Available online at www.sciencedirect.com

Dyes and Pigments 73 (2007) 31–39

www.elsevier.com/locate/dyepig

Acid dyebath effluent pretreatment using Fenton's reagent: Process optimization, reaction kinetics and effects on acute toxicity

Idil Arslan Alaton*, Senem Teksoy

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

Received 23 June 2005; accepted 16 September 2005
Available online 23 November 2005

Abstract

Fenton's reagent (Fe^{2+}/H_2O_2) is known as one of the most effective and most often employed advanced oxidation process (AOPs) for the treatment of textile dyes and dyehouse effluent. In the present study, a synthetic acid dyebath effluent (SADB) bearing two azo and one anthraquinone dye together with two dye auxiliaries was subjected to pretreatment with Fenton's reagent. Firstly, initial Fe^{2+} and H_2O_2 concentrations as well as pH were optimized to achieve highest COD and color removals during Fenton's treatment of SADB. In the second stage of the experimental work, kinetic studies were conducted to elucidate the effect of operating temperature ($20\ ^\circ C < T < 60\ ^\circ C$) on COD, color abatement and H_2O_2 consumption kinetics. Obtained results indicated that 30% COD and practically complete color removal (99%) could be achieved at $T = 50\ ^\circ C$. The kinetic studies revealed that a strong correlation existed between COD removal and H_2O_2 utilization rates. In the final part of the study, the acute toxicity of raw (untreated) and pretreated SADB on heterotrophic biomass was investigated employing a modified (COD-balanced), activated sludge inhibition test. The toxicity experiments demonstrated that the inhibitory effect of SADB towards sewage sludge could be completely eliminated when the effluent was pretreated with Fenton's reagent.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Advanced oxidation processes (AOPs); Acid dyebath effluent; Fenton's pretreatment; Thermal enhancement; Activated sludge inhibition; Acute toxicity

1. Introduction

Textile dyeing is the most water consuming and chemically intensive process among all textile preparation, dyeing, washing and finishing stages. Effluent from textile dyeing contains residuals of dyebath auxiliaries and unfixed dyestuff at significant concentrations [1]. Unfortunately, most chemicals employed for textile dyeing are known for their recalcitrant nature, i.e. they are hardly biodegradable and also resist most physicochemical remediation methods such as adsorption, coagulation or precipitation [2,3]. However, if not treated properly, effluent containing these chemicals will not only inhibit the performance of municipal sewage treatment works accepting primary and/or secondary treated textile effluent, but also seriously deteriorate the aesthetics and threaten the aquatic life of receiving waters. Consequently, the effective and feasible treatment of dyehouse effluent remains a problematic and challenging task for the textile finisher who is confronted with discharge consents that are becoming stricter every day.

Effluent from the textile dyeing and finishing operations can be successfully treated with advanced oxidation processes (AOPs) that have been employed to reduce the pollutant load, recalcitrance and/or toxicity of industrial pollutants for more than two decades now [4–13]. AOPs are defined as ambient temperature oxidation reactions, which generate free radicals (mainly $HO_2^\bullet$, $^\bullet OH$) in sufficient quantities to affect water and wastewater treatment [14]. Among them, the hydroxyl radical ($^\bullet OH$) is one of the most reactive and strongest oxidants (reduction potential = 2.8 eV versus NHE) that aggressively and almost indiscriminately reacts with organic as well as inorganic compounds in aqueous medium [5,15]. They are produced on-site most commonly by combinations

---

* Corresponding author. Tel.: +90 212 285 37 86; fax: +90 212 285 65 87.
E-mail address: arslanid@itu.edu.tr (I.A. Alaton).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.09.027

of ultraviolet irradiation (UV), ozone, hydrogen peroxide and (photo)catalysts (mainly transition metal salts) forming rather compact, homogenous oxidation systems [16]. The heterogeneous type AOPs particularly involve TiO_2-mediated semiconductor (photo)catalytic processes [17]. Both AOP types proved to be very effective for the partial degradation (decolorization) of different textile dyes in the recent past [18]. Among the currently existing AOPs, the Fenton process (Fe^{2+}/H_2O_2) usually applied at acidic pH (2–5) is the method of choice for heavily polluted and highly colored industrial waste streams due to its ease of operation, the high abundance of reactants and relatively low operating costs [19–21]. Different Fenton applications have already been reported in the scientific literature, such as the treatment of wastewaters from the acid manufacturing, pharmaceutical, textile, and pulp and paper industries [22–24].

Acid dyes are commonly used for dyeing polyamide fibers as well as silk, wool and modified acrylics [25]. They are one of the most frequently applied textile dye classes world-wide and have the highest market share in the Turkish polyamide dyeing sector. Acid dyes are employed at pH = 3–5 and at high temperatures ($T = 95–105$ °C) making them ideal candidates for Fenton's oxidation.

There is a huge body of scientific literature reporting the application of Fenton's process for the degradation of commercial textile dyestuffs [10,11,26–28]. However, to our knowledge, none of these studies have investigated the effect of temperature on the relationship between dyebath degradation and oxidant (H_2O_2) consumption rates for Fenton's processes. In addition, there is also no information available on the toxicity and/or biodegradability changes occurring in textile dyebaths after Fenton's pretreatment.

The objective of the present study was to investigate the treatability of a simulated acid dyebath effluent (SADB) with Fenton's reagent and to assess the effect of chemical pretreatment (partial oxidation) on the acute toxicity and biodegradability of SADB. The first part of the experimental work involved the optimization of Fe^{2+} iron (1–10 mM) and H_2O_2 (10–100 mM) concentrations as well as reaction pH (2–5) in terms of overall percent COD and color removal efficiencies for a fixed reaction duration (30 min). In the second part of the study, a kinetic evaluation of the Fenton process at different reaction temperatures ($T = 2–70$ °C) was carried out in order to demonstrate the thermal improvement of Fenton's reaction in terms of COD and color abatement kinetics. Finally, the effect of Fenton's pretreatment on acute toxicity and biodegradability was assessed by means of a modified (balanced for organic loading) activated sludge inhibition test.

2. Materials and methods

2.1. Reagents and supplies

The Fenton's pretreatment experiments were investigated on SADB, an acid dyebath formulation being frequently used to dye polyamide fabrics at Turkish as well as international dye mills. SADB consist of three different acid dyestuffs (C.I. Acid Yellow 242, C.I. Acid Red 360 and C.I. Acid Blue 264) and two dye auxiliaries (a leveling agent and an acid donor). The dyestuffs and dye assisting agents were kindly supplied by a dyehouse located in Istanbul, Turkey. The chemical composition of SADB is given in Table 1.

