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Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes

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Abstract

The effect of untreated and Fenton-treated acid dyes (C.I. Acid Red 183 and C.I. Acid Orange 51) and a reactive dye (C.I. Reactive Blue 4) on aerobic, anoxic and anaerobic processes was investigated. The optimum Fe^{2+}:H_2O_2 molar ratio was selected as 1:5 (4 mM:20 mM) for 10 min Fenton treatment at pH 3, resulting in reduced chemical oxygen demand and dissolved organic carbon removal efficiencies; only acetate was detected as a stable dye oxidation end product. During anaerobic digestion, 100, 29% and no inhibition in methane production was observed for the untreated blue, red and orange dyes, respectively. The inhibitory effect of the blue reactive dye on methane production was ~21% after Fenton treatment. Neither untreated nor treated dyes exhibited an inhibitory effect on denitrification. Aerobic glucose degradation was inhibited by 23–29% by untreated dyes, whereas Fenton-treated dyes had no inhibitory effect on aerobic glucose degradation.

Keywords: Dyehouse effluent; Acid dyes; Reactive dyes; Fenton treatment; Aerobic, anoxic and aerobic treatment processes

1. Introduction

The textile preparation, dyeing and finishing industry is one of the mightiest water consumers among different industrial sectors and produces 50–100 L wastewater/kg of finished product [1]. From the environmental point of view, particularly the textile dyeing process constitutes a major pollution problem due to the variety and complexity of chemicals (dyes, sequestering agents, tannins, dye carriers, leveling agents, dispersing agents, etc.) employed. Among the textile auxiliaries, dyes have attracted the most attention since color in dyehouse effluent not only causes environmental concerns, but also creates a significant aesthetic problem in sewage treatment works and receiving water bodies [2–4].

Conventional chemical (coagulation–flocculation) and biological (activated sludge, sequential bed reactors, anaerobic/anoxic)-based processes are widely used for textile wastewater treatment, however, with a rather limited success [5,6]. Although some of the more biodegradable dye auxiliaries may be completely eliminated from dyehouse effluent, conventional treatment systems cannot achieve ''destructive'' decolorization due to the fact that textile dyes are intentionally designed to resist biological, photolytic and chemical degradation. The nature of textile effluent depends on fashion, technical, technological, social and economical factors. These effluents often require pre-treatment of segregated process streams (e.g. dyebath effluent) using alternative, advanced oxidation processes (AOPs) that have more recently been used to treat refractory and/or toxic pollutants [7–9].

Among the AOPs, the Fenton's process is quite well known and has been successfully applied for the treatment of dyehouse effluent [10–17]. The Fenton's reagent is relatively cheap and easy to handle compared with other AOPs. Fenton's reagent (being a mixture of H_2O_2 and Fe^{2+} and applied at acidic pH) can be effectively used to achieve complete color and partial COD removal from textile effluent and thus an attractive option to prepare recalcitrant process streams to conventional activated sludge treatment of the combined wastewater. However,

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advanced oxidation products might be more toxic and/or inhibitory on the biological treatment systems used for the post-treatment than the original textile dyes. In fact, many studies have recently reported the effect of Fenton pre-treatment of textile (mainly reactive and acid) dyes on aerobic biological treatment processes by coupling the Fenton (or Photo-Fenton) process with an aerobic biological (mainly sequential batch) reactor; however, no study dealing with the influence of Fenton oxidation of textile dyes on anaerobic and anoxic biological process has been published so far [17–22]. Due to the fact that the textile dyer and finisher is mainly confronted with anaerobic and anoxic treatment systems, it is more interesting and important to study the behavior of these dyes and their degradation products under anaerobic and anoxic conditions.

Considering the above mentioned facts, the aim of the present study was to evaluate the effect of Fenton's treatment of three commercially important textile industry dyes on conventional biological (anaerobic, anoxic and aerobic) processes. For this purpose, two acid dyes, namely Acid Red 183 (AR 183) and Acid Orange 51 (AO 51), and one reactive dye, i.e. Reactive Blue 4 (RB 4), were selected as model textile dyes and subjected to Fenton's treatment under different oxidant (H_2O_2) and transition metal catalyst (Fe^{2+}) concentrations. Fenton treatment efficiency was assessed in terms of color, COD (chemical oxygen demand) and DOC (dissolved organic cabon) removal rates. The study also aimed at quantitatively identifying stable advanced oxidation end products that were expected from textile dye degradation such as carboxylic acids (formic, acetic, malic, maleic, etc.) as well as inorganic salts such as sulfate, nitrite, nitrate and chloride. In the second part of the study, the inhibitory effect of untreated and Fenton-treated textile dyes on biological processes was examined in terms of (a) methane production, (b) denitrification and (c) glucose-COD activated sludge treatment rates.

2. Materials and methods

2.1. Textile dyes

Two acid dyes (AR 183 and AO 51) and one reactive textile dye (RB 4) were chosen as refractory model pollutants and all purchased from Aldrich. Particularly these three textile dyes were selected for this study since their molecular structure is exactly known and all three dyes are frequently being applied for the dyeing of cotton, woolen and nylon (polyamide) fabrics worldwide as well as in Turkey. Some important physicochemical properties of the selected textile dyes are presented in Table 1. For the Fenton treatment as well as anaerobic, anoxic and aerobic experiments, 100 mg/L aqueous dye solutions (corresponding to 171 μM AR 183, 116 μM AO 51 and 157 μM RB 4) were prepared in distilled water. The reason why particularly 100 mg/L was selected in the present study are formerly published papers [17,21,23] as well as private communications with technical staff from local dyehouses [24–26] indicating that the dye concentration typically encountered in effluents originating from the cotton and polyamide dyeing factories is in the range of 10–200 mg/L. Environmental characterization of 100 mg/L aqueous solutions of the selected dyes in terms of COD, DOC and absorbance parameters is given in Table 2. The other reagents used in the present study were hydrogen peroxide (H_2O_2; 35% w/w, Fluka), ferrous iron sulfate heptahydrate ($Fe(SO_4)\cdot 7H_2O$, Fluka), and enzyme Catalase (from *Micrococcus lyseidicticus*; 1 AU destroys 1 μmol H_2O_2 at pH = 7 RTP, 100,181 U/mL, Fluka) to destroy residual, unreacted H_2O_2. Peroxide Quant test strips (Aldrich) were used to determine the approximate amount of residual (unreacted) H_2O_2 in the Fenton reaction solutions. Millipore syringe filters with 0.45 μm cutoffs were used to separate supernatant after ferric hydroxide precipitation and to cease the Fenton reaction.

Table 1
Physicochemical properties of the textile dyes AR 183, AO 51 and RB 4

Textile dye	AR 183	AO 51	RB 4
Molecular formula	$C_{16}H_{11}ClN_4Na_2O_8S_2\cdot x$Cr	$C_{36}H_{26}N_6Na_2O_{11}S_3$	$C_{23}H_{14}Cl_2N_6O_8S_2$
Molecular weight (g/mol)	584.84	860.80	637.43
C.I. number	18,800	26,550	2,363,639
λ_{max} (nm)	497	463	595
Molecular structure