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# Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation, and ferrous iron-catalyzed ozonation

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## Abstract

Dyeing and finishing of textile yarns and fabrics are extremely important processes in terms of both quality and environmental concerns. Among the commercial textile dyes, particularly disperse dyestuffs are of environmental interest because of their widespread use, their potential for formation of toxic aromatic amines and their low removal rate during aerobic waste treatment as well as advanced chemical oxidation. Thus, in the present paper ferrous iron coagulation, ozonation and ferrous iron-catalyzed ozonation were employed at varying pH (3–13) and Fe(II)-ion doses (0.09–18 mM) for the treatment of a simulated disperse dye-bath (average initial apparent color as absorbance at 566 nm = 815.4 m<sup>-1</sup>; COD<sub>0</sub> = 3784 mg l<sup>-1</sup>; TOC<sub>0</sub> = 670 mg l<sup>-1</sup>; BOD<sub>5,0</sub> = 58 mg l<sup>-1</sup>) that more closely resembled an actual dyehouse effluent than an aqueous disperse dye solution. Coagulation with 5000 mg l<sup>-1</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O (18 mM Fe<sup>2+</sup>) at pH 11 removed up to 97% color and 54% COD, whereas oxidation via ozonation alone (applied ozone dose = 2300 mg l<sup>-1</sup>) was only effective at pH 3, resulting in 77% color and 11% COD removal. Fe(II)-ion-catalyzed ozonation (3.6 mM Fe<sup>2+</sup> at pH 3; Fe<sup>2+</sup>:O<sub>3</sub> molar ratio 1:14) eliminated 95% color and 48% COD and appeared to be the most attractive option among the investigated chemical treatment methods as for its applicability at the natural acidic pH of the disperse dye-bath effluent and at relatively low Fe<sup>2+</sup>-ion doses as compared to ferrous sulfate coagulation. However, no TOC reduction was observable for ozonation and catalytic ozonation at the investigated reaction conditions (14 g l<sup>-1</sup> O<sub>3</sub> at pH 3). An average six-fold enhancement in the biodegradability parameter of the synthetic dye wastewater expressed in terms of the BOD<sub>5</sub>/COD ratio could be achieved by the investigated chemical treatment methods. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Disperse dyes; Simulated disperse dye-baths; Coagulation; Ozonation; Ferrous iron-catalyzed ozonation

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## 1. Introduction

As many other industrial sectors, growing concern about environmental issues has prompted the textile industry to investigate more appropriate and environmentally friendly treatment technologies to meet the discharge consents becoming stricter every day. Textile preparation, dyeing and finishing plants are currently being forced to treat their effluents at least partially prior to discharge to publicly owned treatment works (POTWs) due to the high organic load, strong and resistant color as well as high dissolved solids content of the discharged wastewater [1–3]. Nowadays efforts are being made to first separate the more “problematic” textile effluent streams as to augment their treatability by conventional methods, since the advanced treatment of such complex and variable wastewater at its typically high flow rates with up to 3000 m<sup>3</sup> per day × textile plant is unaffordable [4,5]. As a consequence, the biodegradability improvement of those streams selected as the most refractory or toxic ones will be economically more advantageous than treating the whole textile industry effluent [6,7].

Since commercial dyestuffs are intentionally designed to be recalcitrant under typical usage conditions, a marked resistance of these dyes to aerobic biological treatment is not unusual [3,5,6]. Many studies have also confirmed that anaerobic degradation products of some dye classes are suspected of being carcinogenic and mutagenic, and the probability that they are moving through treatment systems essentially without alteration into receiving water streams is a matter of significant concern [8,9]. A possible approach to the alleviation of this problem is to apply ozone to dyehouse effluents, either as a pre-treatment or a final polishing step before discharge [10–16], or possibly as a step in an in-plant water reuse system. Several studies have provided some evidence that ozone can de-colorize water-soluble synthetic dyes (i.e. fiber reactive, acid and direct dyestuff preparations) effectively [16,17]. Although the majority of commercial textile dyes are water-soluble (hydrophilic), the hydrophobic disperse dyes employed for dyeing polyester fabrics are most heavily used [3,4,8]. Unfortunately, rather poor treatment efficiencies were reported for the biological treatment of disperse dyes and contradictory results obtained via chemical oxidation methods such as ozonation and Fenton’s reaction [11,16,17]. A review mentions that about twice as much ozone was needed to completely de-colourize disperse dyes than was required for hydrophilic dyes [11]. Other investigators experienced a relatively inefficient color removal for ozone when applied to wastewater samples containing this dye class [10,17].