The acid dyes and auxiliaries were dissolved in boiling Milli-Q water to simulate a typical SADB, making up a total COD of 2747 ± 33 mg/L. Generally speaking, acid dyes are well attained on the targeted fabric and usually only 10–20% of the applied dyestuffs remain in the spent (exhausted) dyebath [25]. However, in the present work it was assumed that all SADB components totally remained in the exhausted dyebaths in order to observe the consequences of a "worst case scenario"; i.e. the Fenton's performance under stressed conditions.

All chemicals used were at least reagent grade and obtained from Fluka, Aldrich, Merck or Riedel depending upon their price, purity and availability. Chemicals used for the Fenton pretreatment experiments were hydrogen peroxide (35% w/w, Fluka), ferrous iron sulphate hepta hydrate (Merck), NaOH pellets (Merck), enzyme Catalase (made from *Micrococcus lysodeikticus*; 1 AU destroys 1 μmol H_2O_2 at pH = 7 RTP, 10 0181 U/mL, Fluka), and sulphuric acid (Merck). Reagents used for the residual H_2O_2 analyses were KI solution (1% w/v), Ammonium molybdate solution (0.12 N), sulphuric acid solution (2 N), starch indicator solution (0.2% w/v) and sodium thiosulphate (0.1 N).

2.2. Experimental procedure

Appropriate amounts of Fenton reagents were taken from the stock solutions of $FeSO_4 \cdot 7H_2O$ (0.36 M) and H_2O_2 (35% w/w) to attain the desired H_2O_2 and Fe^{2+} concentrations. The pH of the medium was adjusted to the desired value before starting the experiment with concentrated (6 N) NaOH and H_2SO_4 solutions. A temperature controllable magnetic stirrer (Yellowline MST Basic, IKA-WERKE) was used to ensure perfect mixing at a constant rate of 300 rpm during all experiments. Thereafter, proper amounts of $FeSO_4 \cdot 7H_2O$ were added to the reaction solution as the ferrous iron source. The reaction was assumed to start with the addition of H_2O_2. After the selected reaction time, usually set as 30 min for the preliminary optimization experiments, the experiment was

Table 1
Chemical components and composition of the SADB

Dyestuff (CI index)	Dye chromophore type	Concentration (mg/L)
Acid Yellow 242	Azo	30
Acid Red 360	Azo	30
Acid Blue 264	Anthraquinone	30
Assisting chemical	**Chemical composition**	**Concentration (mg/L)**
Leveling agent	An oxyethylene derivative with amine and sulphonic properties	1500
Acid donor	A formic ester	500

ceased with the addition of NaOH as to increase the pH to around 10 ± 0.5, where ferrous iron precipitated out as solid $Fe(OH)_3$. After the iron sludge was removed via filtration, the residual (unreacted) H_2O_2 in solution was checked with H_2O_2 strips (Quantofix, Macherey–Nagel) and enzymatically decomposed to $H_2O + O_2$ with appropriate amounts of Catalase in order to prevent the positive interference of H_2O_2 with the COD measurements. H_2O_2 was immediately destroyed in this way in all samples whenever the reaction solution was not analyzed for residual H_2O_2 (its abatement during the reaction).

The preliminary optimization experiments for the SADB were carried out at room temperature (20 °C) for different concentrations of Fe^{2+} (1–10 mM), H_2O_2 (10–100 mM) and at different pH values (pH = 2–5) in 250 mL flasks, and the kinetic (COD and H_2O_2 abatement) experiments were conducted at a temperature range of 20–70 °C for 90 min under pre-determined optimum experimental conditions in 2 L-capacity glass beakers with a fixed SADB volume of 1 L. For these kinetic experiments, 25 mL sample aliquots were withdrawn at specific time intervals up to 90 min, out of which 10 mL was separated and used to determine their residual H_2O_2 concentration.

2.3. Analytical procedure

All samples were filtered through 0.45 μm syringe filters (purchased from Sartorius and Millipore) prior to analyses. COD measurements were conducted in accordance with the titrimetric open reflux method [29]. Changes in color were recorded as absorbance values on a colorimeter (Novaspec II, Pharmacia LKB) in 1 cm disposable cuvettes at the three specific wavelengths $\lambda = 436, 525, 620$ nm corresponding to perceived colors yellow, red and blue, respectively. These three absorption bands were selected for color determination in raw and pre-treated reaction solutions since they are indicated in the discharge consents set for color in the German Guidelines due to the trichromatic nature of color in dyehouse effluent [30]. The Turkish legislation currently has no discharge standard for color, however, within the framework of the adoption of the *European Union Aquis* this particular standard is foreseen in the updated environmental legislation for discharge limit values in receiving water bodies.

2.4. Activated sludge inhibition test

Acute toxicity tests were conducted in accordance with a test procedure described in ISO 8192 [31]. The activated sludge inhibition experiments were run at a constant temperature of 20 ± 2 °C. The heterotrophic biomass used in the activated sludge inhibition test was daily fed with synthetic wastewater (SWW) to simulate a readily biodegradable effluent of domestic nature. The ingredients of SWW (stock solution) are described in Table 2.

Table 2
Synthetic wastewater stock solution ($COD_{tot} = 30{,}000$ mg/L)

Reagent	(g/L)
Peptone	16
Meat extract	11
Urea	3
NaCl	0.7
$CaCl_2 \cdot 2H_2O$	0.4
$MgSO_4 \cdot 7H_2O$	0.2
K_2HPO_4	2.8

SWW was diluted with tap water to obtain the required COD.

The test samples (raw and pre-treated SADB) were diluted with appropriate amounts of SWW ($COD_{SWW} = 500$–1000 mg/L) to obtain a series of different SADB COD fractions thereby keeping a constant total COD in the SADB + SWW mixture. This modification of the standard ISO 8192 tests was necessary to eliminate the effect of changes in organic loading (COD) on activated sludge responses that may cause misinterpretation of dose (COD)–response (of biomass). During the inhibition tests, SWW + raw or pre-treated SADB effluent mixtures were continuously aerated for 30 min in 500 mL-test beakers containing proper amounts of activated sludge that were previously acclimated to SWW for at least 3 months. The *F*/*M* (food-to-microorganisms) ratio was adjusted exactly to 0.19 mg COD/mg MLVSS d^{-1} (active biomass; MLVSS = 600–900 mg/L). The decrease in dissolved oxygen concentration (in mg/L) in the test blank (SWW only) as well as in different dilutions of raw and pre-treated SADB samples was monitored for 2–4 min using a WTW Oxi Digi 2000 model oxygen meter. Oxygen uptake rates (OUR; expressed in mg L^{-1} h^{-1}) in the blank (SWW) and SWW-diluted dyebath samples were calculated based on the linear part of the declining dissolved oxygen curves as a function of the aeration (i.e. biological treatment) time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, was calculated using the following equation:

