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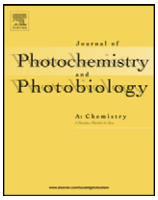

Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology

Idil Arslan-Alaton*, Gokce Tureli, Tugba Olmez-Hanci

Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34469 Maslak, Istanbul, Turkey

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ABSTRACT

Treatability of synthetic azo dye production wastewaters from Acid Blue 193 and Reactive Black 39 production and real Reactive Black 39 production effluent via Photo-Fenton-like process was investigated. Response surface methodology was employed to assess individual and interactive effects of critical process parameters (Fe^{3+}, H_2O_2 concentrations; initial chemical oxygen demand (COD) and reaction time) on treatment performance in terms of color, COD and total organic carbon (TOC) removal efficiencies. Optimized reaction conditions for synthetic AB 193 production wastewater were established as Fe^{3+} = 1.5 mM; H_2O_2 = 35 mM for CODs ≤ 200 mg/L and a reaction time of 45 min. Under these conditions, 98% color, 78% COD and 59% TOC removals were experimentally obtained and fitted the model predictions well. The same model also described the treatment of synthetic Reactive Black 39 production wastewater satisfactorily. Experimentally achieved removals were considerably lower than model predictions for real Reactive Black 39 production effluent due to its high chloride content.

1. Introduction

Dye manufacturing wastewater generally contains residual dyestuffs, dye intermediates as well as unreacted raw materials such as aromatic amines with alkyl-, halogen-, nitro-, hydroxyl-, sulfonic acid-substituents, and inorganic sodium salts [1]. Waste streams being variable in composition and strength are generated at different stages of the dye manufacturing process. The effluent is generally characterized by its high chemical oxygen demand (COD), total dissolved solids (TDS) content, intense color and low biodegradability, implying the presence of recalcitrant organic matter [1,2]. Dyes and dye intermediates can undergo reductive processes in the aquatic environment, resulting in the formation of potentially carcinogenic/mutagenic compounds (e.g. naphthylamines, substituted phenylamines, benzidine analogues) and cause abnormal coloration [3]. Dye manufacturing effluent may also contain free and complexed, toxic heavy metals (i.e. cobalt, chromium and copper) that result from the production of metal-complex azo dyes. Since the environmental characteristics of dye manufacturing wastewater are not suitable for the application of biological treatment technologies, the conventional treatment of dye production wastewater involves adsorption, coagulation and precipitation. However, these phase-transfer methods are not always effective in the removal of polar and hence very water soluble dyes from the effluent. Besides, both treatment processes have major drawbacks such as disposal/treatment of the created chemical sludge or regeneration/replacement of the spent adsorbent [4]. Oxidative treatment with chlorine or ozone is another plausible alternative for dealing with dye manufacturing effluents. Although chlorine is a powerful oxidant, chlorination has the inherent disadvantage of generating organic halogenated byproducts and it application is currently being ruled out. On the other hand, ozonation combined with coagulation is being employed in real practice, providing efficient color but low organic carbon removal. A major drawback of ozonation is its high electrical energy requirement [5,6].

Recent studies indicated that so-called advanced oxidation processes (AOPs) might be a good alternative for treating recalcitrant and/or toxic pollutants [7]. AOPs involve the production of strongly oxidizing agents, mainly hydroxyl radicals ($^{\bullet}OH$) that react rapidly and almost non-selectively with most inorganic and organic compounds including biologically difficult-to-degrade azo dyes and dye intermediates [8]. Among the AOPs, ozonation combined with H_2O_2, UV-C or both, H_2O_2/UV-C oxidation, Fenton and Photo-Fenton treatment, heterogeneous photocatalytic processes