Ozonation has been shown to achieve a very limited mineralization of many organic compounds [18–20]. It is now widely assumed that ozone decomposition induces radical type chain reactions mainly involving the hydroxyl radicals (OH<sup>•</sup>), whose inherent reactivity towards various organic and inorganic compounds has been already proven by many researchers [18,21,22]. Ozone decomposition into OH<sup>•</sup> can be activated via OH<sup>−</sup>, H<sub>2</sub>O<sub>2</sub>, humic substances, short UV light ( $\lambda < 300$  nm) and reduced transition metals [18,22]. Combinations like O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/OH<sup>−</sup> have been studied for the treatment of various organic compounds found in water and industrial wastewater [20,22–24]. More recently, ozonation processes catalyzed by transition metals have been investigated for the degradation of organic pollutants [24–27]. Transition metals such as iron and manganese have been applied in the form of their salt solutions, as metal oxides acting as heterogeneous catalysts, or metals on various supports mostly under acidic reaction conditions. Former

investigators have already evidenced that even very small amount of di- and tetra-valent manganese-ion enhanced the oxidation of toxic organic pollutants through a mechanism different from that reported for non-catalyzed ozonation [28–31]. There is still an ongoing debate about whether transition metal-catalyzed ozonation ( $\text{Mn}^{2+}/\text{O}_3$ ) proceeds via  $\text{OH}^\bullet$  induced radical type chain reactions [32–34] or through the formation of metal oxides and metal–organic complexes [24]. Metal–organic complexes more easily oxidize the organic compounds than molecular ozone and/or might form intermediate oxidation products that are easier oxidized via ozonation [24,34].

Until now, no works have been attempted to apply ozone and coagulants such as iron salts simultaneously for the treatment of disperse dyestuffs or disperse dye-bath effluents. The main reason for investigating such a combination in the present work is the fact that their stand-alone application is expected to be rather insufficient to deal with the de-colourization and effective partial oxidation of these dyestuffs and their corresponding auxiliary chemicals. Considering the beneficial results obtained by the ozonation of several dye classes and actual textile wastewater as mentioned above, this process seems to have a great potential as a pre-treatment method for disperse dyes and/or disperse dye containing textile effluents.

With the above mentioned facts in mind, the experimental investigation described herein aimed to ascertain the treatability of a synthetic disperse dye-bath via (1) coagulation with Fe(II)-iron, (2) ozonation, and (3) Fe(II)-iron-catalyzed ozonation under varying reaction conditions. Each chemical treatment process was optimized for operating conditions such as reaction pH and Fe(II)-iron dose in terms of overall color and COD removal efficiencies. Further, a series of separate time-dependent experiments were conducted to verify the catalytic effect of low doses of  $\text{Fe}^{2+}$ -ions throughout the ozonation reactions. In addition, the changes in the biodegradability parameter (expressed as the  $\text{BOD}_5/\text{COD}$  ratio) were comparatively evaluated before and after application of the selected chemical treatment systems to the simulated disperse dye-bath.

## 2. Experimental

### 2.1. Simulated disperse dye-bath

Since the present study aimed to demonstrate the alternative pre-treatment of one of the most problematic dyehouse effluents, a typical disperse dye-bath was chosen as the surrogate recalcitrant textile effluent stream. The exhausted disperse dye-bath investigated in this study was simulated according to typical disperse dyeing formulae of a local dyehouse (Pisa Tekstil Inc., Istanbul). The chemical composition of such a dye-bath mixture is listed in Table 1.

Artificial disperse dye-baths were prepared due to three reasons: firstly, it enables research to be carried out in the absence of a local source of effluent; secondly, simulated effluents have a constant composition and, hence, enable the effect of treatment to be more readily understood; and thirdly, from the practical point of view it is of utmost importance to assess the treatment performance of the selected treatment systems in the presence of several dye assisting chemicals since disperse dyes are always found in the form of an “exhausted” dye-bath formulation. Because of the proprietary nature of the dyes, additional information

Table 1  
Ingredients of the simulated disperse dye-bath

Ingredient	Chemical properties	Concentration (g l <sup>-1</sup> )	Manufacturer
Serilene Black SBN	Mixture of CI <sup>a</sup> disperse violet 93:1 (5–15%) and CI disperse blue 291 (5–15%); biological elimination <10%	0.50	Yorkshire
Foron Red S-WF	Mixture of two azo dyestuffs, elemental composition: C, Cl, H, N, O, S; biological elimination <10%	0.03	Clariant (Sandoz)
Breviol A69 (dispersing agent)	Condensation product of naphthalene sulphonic acids (>20%)	1.00	Henkel
Rucogal SBM (equalizer)	Mixture of polyacrylate and fatty acid ethoxylates, aromatic carboxylic acid compound, anionic	0.50	Rudolf-Duraner
Acetic acid (pH buffer)	–	1.50	Merck