$$I_{OUR}(\%) = [(R_B - R_T) \times 100]/R_B \quad (1)$$

where R_T is the OUR in the effluent sample mixture (SADB + SWW) and R_B stands for the OUR in the blank sample (SWW only). The I_{OUR} values were thereafter plotted against ln (COD)'s (natural logarithm of the CODs of different SADB dilutions). The COD content of raw and pre-treated SADB resulting in 50% decrease in OURs (i.e. EC_{50} value; in mg/L) was calculated by interpolation of the ln (COD) versus percent I_{OUR} plots obtained for different SADB + SWW sample mixtures. In addition, the COD contributions from SWW were kept above 250 mg/L in order to prevent the interference and/or misinterpretation arising from substrate (COD) limiting conditions. The heterotrophic sludge sensitivity was checked by means of a reference test chemical 3,5-dichlorophenol. Its EC_{50} value (5–30 mg/L) was reconfirmed by applying the above indicated ISO 8192 test procedure and was found as 29 mg/L.

3. Results and discussion

3.1. Pretreatment with Fenton's reagent – optimization experiments

Referring to the Fenton process, it is well known that a higher hydrogen peroxide (oxidant) to pollutant molar ratio results in more thorough substrate degradation; while higher concentrations of ferrous iron (catalyst) yield kinetically faster oxidation rates [32]. As previously mentioned, Fenton's reagent is employed to produce sufficient quantities of $^{\bullet}OH$ to degrade organic substances (R) at diffusion limited rates ($k_{R,\bullet OH} = 10^7–10^{10}\ M^{-1}\ s^{-1}$). In order to achieve maximum treatment performance, particular attention must be paid to Fe^{2+} and H_2O_2 concentrations in order to avoid the following undesired $^{\bullet}OH$-scavenging reactions occurring in the presence of an excess of one of the two reagents [33]:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \quad (k_{20\ ^{\circ}C} = 3.0 \times 10^{8}\ M^{-1}\ s^{-1}) \tag{2}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (k_{20\ ^{\circ}C} = 2.7 \times 10^{7}\ M^{-1}\ s^{-1}) \tag{3}$$

Accordingly, if Fe^{2+} and/or H_2O_2 concentrations are overdosed, the amount of available $^{\bullet}OH$ to oxidize organic matter becomes low. In other words, a pollutant specific optimum molar ratio between H_2O_2 and Fe^{2+} (Fe^{2+}:H_2O_2) must be determined in order to minimize the scavenging effects.

3.1.1. Effect of Fe^{2+} concentration

In order to determine the optimum initial Fe^{2+} concentration, a set of experiments was carried out for SADB for which the concentration of Fe^{2+} (0.5–10 mM) was progressively increased while maintaining the concentration of H_2O_2 constant at an arbitrary value of 30 mM. All experiments were carried out for 30 min and at an initial pH of 3. Percent COD removal efficiencies obtained after 30 min Fenton's treatment of SADB at varying initial Fe^{2+} concentrations are presented in Fig. 1. The iron concentrations studied were in the range of 0.5–20 mM. Control samples without Fe^{2+} addition were also conducted to explore the effect of mere H_2O_2 oxidation.

It is evident from Fig. 1 that COD removal increased with increasing initial Fe^{2+} concentrations. Only at concentrations exceeding 10 mM COD removals did not increase significantly.

Percent color removal efficiencies at the predefined wavelengths are depicted in Fig. 2. Decolorization rates followed a similar trend to COD removals. The optimum ferrous iron concentration was selected as 10 mM corresponding to 24% COD removal ($COD_o = 2741$ mg/L) after 30 min treatment of SADB.

Percent overall COD and color removal efficiencies obtained after 30 min treatment of SADB via Fenton's reagent at varying initial Fe^{2+} concentrations are summarized in Table 3. It is interesting to mention here that although no color removal was obtained for low Fe^{2+} concentrations (0.5–2.0 mM), COD removal was already observed even if Fe^{2+} was totally absent. Although at the first sight this is rather surprising, upon consideration of the fact that dyestuffs are not the sole ingredients of SADB and it might be inferred that the dye auxiliaries may also contribute to the apparent COD removal rates obtained for SADB.

3.1.2. Effect of H_2O_2 concentration

The effect of initial H_2O_2 concentration on treatment efficiency was investigated by trying different concentrations of H_2O_2 at the optimum Fe^{2+} concentration previously determined as 10 mM at pH = 3. The selected H_2O_2 concentration was in the range of 10–100 mM. A separate control experiment was conducted to observe the (coagulating) effect of Fe^{2+} addition only in the absence of H_2O_2. The results are displayed in Fig. 3 in terms of percent COD removal efficiencies obtained after 30 min Fenton's treatment of SADB.

As can be seen from Fig. 3, percent COD removal firstly increased with increasing initial H_2O_2 concentration from 15% at 10 mM to 30 mM, beyond which concentration the COD removal rate started to decrease due to the previously mentioned $OH^{\bullet}$ scavenging effect. Hence an optimum H_2O_2 concentration yielding an overall COD removal efficiency of 24% at pH = 3 and $t = 30$ min ($COD_o = 2745$ mg/L) could

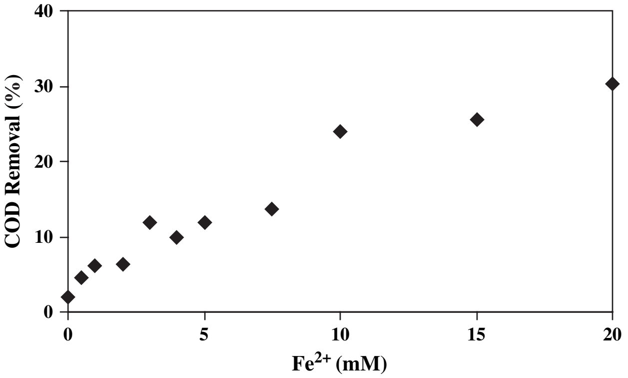

Fig. 1. Effect of Fe^{2+} concentration on COD removal efficiency ($H_2O_2 = 30$ mM; pH = 3; $t = 30$ min; $COD_o = 2741$ mg/L).