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Abbreviations: ANOVA, Analysis of Variance; CCD, Central Composite Design; COD, chemical oxygen demand (mg/L); TOC, total organic carbon (mg/L); *k*, reaction rate constant (time^{-1}); *K*, equilibrium constant; TDS, total dissolved solids (mg/L); λ_{max}, the wavelength of the maximum absorption band (nm); R^2, correlation coefficient; RSM, response surface methodology; DF, degrees of freedom; Prob > *F*, probability value; *F*-value, Fisher variation ratio; COD_o, initial chemical oxygen demand (mg/L); pH_o, initial pH; $[Fe^{3+}]_o$, initial ferric ion concentration (mmol/L); $[Fe^{3+}]$, ferric ion concentration (mmol/L); $[H_2O_2]$, hydrogen peroxide concentration (mmol/L); $[H_2O_2]_o$, initial hydrogen peroxide concentration (mmol/L); t_r, reaction time (min); ϕ, quantum yield for photoreduction of Fe^{3+} to Fe^{2+}; $^{\bullet}OH$, hydroxyl radical; $HO_2^{\bullet}$, hydroperoxyl radical; $^{\bullet}OH$, hydroxyl radical; $HO_2^{\bullet}$, hydroperoxyl radical; $Cl^{\bullet}$, chloride radical; $Cl_2^{\bullet-}$, chlorine radical.

* Corresponding author. Tel.: +90 212 285 37 86; fax: +90 212 285 65 45.
E-mail address: arslanid@itu.edu.tr (I. Arslan-Alaton).

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mediated by the semiconductors TiO_2, ZnO and CdS, electrochemical processes, catalytic ultrasound (sonolysis), wet air oxidation and supercritical water oxidation have been reported in the scientific literature as effective means for the treatment of colored aromatics such as textile azo dyes [9–12]. The advanced oxidation of textile dyes and dyehouse effluent with Fenton and Photo-Fenton processes have recently received great attention because of their high efficiency in decolorization, ease of operation and relatively low operating costs [13]. However, only few studies are available in scientific literature dealing with the application of AOPs to treat dye manufacturing wastewater [4,14,15] although the application of AOPs to this type of wastewater is definitely more attractive than treating dyehouse effluent, owing to the low volume and high recalcitrance of dye manufacturing wastewater. In fact, some dye manufacturing effluent streams (i.e. wastewater created during reactor rinsing as well as dye separation/purification-reverse osmosis-outflows) are quite suitable for photochemical oxidation due to their relatively low volume and lower pollution load (COD $\leq$ 500 mg/L) despite their intense color.

Fenton's reagent (Fe^{2+}/H_2O_2) involves the catalytic decomposition of hydrogen peroxide by ferrous ions under acidic pH conditions [16–18], whereas Photo-Fenton (Fe^{2+}/H_2O_2/UV) and Photo-Fenton-like (Fe^{3+}/H_2O_2/UV) processes are its "photochemically enhanced version" [19,20]. Fenton as well as Photo-Fenton type processes are favored by acidic pH conditions (2–5) with a distinct optimum range of pH 2.8–3.0 [20]. However, as the solution pH is higher in many cases, the necessity to acidify the reaction medium limits the applicability of the Fenton process in practice. Besides this strict limitation, iron hydroxide sludge is produced at the end of the reaction which needs further treatment and disposal as solid waste [21]. The application of UV-C and even UV-A (near-UV) radiation during the Fenton process causes a dramatic increase in the $^{\bullet}OH$ formation efficiency thus enabling the use of lower iron catalyst concentrations [22]:

$$\mathrm{Fe(III)OH^{2+}} + h\upsilon \rightarrow \mathrm{Fe^{2+}} + {}^{\bullet}\mathrm{OH} \text{ with } \phi \text{ at } 347\,\mathrm{nm} = 0.2 \text{ and } k = 0.0012\,\mathrm{s^{-1}} \tag{1}$$

The above reaction results in the continuous support of Fe^{2+} iron for the direct Fenton reaction, thus minimizing the required Fe^{2+} concentration, enhancing the catalytic oxidation cycle and providing additional $^{\bullet}OH$. The photoreduction of ferric iron complexes is a strong function of the irradiation wavelength (e.g. the emission band of the UV light source) as well as reaction pH [22,23].