<sup>a</sup> Color index.

such as molecular weight and structures is not available. The original (natural) pH of the simulated dye-bath was 3.34 (pH 3), but this value was adjusted with H<sub>2</sub>SO<sub>4</sub> or NaOH solutions according to the experimental requirements. Although this dye-bath was prepared to simulate concentrations that could be present in an unrinsed dye-bath, the concentrations in an actual spent dye-bath effluent would in fact be lower because the degree of disperse dye fixation is relatively high. The average dye loss typically ranges between 4 and 20% after the dyeing process is complete [3,4]. Thus, the results are anticipated to represent the worst case of unspent disperse dyes in the dye-bath effluent.

## 2.2. Coagulation procedure

Coagulation experiments were conducted by using Merck grade FeSO<sub>4</sub>·7H<sub>2</sub>O as the coagulant at five different doses (250–5000 mg l<sup>-1</sup>) and varying initial pH (3–13). The optimum coagulant concentration and pH were determined by jar tests on the basis of percent apparent color and COD removal efficiency after treatment. The conventional jar tests were started by pipetting varying amounts of FeSO<sub>4</sub>·7H<sub>2</sub>O from its 0.36 M (10% w/w) stock solution to 400 ml pH-adjusted wastewater samples. After pH adjustment and coagulant addition, the jar test was carried out as follows: first, rapid mixing (250 rpm impeller speed) was continued for 1 min followed by slow mixing that was applied for 10 min at 25 rpm. Thereafter, the impeller was removed and the formed flocs were allowed to settle for another 45 min. At the end of the settling period the supernatant water sample was withdrawn and centrifuged for 20 min at 2000 rpm and analyzed for residual color and COD.

## 2.3. Ozonation and catalytic ozonation procedure

Simulated disperse dye-baths were ozonated for 10 min unless otherwise stated, in a 300 ml capacity gas washing bottle fitted with a fine porosity, sintered glass plate diffuser.

Two separate gas washing bottles containing 2% KI solution were connected in series with the washing bottle with the reaction solution (250 ml) to collect all off-gas ozone passing through the simulated dye-bath. Another single gas washing bottle with 20% KI was employed for measuring the (input) ozone concentration in the feed gas in separate runs. The introduced ozone input rate was determined iodometrically [35] as  $3.5 \text{ g h}^{-1}$  corresponding to a specific dose of  $0.62 \text{ g ozone per g initial COD}$  ( $0.62 \text{ g O}_3 \text{ g}^{-1} \text{ COD}_0$ ) of the simulated wastewater after 10 min ozonation of the simulated dye-bath. Short lengths of Tygon<sup>®</sup> tubing were used for all connections to ensure minimal  $\text{O}_3$  loss from the system. Ozone was generated from pure  $\text{O}_2$  with a Fischer OZ 500M model  $\text{O}_3$  generator at a flow rate of  $70 \text{ l min}^{-1}$ . The  $\text{O}_2 + \text{O}_3$  gas flow rate was continuously monitored with a rotameter incorporated into the ozone generator. Ozonation tests were also conducted in the presence of Fe(II)-ion applied as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  at concentrations ranging between 0.09 and 3.6 mM  $\text{Fe}^{2+}$  (i.e.  $25\text{--}1000 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  from a  $0.36 \text{ mole l}^{-1}$  stock solution) and varying pHs ranging between pH 3 and 11.

#### 2.4. Analyses

A volume of 20 ml aliquots of raw and treated wastewater samples were analyzed for apparent color (optical density including turbidity), COD and TOC. Further, to evaluate whether changes in biodegradability (expressed herein as the  $\text{BOD}_5/\text{COD}$  ratio) occurred after application of the three chemical treatment methods, initial and final  $\text{BOD}_5$ -values of the raw and treated synthetic dye-bath effluent samples were also measured. The visible light absorbance at the characteristic wavelength of the raw and treated simulated disperse dye-bath ( $\lambda = 566 \text{ nm}$ ) was measured to follow up the progress of de-colourization during the application of different treatment methods. Changes in the visible absorption spectra of the synthetic dyehouse effluent samples were monitored with a Perkin-Elmer Lambda 12 double beam UV–VIS spectrophotometer in 1 cm quartz cells after centrifugation for 20 min at 4000 rpm (Heraeus Labofuge) and 10-fold dilution with de-ionized water (Millipore Corp.). TOC was determined by organic carbon cuvette tests (CADAS, Germany), whereas COD measurements were conducted by using the closed reflux, colorimetric method in accordance with standard methods [36]. The  $\text{BOD}_{5\text{s}}$  of the initial and chemically pre-treated samples were determined iodometrically according to the modified Winkler Method [36].