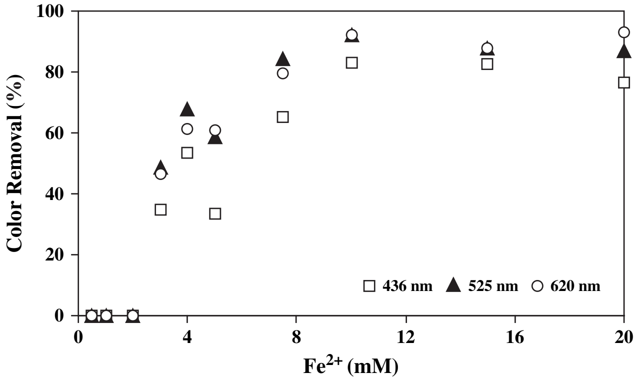

Fig. 2. Effect of Fe^{2+} concentration on color removal ($H_2O_2 = 30$ mM; pH = 3; $t = 30$ min; $COD_o = 2741$ mg/L; $A_{436,\ o} = 0.83\ cm^{-1}$; $A_{525,\ o} = 0.61\ cm^{-1}$; $A_{620,\ o} = 0.28\ cm^{-1}$).

Table 3
Effect of initial Fe^{2+} concentration on percent COD and color removal efficiencies

Fe^{2+} concentration (mM)	COD		Color			
	Final COD (mg/L)	Removal efficiency (%)	Final absorbance at λ (cm^{-1})			Removal efficiency (%)
			436 nm	525 nm	620 nm	620 nm
0.0	2692	2	—[a]	—	—	—
0.5	2621	5	—[a]	—	—	—
1.0	2582	6	—[a]	0.498	0.273	—
2.0	2573	6	—[a]	0.520	0.215	—
3.0	2419	12	0.544	0.315	0.150	46
4.0	2477	10	0.389	0.196	0.108	61
5.0	2419	12	0.554	0.253	0.109	61
7.5	2371	14	0.29	0.097	0.057	80
10	2107	23	0.14	0.049	0.022	92
15	2189	26	0.241	0.091	0.040	88
20	2078	30	0.203	0.065	0.019	93

$H_2O_2 = 30$ mM; pH = 3; reaction duration = 30 min; $COD_o = 2746$ mg/L; $A_{436,\ o} = 0.83\ cm^{-1}$; $A_{525,\ o} = 0.61\ cm^{-1}$; $A_{620,\ o} = 0.28\ cm^{-1}$.

[a] No reduction observed.

be established. Percent color removal efficiencies obtained at varying H_2O_2 concentrations during Fenton's oxidation of SADB is displayed in Fig. 4.

As is evident in Fig. 4, unlike in the case of COD removal, color removal took place even for the case when no H_2O_2 was added and decolorization efficiency did not increase for H_2O_2 concentrations above 30 mM. From these findings it can be inferred that the optimum H_2O_2 concentration (to achieve highest color removal) was found as 30 mM, coinciding with the highest COD removal efficiency. Thus the most suitable Fe^{2+}:H_2O_2 molar ratio in terms of both COD and color removals from SADB at pH = 3 was determined to be 1:3. Exactly the same molar ratio was obtained for phenol oxidation by Eisenhauer [34]. Similarly, Sedlak and Andren [35] found a ratio of 1:4 for the degradation of chlorinated biphenyls. The molar ratios determined for the degradation of different types of textile dyes were determined as follows: 1:5 for the oxidation of Vat Blue BO [36]; around 1:5 and 1:7 for Disperse Blue 106 and Disperse Yellow 54, respectively [28], coinciding with the molar ratios of 1:7 and 1:5 established for Reactive Blue 49 and Reactive Yellow 84, respectively, as obtained in the same experimental work. The results of Fenton's pretreatment of SADB at varying initial H_2O_2 concentrations are presented in Table 4. Owing to the fact that color removal could be best followed at $\lambda = 620$ nm, results in terms of color removal were shown for this particular wavelength in the forthcoming tables.

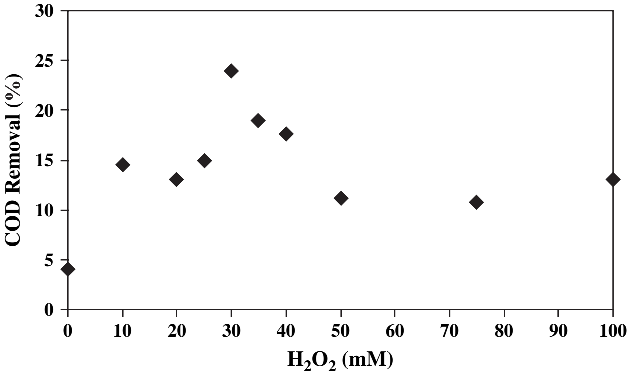

Fig. 3. Effect of H_2O_2 concentration on COD removal efficiencies during Fenton's pretreatment of SADB ($Fe^{2+} = 10$ mM; pH = 3; $t = 30$ min; $COD_o = 2745$ mg/L).

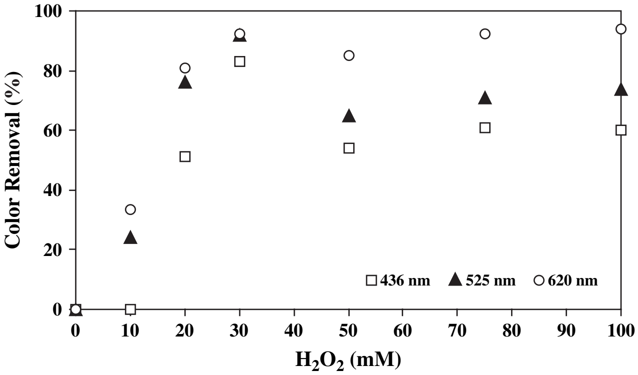

Fig. 4. Effect of initial H_2O_2 concentration on percent color removal efficiency ($Fe^{2+} = 10$ mM; pH = 3; $t = 30$ min; $A_{436,\ o} = 0.833\ cm^{-1}$; $A_{525,\ o} = 0.612\ cm^{-1}$; $A_{620,\ o} = 0.28\ cm^{-1}$).

3.1.3. Effect of pH

As indicated before, pH has a significant effect on the performance of Fenton's reactions and the most suitable pH range for the removal of various organics was found between 2 and 5 [18–21]. On the other hand, pH re-adjustment usually done in order to neutralize the pH after Fenton's treatment and to remove iron from the oxidized effluent may result in an additional coagulation + precipitation effect [31].

