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Case Study

Color, organic matter and sulfate removal from textile effluents by anaerobic and aerobic processes

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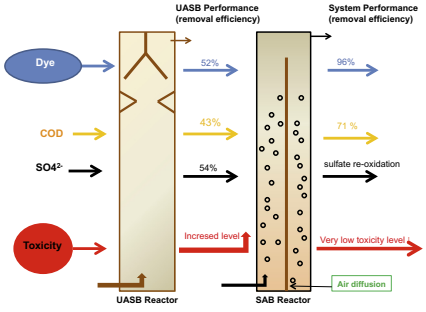
HIGHLIGHTS

- We treat real textile wastewater rich in sulfate, dye and organic matter.
- We use the combination of anaerobic and aerobic process.
- A precipitate material (sulfur and metals) was detected inside the UASB reactor.
- The precipitate impaired the dye removal under anaerobic conditions.
- The system was efficient in removing the textile effluent toxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

An upflow anaerobic sludge blanket (UASB)–submerged aerated biofilter (SAB) system was evaluated to remove color and chemical oxygen demand (COD) from real textile effluent. The system was operated for 335 days in three phases (P-1, P-2, P-3) with total hydraulic retention time varying from 21 h to 14 h. The results showed that high sulfate levels (>300 mg SO_4^{2-}/L) impaired the dye reduction. The best color removal efficiencies of 30% and 96% for the UASB and the reactor system, respectively, were obtained in P-1; the SAB higher efficiency was associated with adsorption. The best COD removal efficiency of 71% for the reactor system was obtained in P-2. Precipitation of some material composed mostly of sulfur (98%) and some metals occurred in the UASB. However, the precipitated sulfur was again oxidized in the SAB. The system also showed an effective toxicity reduction in tests (*Daphnia magna*) with the treated effluent.

1. Introduction

The textile industry has been growing extensively in recent decades. According to Textile Manufacturers, Exporters and Supplier (TMES, 2014) the global textile market expect to negotiate around $800 billion dollars in 2014, with a global textile production increase of 25% from 2010 to 2014. However, a proportional increase in the industrial effluents has been observed, releasing a correspondingly large amount of chemicals that can have negative effects on the environment. Each kilogram of goods produced can be the source of approximately 100 L of waste from dyeing and rinsing processes alone. Facilities that are involved in the dyeing of goods often turn out more than 3.7 million liters of wastewater each day (U.S.EPA, 1997).

The composition of textile effluents depends on the different organic-based compounds, chemicals, and dyes used in the industrial process. The dyes characterize the textile effluents as highly colored and are responsible for many problems in water bodies, making regulatory agencies increasingly concerned, especially

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about the possible carcinogenicity of some of the compounds (Peng et al., 2008; Rauf and Ashraf, 2009). The azo dyes are the most used for coloring clothes. In general, the biodegradation process of azo dyes by microbes occurs in two stages. The first stage involves the reductive cleavage of the bonds (N=N) under anaerobic conditions, resulting in the formation of aromatic amines; these compounds are generally free of color but are nonetheless toxic (Mendez-Paz et al., 2005; Razo-Flores et al., 1996). In the second stage, aerobic microorganisms transform such amines into organic acids or CO_2 and H_2O (Tan et al., 2000).

Although already proved to be a feasible method, the biological process for treating textile effluents is not commonly applied in real scale due to significant variation in wastewater composition, including the presence of high salinity levels, some bactericidal compounds and sulfate. Physicochemical processes such as coagulation, flocculation and sedimentation are the most used in real scale (Solanki et al., 2013), generating large amounts of sludge, an undesirable by-product. However, the availability of organic matter that is easily degradable in this type of effluent, highlights the challenge to keep looking for technological alternatives to the biological treatment (Senthilkumar et al., 2011). Regarding the treatment of real textile wastewater, few studies have reported good removal efficiencies for chemical oxygen demand (COD), color and toxicity through the use of anaerobic–aerobic reactors (Frijters et al., 2006; Ferraz Jr. et al., 2011). However, the influence of sulfate, especially at high concentrations, was not evaluated in those studies.

Both azo dyes and sulfates are electron acceptors and may compete for the source of organic matter in anaerobic reactors. The occurrence of sulfate reduction depends on the ability of the microbial population and the availability of easily degradable organic matter. As starch is commonly found in textile wastewater (from degumming), it can easily be converted into volatile acids, mainly acetic, propionic and butyric acids, under anaerobic conditions, thus, providing a substrate for sulfate reduction. Depending on the thermodynamic conditions, sulfate removal can overhang the dye reduction. However, sulfide generated from sulfate reduction may also donate electrons for the reduction of azo dye.