### 3. Results and discussion

#### 3.1. Ferrous iron coagulation

Ferrous sulfate coagulation of the simulated disperse dye-bath was examined at pH 3, 5, 7, 9, 11 and 13 at a coagulant dose of  $2500 \text{ mg l}^{-1}$ . As is apparent in Table 2, color (97%) and COD removal (54%) of the dyehouse effluent exhibited a distinct maximum at pH 11, whereas relatively low COD removal rates were obtained at the other investigated pH-values.

Color removal was 73% at a range of pH 3–7 and increased to 78% at pH 9. Color (83%) and COD (25%) removal efficiencies at pH 13 were still higher than in the range of pH 3–9.

Table 2

Effect of initial pH on the overall percent apparent color and COD removal efficiencies obtained by ferrous iron coagulation with  $2500 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $A_{566,0} = 806.6 \text{ m}^{-1}$ ;  $\text{COD}_0 = 3780 \text{ mg l}^{-1}$ )

pH	Final color ( $\text{m}^{-1}$ )	Final COD ( $\text{mg l}^{-1}$ )	Color removal (%)	COD removal (%)
3	218.9	3533	72.9	6.5
5	216.0	3665	73.2	3.0
7	209.0	3549	74.1	6.1
9	178.2	3409	77.9	9.8
11	24.8	1739	96.9	54.0
13	141.4	2831	82.5	25.1

The increasing coagulation efficiency at elevated pHs with an optimum at pH 11 is attributable to the fact that disperse dyes tend to aggregate at alkaline pHs as a consequence of their reduced solubility and ionization rate at a specific elevated pH. Similar to the present work, Kuo investigated the Fenton's ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  reagent) reaction of dyestuffs originating from five different classes as well as simulated textile wastewater. He stated that among the selected dyestuffs, in particular de-colourization of the disperse dye-containing effluent might be mainly completed by ferrous sulfate coagulation during Fenton's treatment [37].

In separate runs, the effect of increasing ferrous iron coagulant dose upon color and COD reduction rates was studied at pH 11 and presented in Table 3.

As expected, increasing the ferrous sulfate dose had a dramatic positive impact on the achieved removal efficiencies. Moreover, at pH 11 the disperse dyes tended to precipitate even without the addition of coagulant resulting in an average of 72% color and 6% COD removal, respectively. As can be seen in Table 3, the coagulating effect of ferrous sulfate was apparent only beyond a "critical" dose of  $1000 \text{ mg l}^{-1}$ . Practically, no difference in treatment efficiencies was observable for 2500 and  $5000 \text{ mg l}^{-1}$  ferrous sulfate revealing that the optimum coagulation conditions were already achieved with  $2500 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  and at pH 11. Comparatively, low removal efficiencies in apparent color (40–55%) and COD (3–6%) were obtained for varying coagulant doses between 0 and  $2000 \text{ mg l}^{-1}$  at pH 3.

Table 3

Effect of coagulant dose on the overall percent apparent color and COD removal efficiencies obtained by ferrous iron coagulation at pH 11 ( $A_{566,0} = 824.9 \text{ m}^{-1}$ ;  $\text{COD}_0 = 3791 \text{ mg l}^{-1}$ )

Coagulant dose ( $\text{mg l}^{-1}$ )	Final color ( $\text{m}^{-1}$ )	Final COD ( $\text{mg l}^{-1}$ )	Color removal (%)	COD removal (%)
0	230.2	3572	71.6	5.6
250	235.1	3539	71.0	6.4
500	217.4	3467	73.1	8.3
1000	154.4	3090	80.9	18.3
1750	81.0	2411	90.0	36.3
2500	25.6	1826	96.8	51.7
5000	18.7	1752	97.7	53.7

### 3.2. Ozonation

Simulated disperse dye-baths were subjected to ozonation in a semi-continuous manner (applied  $O_3$  dose =  $2300 \text{ mg l}^{-1}$ ; specific input rate =  $0.62 \text{ g } O_3 \text{ g}^{-1} \text{ COD}$  after 10 min ozonation) at varying pH-values (pH 3, 5, 8 and 11). In contradiction to the coagulation experiments, highest color (77%) as well as COD (11%) removals were achieved via ozonation at acidic pH (pH 3; Table 4), whereas no color and COD removals were obtained at pH 11. The decrease in color and COD at pH 11 occurred only via precipitation of the disperse dyes as a consequence of the elevated pH.