The effect of pH on COD and color removals during Fenton's treatment of SADB was examined for already optimized initial Fe^{2+} and H_2O_2 concentrations. The tested pH values ranged between 2 and 5. The effect of pH on percent

Table 4
The effect of initial H_2O_2 concentration on percent COD and color removal efficiencies obtained for Fenton's oxidation of SADB

H_2O_2 concentration (mM)	COD		Color	
	Final COD (mg/L)	Removal efficiency (%)	Final absorbance (cm^{-1}) at $\lambda = 620$ nm	Removal efficiency (%)
0	2636	4	0.267	5
10	2347	15	0.186	34
20	2386	13	0.054	81
25	2405	15	—[a]	—[a]
30	2086	24	0.022	92
35	2290	19	—[a]	—[a]
40	2328	18	—[a]	—[a]
50	2438	11	0.042	85
75	2448	11	0.022	92
100	386	13	0.017	94

$Fe^{2+} = 10$ mM; pH = 3; reaction duration = 30 min; $COD_o = 2745$ mg/L; $A_{620,\ o} = 0.28\ cm^{-1}$.

[a] Not determined.

overall COD and color removal efficiencies are presented in Figs. 5 and 6, respectively.

As can be clearly seen in Figs. 5 and 6, an optimum pH to achieve the highest COD and color removal efficiencies was found at around pH = 3. Unlike in the case of Fe^{2+} and H_2O_2 concentrations, COD and color abatement rates were not very sensitive to the variations in pH. However, both decreasing the pH to below 3 or increasing the pH above 3 resulted in slightly worsening effects in terms of COD removal rates, whereas color abatement was not appreciably higher at pH values ≤ 3 than at pH > 3. Table 5 summarizes the experimental results obtained for pretreatment of SADB with Fenton's reagent at varying pH.

The results given in the above table again emphasize that color and COD removal efficiencies were fortunately not very sensitive to pH, implying that the pH range encountered in typical acid dyebaths is suitable for oxidation via Fenton's reaction.

3.2. Kinetic studies

Kinetic experiments were conducted for 90 min at predetermined, optimized reaction conditions ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; pH = 3) in order to examine the effect of SADB temperature (20–70 °C) on COD, color and H_2O_2 abatement rates. It was aimed to determine the fate of COD and H_2O_2 at varying reaction temperatures for two major reasons; namely, in order to question whether a positive correlation existed between COD removal and H_2O_2 (oxidant) consumption. The other reason for a kinetic evaluation at elevated temperatures was the fact that acid dyestuffs are typically used at elevated temperatures (>90 °C). Fig. 7 shows COD abatement rates versus treatment time for the oxidation of SADB at varying temperatures (20–60 °C).

It was observed from Fig. 7 that COD removal from SADB leveled off after 30 min treatment for all operating temperatures. It is also important to note that the positive effect in COD removal rates with increasing reaction temperature was more pronounced within the first minute of Fenton's reaction. The highest COD removal efficiency was obtained at $T = 50$ °C as 30% with a final COD value of 1843 mg/L after 30 min as well as 90 min indicating the presence of an optimum reaction temperature.

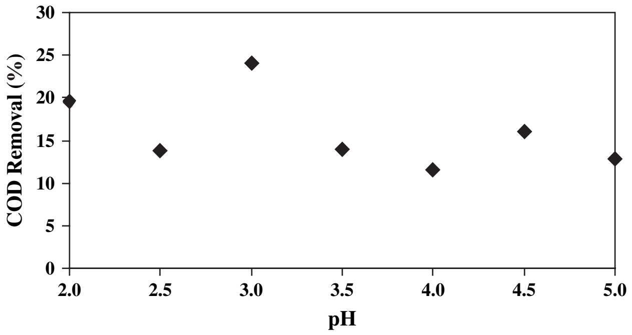

Fig. 5. Effect of pH on percent COD removal efficiencies ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; $t = 30$ min; $COD_o = 2731$ mg/L).

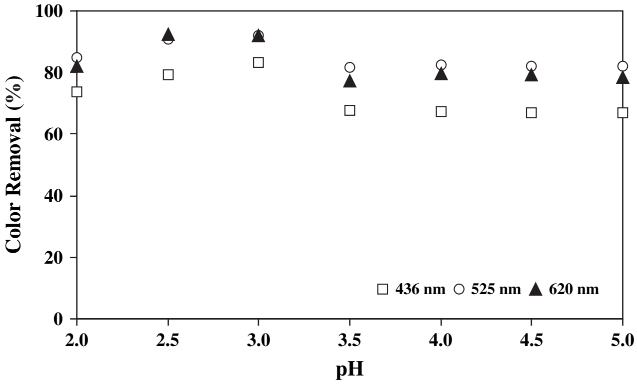

Fig. 6. Effect of pH on percent color removal efficiencies ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; $t = 30$ min; $COD_o = 2731$ mg/L; $A_{436,\ o} = 0.833$ cm^{-1}; $A_{525,\ o} = 0.612$ cm^{-1}; $A_{620,\ o} = 0.28$ cm^{-1}).

Corresponding color removal efficiencies at the most representative wavelength ($\lambda = 620$ nm) with respect to varying reaction temperatures are presented in Fig. 8. It may be observed from Fig. 8 that the highest color removal (99%) was already achieved at $T = 50$ °C after 30 min reaction.

The residual H_2O_2 concentration was also determined at varying temperatures as a function of treatment time. For that purpose parallel samples were taken for the determination of remaining (unreacted) H_2O_2 in SADB. Fig. 9 presents H_2O_2 abatement (consumption) rates as a function of Fenton's treatment of SADB at varying temperatures.

Both COD and H_2O_2 abatement followed first-order kinetics for the first 30 min of the reaction. Reaction kinetics could be formulated as follows:

$$\ln\left(\frac{C}{C_0}\right) = -k \times t \qquad (4)$$

where C and C_0 stand for COD or H_2O_2 concentrations at $t = t$ and $t = 0$, respectively, and k is the first-order COD or H_2O_2 abatement rates constant, expressed in min^{-1}. Percent overall COD removal efficiencies, final CODs, together with first-order COD and H_2O_2 abatement rate constants (i.e. k_{COD} and $k_{H_2O_2}$, in min^{-1}) are summarized in Table 6.

Table 5
Effect of pH on percent COD and color removal efficiencies for Fenton's oxidation of SADB

pH	COD		Color	
	Final COD (mg/L)	Removal efficiency (%)	Final absorbance (cm^{-1}) at $\lambda = 620$ nm	Removal efficiency (%)
2.0	2185	20	0.05	82
2.5	2349	14	0.021	93
3.0	2076	24	0.022	92
3.5	2348	14	0.064	77
4.0	2403	12	0.057	80
4.5	2294	16	0.058	79
5.0	2376	13	0.060	79

$Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; reaction duration = 30 min; $COD_o = 2731$ mg/L; $A_{620,\ o} = 0.28$ cm^{-1}.