Using ferric iron was preferred in this experimental study considering our previous experimental findings [9] reporting that hydrogen peroxide consumption is more efficient during the Photo-Fenton-like process as compared with the Photo-Fenton process since initially there is no ferrous iron in the reaction solution and its formation depends on the photoreduction of Fe^{3+}-complexes and the dark Fenton-like process;

$$\mathrm{Fe^{3+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H^+} + \mathrm{HO_2}^{\bullet} \tag{2}$$

Since Photo-Fenton-like oxidation is affected by numerous process parameters such as iron (catalyst) concentration, hydrogen peroxide (oxidant) concentration, reaction pH and initial pollutant concentration (COD and TOC); working conditions are case-specific and need to be carefully optimized. The majority of recent studies concerned with the effect of these process variables on the treatment efficiency and reaction kinetics were performed using a rather one-factor-at-a-time approach, where one parameter was varied thereby keeping the others constant. However, the process parameters may involve synergistic effects, as a result of complex interactions between the process variables. Hence, the application of conventional optimization techniques is not adequate for process optimization, very time consuming, and does not necessarily allow a precise process optimization. As to overcome these drawbacks, experimental process optimization should be based on statistical design tools. In the design and statistical evaluation of experiments, response surface methodology (RSM) can be used for process optimization and prediction of the interaction between process variables, reducing the numbers and thus the time and associated costs spent for conducting these experiments [24]. RSM has already proven to be a reliable statistical tool in the investigation of chemical treatment processes [25]. RSM has been applied in numerous studies to optimize treatment of textile dyes and simulated/real dyehouse effluent [26–31]. As far as we are concerned, no scientific work has been published dealing with the application of RSM to treat azo dye manufacturing wastewater so far. The relatively low volume, neutral-to-slightly acidic pH as well as refractory organic carbon content of textile production effluent render it an ideal candidate for treatment with iron-based advanced oxidation processes.

Considering the above-mentioned facts, the present work aimed at investigating the treatability of synthetic and real azo dye production wastewaters with the Photo-Fenton-like process. RSM was applied to assess the individual and interactive effects of several operating parameters on treatment efficiency. Central Composite Design (CCD), which is the most widely used form of RSM, was employed to evaluate the effect of important process variables (irradiation time, catalyst and oxidant concentration, organic carbon content of the wastewater) on color, COD and TOC removal efficiencies. Process modeling and optimization studies focused on synthetic effluent originating from Acid Blue 193 production (reactor washing stage) and model predictions were experimentally validated. Photo-Fenton-like oxidation of synthetic Reactive Black 39 (reactor washing stage) and real Reactive Black 39 (reverse osmosis purification stage) production effluent was also performed under optimized working conditions established by the model for Acid Blue 193 production effluent. In this context, the applicability of the derived model predictions on Photo-Fenton-like treatment of several azo dye production effluents could be explored more comprehensively.

2. Materials and methods

2.1. Azo dye production wastewaters

Synthetic Acid Blue 193 (a chromium complex disazo dye; AB 193) and Reactive Black 39 (a disazo dye; RB 39) production wastewaters were prepared to simulate effluent originating from the azo dye synthesis reactor washing stages. In order to attain uniformity throughout the optimization experiments, synthetic wastewaters were prepared by dissolving the synthesized, azo dye formulations (obtained prior to their purification) supplied by a local dye manufacturing company, in distilled water. Synthetic AB 193 production effluent samples that were used throughout the optimization runs were daily prepared to attain effluent CODs of 100, 150, 200, 250 and 300 mg/L. The studied COD range was selected upon consideration of typical process and effluent conditions at textile dye manufacturing plants, while increments of 50 mg/L COD were determined according to the employed RSM. Synthetic RB 39 production wastewater was prepared to attain a COD of around 200 mg/L, so that optimum Photo-Fenton-like conditions established for the COD range 150–200 mg/L via RSM could be applied.

Real RB 39 dye production wastewater (RB 39-RO) was provided by the same company from where the raw RB 193 and RB 39 dyes were obtained. The real effluent was taken from a holding tank containing the permeate produced during reverse osmosis RB 39 purification. This effluent was diluted three times with distilled water in order to attain a COD of $\leq$200 mg/L. Some environmental char-