Here it should be pointed out that since enhanced ozone decomposition at elevated pH-values results in the formation of  $OH^\bullet$  and, thus, is expected to enhance pollutant oxidation rates, the obtained results might be confusing on the first sight. However, it should be also kept in mind that organic dyes having polyaromatic structures and  $-N=N-$  and  $-C=C-$  type double bonds in their chromophoric groupings, will readily react via both molecular  $O_3$  that is dominant at acidic pH, as well as  $OH^\bullet$  that is the major oxidizing agent at basic pH. Considering the presence of  $OH^\bullet$  scavengers/competitors (acetic acid, equalizer, dispersing agent) being present in the disperse dye-bath formulation, no significant difference should be expected between the reaction rates throughout the whole studied pH range. Consequently, molecular  $O_3$  will react more selectively with the disperse dye at acidic pH, whereas acetic acid and the other dye auxiliary chemicals that contributed to 83% of the total COD load of the studied disperse dye-bath formulation, will possibly compete for  $OH^\bullet$  at the higher pH-values and, thus, significantly less  $OH^\bullet$  will be available for the oxidation of the disperse dye.

For instance, Chu and Ma [16] examined the ozonation of various dyestuffs in aqueous solutions at different initial pH-values. They concluded that the enhanced solubility of the selected disperse dyes at acidic pH might contribute to the higher oxidation rate achieved at low pH via ozonation of this dye class. In another study, the initial pH-value had to be adjusted down to around pH 2–3 for effective de-colourization of textile wastewater from a polyester dyeing and finishing plant via ozonation [16]. Snider and Porter also evidenced an improved COD removal efficiency at lower pH-values for actual textile wastewater containing disperse dyes and for aqueous solutions of disperse dyes [24].

Considering the above mentioned facts and examples, the absence of an acceleration effect during ozonation at high pH, the even higher overall color and COD removal efficiency obtained for ozonation at acidic pH, together with the relatively high overall treatment efficiencies achieved at pH 11 in the case of coagulation, justify the belief that the effectiveness

Table 4

Effect of initial pH on the overall percent apparent color and COD removal efficiencies obtained by ozonation with  $2340 \text{ mg l}^{-1} O_3$  ( $A_{566,0} = 809.5 \text{ m}^{-1}$ ;  $COD_0 = 3782 \text{ mg l}^{-1}$ )

pH	Final color ( $\text{m}^{-1}$ )	Final COD ( $\text{mg l}^{-1}$ )	Color removal (%)	COD removal (%)
3	189.7	3357	77.0	11.4
5	221.8	3487	73.1	8.0
8	218.6	3522	73.5	7.1
11	221.8	3672	73.1	3.1

Table 5

Effect of initial pH on the overall percent apparent color and COD removal efficiencies obtained by ferrous-iron-catalyzed ozonation ( $\text{Fe}^{2+}:\text{O}_3$  molar ratio = 1:54; ferrous sulfate dose =  $250 \text{ mg l}^{-1}$ ; applied ozone dose =  $2300 \text{ mg l}^{-1}$ ;  $A_{566,0} = 797.8 \text{ m}^{-1}$ ;  $\text{COD}_0 = 3777 \text{ mg l}^{-1}$ )

pH	Final color ( $\text{m}^{-1}$ )	Final COD ( $\text{mg l}^{-1}$ )	Color removal (%)	COD removal (%)
3	162.3	3188	79.7	15.6
5	188.5	3424	76.4	9.5
8	197.9	3508	75.2	7.3
11	198.9	3490	75.1	7.8

of each investigated chemical treatment process may strongly depend upon the molecular structure and solubility of the specific dye(s) in the simulated dye-bath. In addition, the impact of oxidant competitors/scavengers present in the reacting medium should also be considered specifically when the ozonation process of a multi-component reaction solution at varying pH is examined.

### 3.3. Ferrous iron-catalyzed ozonation

Ozonation experiments were also performed in the presence of  $250 \text{ mg l}^{-1}$   $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  serving as the  $\text{Fe}^{2+}$ -ion source at varying initial pHs (pH 3–11). As can be seen in Table 5, removal efficiencies were slightly higher than in the absence of ferrous iron (Section 3.2) and exhibited the same decreasing trend with increasing pH as for mere ozonation, especially when increasing the pH from 3 and 5 to pH 8.