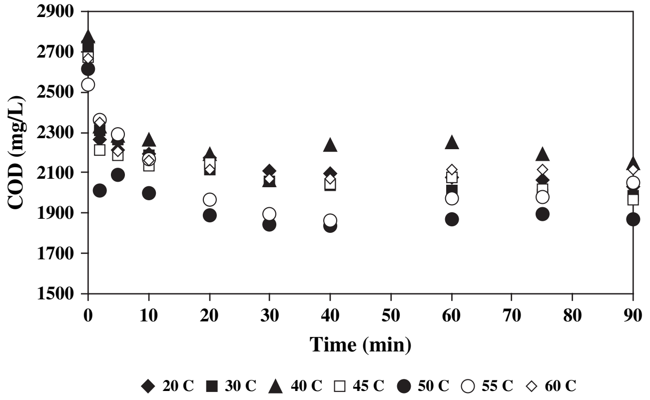

Fig. 7. COD abatement kinetics at different temperatures at optimum reaction conditions ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; pH = 3; $t = 90$ min).

Table 6 indicated that both k_{COD} and $k_{H_2O_2}$ had the highest values at 50 °C and tended to decrease at temperatures above, indicating a 'sharp' optimum temperature value. Apparently, there seemed to be a positive correlation between COD and H_2O_2 abatement rates that can be evaluated in terms of the reaction coefficient ratio, i.e. "$k_{COD}/k_{H_2O_2}$". Fig. 10 illustrates $k_{COD}/k_{H_2O_2}$ obtained for SADB oxidation at varying temperatures.

As is evident in Fig. 10, the ratios of the calculated first-order reaction rate coefficients remained practically constant at around 0.1 $min^{-1}(-COD)/min^{-1}(-H_2O_2)$, speaking for a fair correlation between H_2O_2 consumption and COD removal rates, also revealing that H_2O_2 consumption is 10 times faster than COD removal. Nevertheless, it should be pointed out here that the actual (and active) oxidant responsible for COD abatement is not H_2O_2, but in situ formed $^{\bullet}OH$, that may explain that the obtained ratio is considerably less than unity (theoretical H_2O_2 requirement or equivalent H_2O_2 on mass basis = 2.12 × COD).

3.3. Effects on acute toxicity

As already known, xenobiotic chemicals such as antibiotics, commercial brighteners, anti-chelating agents or organic textile dyestuffs are reluctant to aerobic biodegradation. However, pretreatment of toxic industrial wastewater bearing non-biodegradable pollutants by AOPs fortunately leads to less toxic oxidation intermediates that are more accessible to biological treatment, as was recently reported for synthetic textile wastewater [37]. Besides biodegradability, the toxicity of wastewater is a crucial parameter to evaluate the effectiveness of AOPs. This was already demonstrated by several investigations including Fenton's treatment [38], ozonation [39], perozonation (H_2O_2-assisted ozonation) [40], TiO_2-mediated heterogeneous UV-A-photocatalysis [41], H_2O_2/UV-C treatment [42], and ultrasonic irradiation [43] of textile dyes and dyebath effluent using standard *Daphnia magna* toxicity test procedures or the Microtox® technique by employing the luminescent bacteria *Vibrio fischeri* (i.e. *Photobacterium phosphoreum*).

To elucidate the effect of Fenton's oxidation on both acute toxicity and biocompatibility at the same time, the untreated and Fenton's pre-treated SADB was subjected to a modified (COD-balanced) activated sludge inhibition test using heterotrophic biomass under conventional aerobic biotreatment conditions (*F*/*M* ratio = 0.19 mg COD/mg MLVSS d^{-1}), where the total COD of the SADB + SWW sample mixtures was kept constant at 700 mg/L thereby incrementally increasing the COD fraction coming from SADB effluent. The OURs in raw (SADB + SWW), treated (SADB + SWW) and blank (SWW) samples were measured in parallel after 30 min

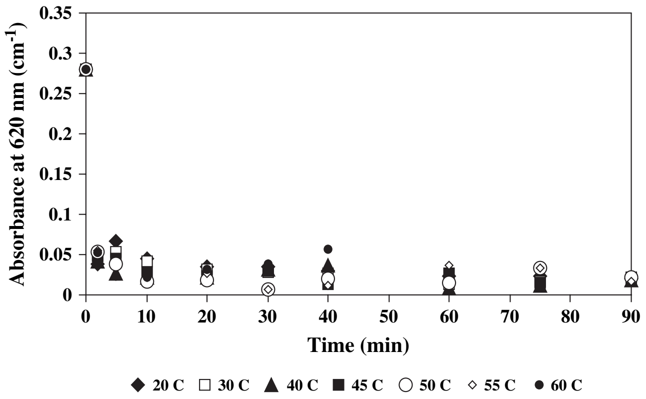

Fig. 8. Color removal for SADB at different operating temperatures ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; pH = 3; $t = 90$ min; $A_{620,\ o} = 0.28$ cm^{-1}).

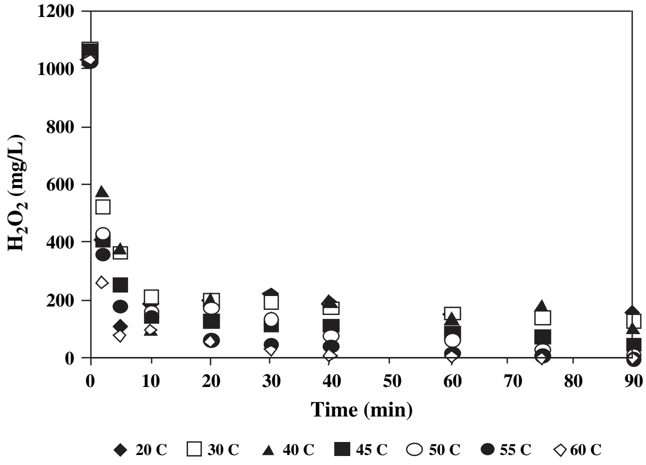

Fig. 9. H_2O_2 consumption rates at different temperatures ($Fe^{2+} = 10$ mM; $H_2O_{2,\ o} = 30$ mM (1020 mg/L); pH = 3; $t = 90$ min).