Recent publications have focused on the use of technological applications to improve the biological removal of azo dyes, including the use of electrodes (Wang et al., 2013), electrodes plus redox mediators (Sun et al., 2013) and new materials such as carbon nanotubes (Pereira et al., 2014). However, very few studies have been published regarding the treatment of real textile wastewater, and even fewer have reported on the additional influence of high sulfate levels on the performance of biological systems.

In the present study, a system with an upflow anaerobic sludge bed reactor (UASB) followed by a submerged aerated biofilter (SAB) was operated to evaluate the behavior of removing color, organic matter and toxicity from real textile effluents subjected to high sulfate concentrations (>300 mg SO_4^{2-}/L).

2. Methods

2.1. Experimental setup

The UASB–SAB reactor system was installed in a textile laundry facility, which is classified as a midsized company, in the city of Caruaru, semi-arid region of Pernambuco, Brazil. The laundry average monthly water consumption was 500 m^3, reaching 1050 m^3 at peak production during the experimental period.

The industrial effluents generated from all processing stages (degumming, dyeing, neutralization and softening) were equalized in a tank from where they were pumped into a 500-L reservoir. The equalized effluent was then fed into the UASB and SAB by gravity.

The reactors' diameter was 0.4 m; the heights were 2.0 m and 1.5 m, and the working volumes were 250 L and 187 L, for the UASB and SAB reactors, respectively. The SAB expanded clay support materials were spheres (2-cm diameter, 0.389-g m^{-3} density, and water uptake of 10.8%), which remained drowned during the entire period of operation. The clays particles were chosen because of the easier local availability; and they are reported as a good material for biomass immobilization (Amorim et al., 2009). The SAB was provided with a radial aeration system. A compressor (MS 2.3 Air Plus – Schulz) supplied diffused air, carried by a perforated PVC pipe. Dissolved oxygen (DO) was continuously measured in the SAB effluent pipe by an oximeter (model LDO HQ10 – Hach); the concentration of 3.0 mg L^{-1} was maintained in that point, by adjusting the air flow through the SAB reactor.

The UASB reactor was inoculated with anaerobic sludge from a municipal wastewater treatment plant, which had significant microbial diversity (Lucena et al., 2011). The SAB reactor was not inoculated.

The reactors UASB and SAB were operated for 335 days with hydraulic retention times (HRT) respectively of 12 h and 9 h during Phase 1 (P-1, 140 days, from months 1 to 5) and Phase 2 (P-2, 60 days, from months 8 to 9), and of 8 h and 6 h during Phase 3 (P-3, 135 days, from months 10 to 14). The reactors were out of operation for two months between P-1 and P-2 due to operational problems (months 6 and 7). The phase P-2 was changed to P-3 when the apparent steady state was reached for the COD parameter.

The reactors were monitored daily by measuring the flow rate and pH, as well as by analyzing color, COD, sulfate, turbidity, total nitrogen, and phosphate, twice a week. Volatile fatty acids were analyzed on a weekly basis by titration (Dilallo and Albertson, 1961) during the P-1 phase, as well as by gas chromatography (Moraes et al., 2000) during the P-2 and P-3 phases. At the end of each experimental phase iron was also analyzed and the effluent toxicity levels, using *Daphnia magna* as an indicator, were determined. Biomass profile, measured as total volatile solids (TVS), was conducted in the end of each experimental phase only in the UASB due to the reactor's configuration with available ports. The SAB reactor, however, did not allow the sludge sampling. All parameters were determined according to the Standard Methods for The Examination of Water and Wastewater (APHA, 2005). Scanning with light absorption in the range of 200–350 nm was performed with samples of the influent system and effluent of each reactor. The samples were filtered through a 0.45-μm membrane, to qualitatively evaluate the formation of aromatic amines, as suggested by Pinheiro et al. (2004).

The chemical composition of the precipitated material was determined by X-ray fluorescence using aX ZSX Mini II – Rigaku-rays fluorescence spectrophotometer and X-ray diffraction (Shimadzu XRD) with Cu–Ka radiation (λ = 1.54056 A), voltage of 40 kV, current of 20 mA and scanning angle (2θ) ranging from 3° to 70°. The results were statistically analyzed using a *t*-test (Montgomery and Runger, 2013).

3. Results and discussion

All dyes used in the laundry during the experimental period were water-soluble azo compounds, set during the washing operation by using NaCl. The dye most commonly used during the experimental period was Direct Black 22 (DB22, $C_{44}H_{32}N_{13}Na_3O_{11}S_3$; C. I. 35435; CAS 6473-13-8; molecular weight of 1083.97 g mol^{-1}), which is a tetra-azo dye. During the period of the reactors' operation, 779 kg of this dye and over 35 tons of NaCl were consumed. Another important consumption is concerned with 2764 kg of