From the additional experimental runs covering a range of  $\text{Fe}^{2+}:\text{O}_3$  molar ratios of 1:542 to 1:14 at pH 3 as shown in Table 6, a fair enhancement of the treatment efficiency is clearly evident at the higher end of the explored  $\text{Fe}^{2+}$  doses.

From the obtained results it is clearly evident that during ozonation in the presence of ferrous iron at a relatively low dose ( $200 \text{ mg l}^{-1}$  as  $\text{Fe}^{2+}$ -ions) at pH 3 and the coagulation experiments at pH 11 and higher  $\text{Fe}^{2+}$  concentrations (i.e.  $1000 \text{ mg l}^{-1}$  as  $\text{Fe}^{2+}$ -ions) almost identical overall removal rates were achieved. It might be further speculated that the additional positive effect of ferrous sulfate which was tried at low doses during the

Table 6

Effect ferrous iron dose on the overall percent apparent color and COD removal efficiencies obtained by ferrous-iron-catalyzed ozonation at pH 3 (applied  $\text{O}_3$  dose =  $2300 \text{ mg l}^{-1}$ ;  $A_{566,0} = 838.2 \text{ m}^{-1}$ ;  $\text{COD}_0 = 3790 \text{ mg l}^{-1}$ )

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dose ( $\text{mg l}^{-1}$ )	$\text{Fe}:\text{O}_3$ molar ratio (mole $\text{Fe}^{2+}$ :mole $\text{O}_3$ )	Final color ( $\text{m}^{-1}$ )	Final COD ( $\text{mg l}^{-1}$ )	Color removal (%)	COD removal (%)
0	0	23.32	3307	72.2	12.7
25	1:542	174.2	3278	79.2	13.5
100	1:136	156.2	3350	81.4	11.6
250	1:54	190.0	3236	77.3	14.6
500	1:27	199.5	2836	76.2	25.2
1000	1:14	45.4	1977	94.6	47.8



ozonation process, was not only a consequence of its properties as a coagulant for the fact that chemical coagulation employing  $200 \text{ mg l}^{-1} \text{ Fe}^{2+}$  ( $1000 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) at pH 3 resulted in only 55% color and 4% COD overall treatment efficiency, instead of 95% color and 48% COD removal obtained for catalytic ozonation at the same pH and  $\text{Fe}^{2+}$  dose. Treatment efficiencies obtained during the  $\text{Fe}^{2+}/\text{O}_3$  process were even higher than that achieved for chemical coagulation with  $2500 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  (equivalent to an  $\text{Fe}^{2+}$  dose of  $500 \text{ mg l}^{-1}$ ) at pH 3 (see Table 2).

It can be further inferred that from the practical point of view, it seems more advantageous to apply ozonation at the natural acidic pH of the disperse dye-bath effluent (pH 3–4) and thereby reducing the required amount of ferrous iron by a factor of at least 2–3, instead of increasing the pH to >11 and employing  $2500\text{--}5000 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$  for effective treatment via chemical coagulation, as to obtain the same treatment performance. Furthermore, by employing the  $\text{Fe(II)}/\text{O}_3$  combined system, a costly pH adjustment necessary for effective coagulation would also be avoided at the same time.

To demonstrate the evidence of  $\text{Fe(II)}$ -iron catalysis on the ozonation of simulated disperse dye-bath effluents, separate experiments were performed where color, COD as well as TOC abatement rates were followed as a function of ozonation time. For this purpose, the dye-bath effluent was ozonated for 1 h (i.e. total applied specific ozone dose =  $3.7 \text{ g O}_3 \text{ g}^{-1} \text{ COD}_0$ ) in the presence of  $1.8 \text{ mM}$  ( $100 \text{ mg l}^{-1}$ )  $\text{Fe}^{2+}$  at pH 3. Though total removal efficiencies were expected to remain rather low, the introduction of ferrous-ion at a concentration lower than that at which the highest catalytic ozonation efficiency was observed in the present study ( $3.6 \text{ mM Fe}^{2+}$  at pH 3), allowed to further distinguish between the positive catalytic effect achieved via  $\text{Fe(II)}$ -iron addition and ferrous-iron chemical coagulation that would become effective when  $\text{Fe(II)}$ -iron is applied at higher doses. The obtained kinetic data were compared with mere ozonation at the same specific ozone dose and a reaction at pH 3 and with two separate runs indicated as  $\text{Fe}/\text{O}_2/\text{pH 3}$  and  $\text{Fe}/\text{O}_2/\text{pH 11}$ . During these experiments the disperse dye-bath together with  $500 \text{ mg l}^{-1}$  ferrous sulfate ( $1.8 \text{ mM Fe}^{2+}$ ) being added at the beginning of the reaction ( $t = 0 \text{ min}$ ), was continuously sparged with  $\text{O}_2$  instead of the usual  $\text{O}_2 + \text{O}_3$  mixture applied during ozonation ( $\text{O}_2$  or  $\text{O}_2 + \text{O}_3$  rate =  $70 \text{ l h}^{-1}$ ). These experiments were conducted as to differ between  $\text{Fe(II)}$ -iron or  $\text{Fe(II)} + \text{O}_2 = \text{Fe(III)}$ -iron coagulation at acidic and alkali pH conditions, and  $\text{Fe(II)}$ -catalyzed ozonation. Fig. 1(a) and (b) display color (a) and COD (b) abatement kinetics observed at the selected reaction conditions. Here it should be noted that the initial COD and apparent color ( $A_{566}$ ) values indicated in Fig. 1 at  $t = 0 \text{ min}$  were those obtained directly after centrifugation of the raw and treated samples and, thus, appear to be lower than their original values at pH 3 and 11.