Table 6
Percent COD removal efficiencies, final CODs, k_{COD} and $k_{H_2O_2}$ obtained for Fenton's treatment of SADB at varying reaction temperatures

T (°C)	COD removal (%)	Final COD (mg/L)	k_{COD} (min^{-1})	R^2	$k_{H_2O_2}$ (min^{-1})	R^2
20	23	2109	0.0204	0.95	0.152	0.90
30	24	2056	0.0214	0.90	0.148	0.92
40	26	2061	0.0205	0.90	0.198	0.96
45	25	1872	0.0224	0.88	0.272	0.91
50	30	1843	0.0268	0.90	0.344	0.99
55	25	1895	0.0198	0.90	0.338	0.95
60	22	2070	0.0210	0.85	0.231	0.85

$Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM (1020 mg/L); pH = 3; $t = 30$ min; $COD_o = 2747 \pm 33$ mg/L.

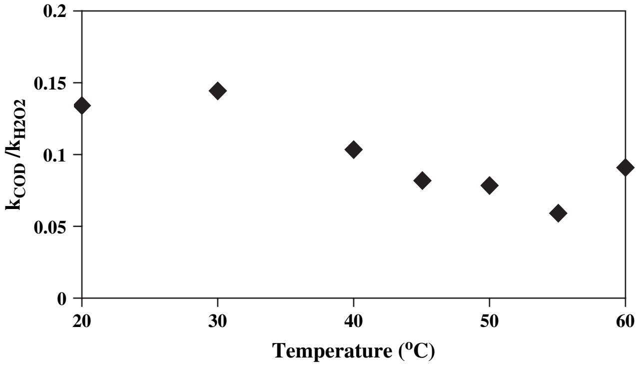

Fig. 10. Effect of reaction temperature on $k_{COD}/k_{H_2O_2}$ ($Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM; pH = 3).

aeration in activated sludge. Fig. 11 presents the ln COD versus I_{OUR} plots established for different COD dilutions of raw SADB with SWW.

According to Fig. 11, the EC_{50} (for $t = 30$ min) for raw SADB was found as 311 mg/L COD. Considering that the COD contribution of SADB in the final, total wastewater of the dyeing and finishing mill without Fenton's pretreatment of SADB was estimated to be 687 mg/L COD (the volumetric contribution of the dyebath effluent to the total dyehouse effluent is 25%) it may be concluded that SADB is expected to exhibit a considerable toxicity (inhibitory effect) on the biosludge of the local treatment plant or of the municipal sewer exposed to dyehouse effluent containing SADB. On the other hand, no inhibition in OURs was found for the samples containing SADB exposed to Fenton's pretreatment (relative to the OUR measured for SWW under the same conditions). It may be concluded from the above mentioned experimental results that the inhibitory effect of SADB on activated sludge microorganisms was totally eliminated after Fenton's pretreatment, coinciding with former related studies.

4. Summary and conclusions

The present work aimed at exploring the effect of Fenton's pretreatment on the degradability and toxicity of a simulated acid dyebath effluent. The following conclusions may be drawn from the experimental studies:

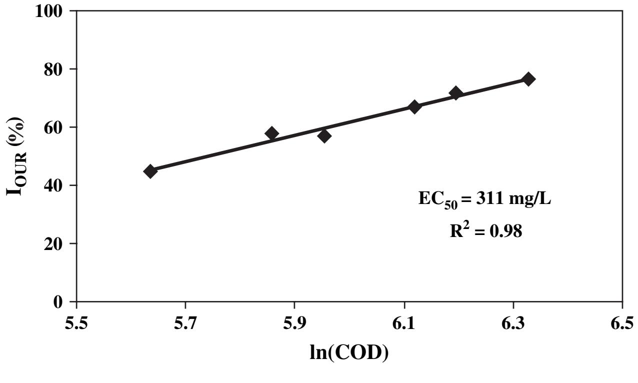

Fig. 11. I_{OUR} (%) versus ln (COD) plot for raw (untreated) SADB ($F/M = 0.19$ mg COD/mg MLVSS d^{-1}, test duration = 30 min).

1. Optimization of process conditions: optimum experimental conditions for the simulated acid dyebath effluent were established as follows: $Fe^{2+} = 10$ mM; $H_2O_2 = 30$ mM and pH = 3 at room temperature ($T = 20$ °C), which yielded an overall COD removal efficiency of 23%. The corresponding color removal efficiency was 92%.
2. Effect of temperature/thermal enhancement: overall COD removal efficiency increased from 23 to 30% upon elevation of the reaction temperature from 20 °C to 50 °C at optimized reaction conditions. The accelerating thermal effect on COD removal was more pronounced at the beginning of Fenton's reaction (first few minutes). COD abatement did not show any improvement upon further increase in temperature and reaction time confirming an optimum value for Fenton's pretreatment of the dyebath effluent.
3. Assessment of reaction kinetics and oxidation rate–oxidant consumption relationship: the first-order COD abatement rate constant increased from 0.02 min^{-1} to 0.03 min^{-1} by increasing the temperature from 20 to 50 °C. The first-order reaction rate constant for H_2O_2 consumption increased from 0.15 min^{-1} to 0.34 min^{-1} by increasing the temperature from 20 to 50 °C. Further increase in temperature did not improve oxidation and oxidant consumption rates. H_2O_2 consumption ran parallel to COD removal; at approximately 10 times faster rate than COD abatement.
4. Effects of pretreatment on acute toxicity and biodegradability: according to the activated sludge inhibition test (ISO 8192), the EC_{50} value obtained for untreated acid dyebath effluent was 311 mg/L in terms of COD, whereas the pre-treated samples of dyebath effluent exerted no inhibition, indicating that the inhibitory effect of the spent acid dyebath was totally eliminated with Fenton's pretreatment. Biocompatibility of the acid dyebath effluent was restored to that of readily biodegradable effluent of domestic character upon exposure to Fenton's pretreatment under optimized reaction conditions.

Acknowledgements and credits

We are thankful to Dr. Izzet Alaton, Head of the Research & Development Department of Pisa Tekstil for his courtesy of supplying the dyes and auxiliaries. The present study was financially supported by TUBITAK (Turkish Scientific and Technical Research Council) under project Nr. ICTAG-C-075 for our participation in COST Action 628 "*Life Cycle Assessment (LCA) of textile products, eco-efficiency and definition of Best Available Technology (BAT) of textile processing*".

References

[1] Grau P. Textile industry wastewater treatment. Water Sci Technol 1991;24:97–103.

[2] Ince NH, Gonenc DT. Treatability of textile azo dye by UV/H_2O_2. Environ Technol 1997;18:179–85.

