of the main components at species level and gives information regarding the structure and diversity of the community [8]. This information may be used to understand the functioning of a biological process as shown in the examples found in a review by Koch et al. [9], where correlation between relative abundance of certain bacteria and process efficiency is two anaerobic systems is reported. Bacteria are expected to be the dominant microorganisms in biological wastewater treatment processes, but the importance of archaea, algae and especially fungi should not be underestimated [10]. In most studies, only the bacterial community is analyzed [11,12] even if fungi are expected to play a more important role in the biotransformation of azo dyes and other complex organic pollutants [10].

Advanced oxidation processes (AOPs) hold the potential of degrading even complex organic compounds to small inorganic molecules by using the oxidative power of the hydroxyl radicals [13]. However, due to the complexity of some industrial effluents, e.g. textile effluent, high consumption of chemicals and energy may be required. This requirement can be substantially reduced by combining AOPs with biological treatments [14].

Photo-Fenton reaction is simple and highly efficient. In short, ferrous ions catalyze the decomposition of hydrogen peroxide and hydroxyl radicals are generated. With the help of light, the catalyst is regenerated and the reaction continues [13]. The relative low cost of the reagents, ferrous sulfate and hydrogen peroxide makes photo-Fenton a cheaper alternative than equally efficient processes like ozonation, in particular when sunlight is used. The use of Fenton or photo-Fenton treatment to enhance biological degradation of textile wastewater has been suggested. In most studies, the Fenton oxidation was conducted before a biological treatment to enhance the biodegradability of the dyes [15,16], although the photo-treated wastewater is not always biodegradable [17]. Considering that azo dyes do not inhibit microbial activity at the concentrations usually found in textile effluents [18], the use of a biological process as first treatment step gives some advantages. In particular, removal of easily degradable COD and nutrients during biological treatment is important for reducing the reagent requirements of the following photo-Fenton oxidation. In addition, during biological treatment azo dyes can be transformed into compounds that are toxic and can inhibit any further biodegradation making it essential to have a physical–chemical post-treatment.

The toxicity of textile effluents is associated with the dyes and their degradation products. These molecules represent only a small part of the total organic content, thus, it is important to run toxicity tests as an additional tool to evaluate the treatment efficiency. The target organisms of the toxicity tests should be chosen with care so that they are not sensitive to high sodium chloride concentration and are representative of more than one trophic level.

This study explores the possibility of treating textile wastewater with a continuous anaerobic biofilm reactor followed by photo-Fenton oxidation. Synthetic effluent composed of the industrial azo dye Remazol Red, starch and sodium chloride was used. The anaerobic treatment was used to reduce COD, whereas the photo-Fenton oxidation was used to achieve further dye mineralization. The impact of phosphate and chloride ions, which may reduce the iron availability, as well as Fenton reagent concentration on the quality of the treated effluent, was evaluated. The effectiveness of the single steps and of the overall treatment was evaluated through two acute toxicity tests. DGGE was used to assess the biodiversity of the reactors and improve our understanding of this biological process by identifying those microorganisms able to grow in presence of azo dyes and possibly playing a role in their biotransformation.

2. Materials and methods

2.1. Chemicals

Remazol Red was provided from a textile factory in Tirupur, India. According to the manufacturer it is a mixture of azo dyes composed of 50–60% dyestuff, 30–40% inorganic salts and up to 5% functional additives. In the experiment it was used as received, without further purification.

$Fe_2SO_4{\cdot}7H_2O$ (ICN Biochemicals Inc., USA), H_2O_2 30% (Merck, Germany) and Na_2SO_3 (Merck, Germany) were used for photo-Fenton experiments.

Anaerobic medium was prepared according to Jonstrup et al. [19]. Starch (BDH Chemicals Ltd., England) was used as carbon source at 0.465 g/l. The starch was dissolved in water by heating at 150 °C for 2 h, autoclaved and then hydrolyzed overnight by adding NaOH 1 M until reaching pH 12.

2.2. Biological treatment

Two anaerobic reactors were used in this study. The reactors were made of glass and had a total volume of 0.6 l of which 0.1 l was head space. The reactors were filled with Poraver carriers (Dennert Poraver GmbH, Schlüsselfeld, Germany) covered by a biofilm; the working volume of reactor A and B was 0.340 l and 0.345 l, respectively. The temperature was kept at 37 °C using a