For the ozonation and ferrous iron-catalyzed ozonation processes, initial color abatement rates were determined as  $0.0335$  and  $0.0722 \text{ m}^{-1} \text{ min}^{-1}$ , respectively, from the initial slopes of the kinetic degradation curves. The initial COD removal rates were found as  $0.0026 \text{ m}^{-1} \text{ min}^{-1}$  (ozonation) and  $0.0127 \text{ m}^{-1} \text{ min}^{-1}$  (catalytic ozonation) in the same manner. The 2–5 times higher initial color and COD reduction rates obtained by the ferrous iron-catalyzed oxidation process reveal that  $\text{Fe}^{2+}$ -ion addition accelerates the oxidation kinetics significantly even at a dose of  $1.8 \text{ mM Fe(II)}$ -ion corresponding to only 1.84% of the stoichiometric amount required for the  $\text{O}_3/\text{Fe}^{2+}$  oxidation system [24]. In the case of  $\text{Fe}/\text{O}_2/\text{pH 3}$  and  $\text{Fe}/\text{O}_2/\text{pH 11}$ , no decrease in color and COD was observed after an initial ( $t = 0$ ) removal of 63.3% (pH 3) to 72.6% (pH 11) color and 8.5% (pH 3) to 12.7%

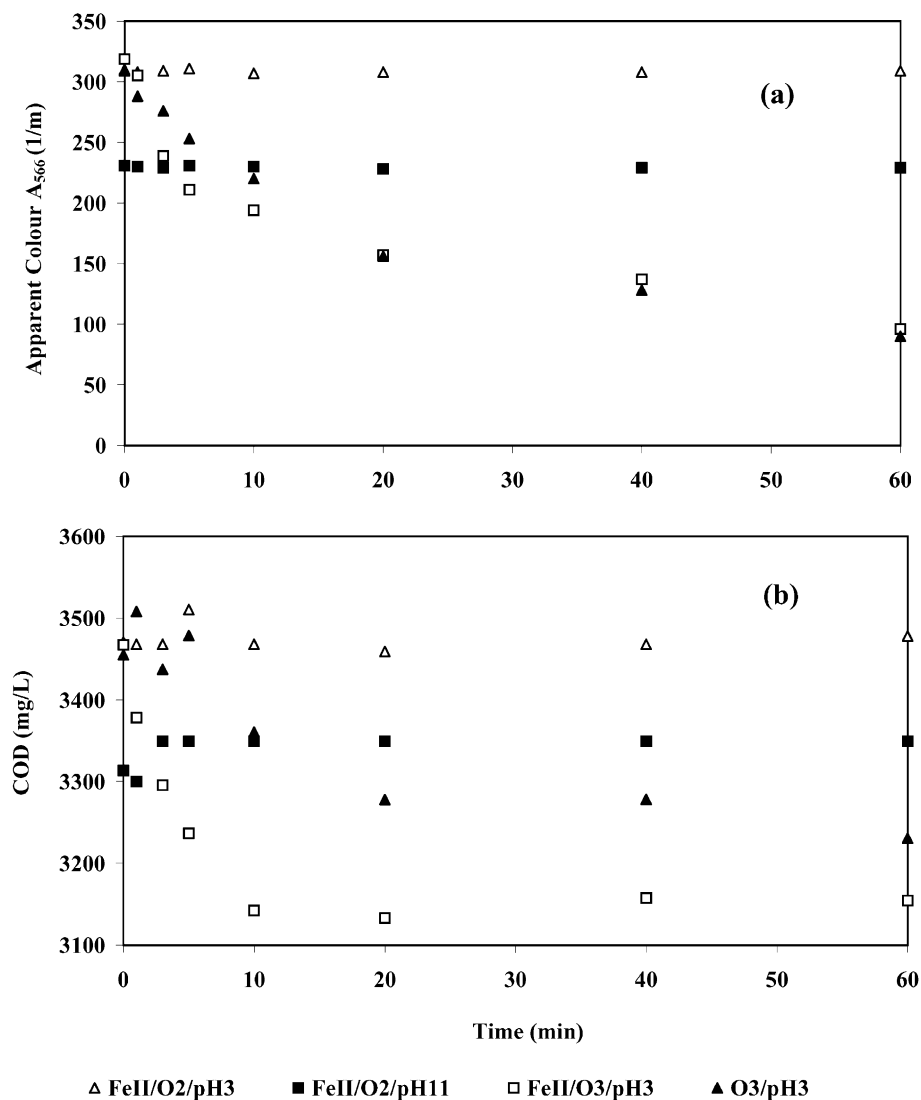


Fig. 1. Time-dependent changes in apparent color (a) and COD (b) during ozonation, catalytic ozonation (applied ozone dose =  $14 \text{ g l}^{-1}$ ; ferrous sulfate dose =  $500 \text{ mg l}^{-1}$ ;  $A_{566,0} = 817.6 \text{ m}^{-1}$ ;  $\text{COD}_0 = 3790 \text{ mg l}^{-1}$ ) and the control experiments Fe(II)/O<sub>2</sub>/pH 3 and Fe(II)/O<sub>2</sub>/pH 11.

(pH 11) COD, respectively. This preliminary removal only accounted for aeration with O<sub>2</sub> and ferrous–ferric iron precipitation and, hence, did not vary as a function of treatment time. A quite similar enhancement in color and COD removal rates by the addition of iron or manganese salts to the ozonation process at concentrations in the millimolar range was found in a previous work conducted with water-soluble reactive dye waste effluents [26]. However,

Table 7  
Results of the biodegradability studies