[3] Pagga U, Brown D. The degradation of dyestuffs. Part II. Behaviours of dyestuffs in aerobic biodegradation tests. Chemosphere 1986;15:479–91.

[4] Vandevivere PC, Bianchi R, Verstraete W. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. J Chem Technol Biotechnol 1998;72:289–302.

[5] Legrini O, Oliveros E, Braun AM. Photochemical processes for water treatment. Chem Rev 1993;93:671–98.

[6] Shu HY, Huang CR. Degradation of commercial azo dye in water using ozonation process. Chemosphere 1995;31:3813–25.

[7] Galindo C, Kalt A. UV–H_2O_2 oxidation of monoazo dyes in aqueous media: a kinetic study. Dyes Pigments 1998;40:27–35.

[8] Shu HY, Huang CR, Chang MC. Decolorization of mono-azo dyes in wastewater by advanced oxidation process: a case study of acid red 1 and acid yellow 23. Chemosphere 1994;29:2597–607.

[9] Ince NH. Critical effect of hydrogen peroxide in photochemical dye degradation. Water Res 1999;33:1080–4.

[10] Neamtu M, Siminiceanu I, Yediler A, Kettrup A. Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H_2O_2 oxidation. Dyes Pigments 2002;53:93–9.

[11] Cisneros RL, Espinoza AG, Litter MI. Photodegradation of an azo dye of the textile industry. Chemosphere 2002;48:393–9.

[12] Mohey El-Dein A, Libra JA, Wiesmann U. Mechanism and kinetic model for the decolorization of the azo dye Reactive Black 5 by hydrogen peroxide. Chemosphere 2003;52:1069–77.

[13] Azbar N, Yonar T, Kestioglu K. Comparison of various advanced processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. Chemosphere 2004;55:35–43.

[14] Huang CP, Dong C, Tang Z. Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. Waste Manag 1993;13:361–77.

[15] Safarzadeh-Amiri A, Bolton JR, Cater SR. Ferrioxalate mediated photodegradation of organic pollutants in contaminated water. Water Res 1997;31:787–98.

[16] Venkatadri R, Peters RW. Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent, and titanium dioxide-assisted photocatalysis. J Hazard Mater 1993;10:107–49.

[17] Pirkanniemi K, Sillanpää M. Heterogeneous water phase catalysis as an environmental application: a review. Chemosphere 2002;48:1047–60.

[18] Arslan-Alaton I. Advanced oxidation of textile industry dyes. In: Parsons S, editor. Advanced oxidation processes for water and wastewater treatment. UK: IWA Publishing; 2004. p. 302–28.

[19] Arslan-Alaton I. The effect of pre-ozonation on the biocompatibility of reactive dye hydrolysates. Chemosphere 2003;51:825–33.

[20] Arslan I, Balcioglu IA. Degradation of commercial reactive dyestuffs by heterogeneous and homogenous advanced oxidation processes: a comparative study. Dyes Pigments 1999;43:95–108.

[21] Arslan I, Balcıoglu AI, Bahnemann DW. Photochemical treatment of simulated dyehouse effluents by novel TiO_2 catalyst. Water Sci Technol 2001;44:171–8.

[22] Perez M, Torrades F, Domenech X, Peral J. Fenton and photo-Fenton oxidation of textile effluents. Water Res 2002;36:2703–10.

[23] Arslan-Alaton I, Gurses F. Fenton-like and photo-Fenton-like oxidation of procaine penicillin G formulation effluent. J Photochem Photobiol A Chem 2004;165:165–75.

[24] Yu G, Zhu W, Yang Z. Pretreatment and biodegradability enhancement of DSD acid manufacturing wastewater. Chemosphere 1998;37:487–94.

[25] Fan Q, Hoskote S, Hou Y. Reduction of colorants in nylon flock dyeing effluent. J Hazard Mater 2004;112:123–31.

[26] Kang SF, Liao CH, Chen MC. Pre-oxidation and coagulation of textile wastewater by the Fenton process. Chemosphere 2002;46:923–8.

[27] Swaminathan K, Sandhya S, Sophia AC, Pachhade K, Subrahmanyam YV. Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. Chemosphere 2003;50:619–25.

[28] Kim T, Park C, Yang J, Kim S. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. J Hazard Mater 2004;112:95–103.

[29] ISO 6060. Water quality – determination of the chemical oxygen demand; 1986.

[30] Gaehr F, Hermanutz F, Oppermann W. Ozonation – an important technique to comply with new German Laws for textile wastewater treatment. Water Sci Technol 1994;30:255–63.

[31] ISO 8192. Water quality—oxygen demand inhibition assay by activated sludge; 1986.

[32] Chan KH, Chu W. Modeling the reaction kinetics of Fenton's process on the removal of atrazine. Chemosphere 2003;51:305–11.

[33] Tang WZ, Huang CP. 2,4-Dichlorophenol oxidation by Fenton's reagent. Environ Technol 1996;17:1373–8.

[34] Eisenhauer HR. Oxidation of phenolic wastes. J Water Pollut Control Fed 1964;36:1116–28.

[35] Sedlak DL, Andren AW. Oxidation of chlorobenzene with Fenton's reagent. Environ Sci Technol 1991;25:777–82.

[36] Xu XR, Li HB, Wang WH, Gu J. Degradation of dyes in aqueous solutions by the Fenton process. Chemosphere 2004;57:595–600.

[37] Ledacowicz S, Solecka M. Impact of advanced oxidation processes on the biodegradation kinetics of industrial wastewater. Water Sci Technol 2000;41:157–64.

[38] Meric S, Kaptan D, Olmez T. Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. Chemosphere 2004;54:435–41.

[39] Gomes de Moraes S, Freire RS, Duran N. Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes. Chemosphere 2000;40:369–73.

[40] Arslan I, Balcioglu IA, Tuhkanen T. Advanced oxidation of synthetic dyehouse effluent by O_3, H_2O_2/O_3 and H_2O_2/UV processes. Environ Technol 1999;20:921–32.

[41] Peralta-Zamora P, de Moraes SG, Reyes J, Duran N. Removal of organic pollutants by coprecipitation with metallic hydroxides and photochemical treatment. Environ Technol 1997;18:461–6.

[42] Ince NH, Stefan MI, Bolton JR. UV/H_2O_2 degradation of and toxicity reduction of textile azo dyes: Remazol Black B, a case study. J Adv Oxid Technol 1997;2:442–8.

[43] Tezcanli-Guyer G, Ince NH. Degradation and toxicity reduction of textile dyestuff by ultrasound. Ultrason Sonochem 2003;10:235–40.