Chemical treatment process	Coagulation (pH 11; 1000 mg l <sup>-1</sup> FeSO <sub>4</sub> ·7H <sub>2</sub> O)	Coagulation (pH 11; 5000 mg l <sup>-1</sup> FeSO <sub>4</sub> ·7H <sub>2</sub> O)	Ozonation (pH 3; 2300 mg l <sup>-1</sup> )	Fe <sup>2+</sup> -catalyzed ozonation (pH 3; 500 mg l <sup>-1</sup> FeSO <sub>4</sub> ·7H <sub>2</sub> O)
Final BOD <sub>5</sub> <sup>a</sup> (mg l <sup>-1</sup> )	207	201	266	289
Final COD (mg l <sup>-1</sup> )	3090	1752	3357	2836
Final BOD <sub>5</sub> /COD	0.07	0.12	0.08	0.10

<sup>a</sup> Average BOD<sub>5,0</sub> = 28 mg l<sup>-1</sup>; average BOD<sub>5,0</sub>/COD<sub>0</sub> = 0.015.

no TOC reduction was observed throughout the course of the O<sub>3</sub> and Fe(II)/O<sub>3</sub> reactions indicating that for mineralization of the wastewater substantially higher ozone doses (i.e. longer exposure to ozone) are required than those applied in the present investigation.

### 3.4. Effect of chemical pre-treatment on simulated disperse dye-bath biodegradability

Although only partial reductions in COD- and TOC-values have been established for the ozonation of textile effluents, ozone has been demonstrated to have the ability to enhance the biotreatability of certain complex organic chemicals [38–40], priority pollutants [41,42] and industrial wastewater [38,43,44]. In fact, the by-products of some partially ozonated compounds can be oxidized more economically and effectively by biological treatment processes. Table 7 presents the final values in BOD<sub>5</sub>, COD and the corresponding BOD<sub>5</sub>/COD (defined here as the specific biodegradability of the effluent in question) obtained for the coagulation of the simulated disperse dye-bath wastewater at two different coagulant doses and pH 11, ozonation at pH 3 and ferrous iron-catalyzed ozonation at pH 3 of the simulated disperse dye-bath.

From the above table it is obvious that the products of chemical coagulation, ozonation as well as Fe<sup>2+</sup>-catalyzed ozonation were much more biocompatible than the original dye-bath components. Final biodegradability varied between 0.07 and 0.12 and to reach a moderate biodegradability >0.1, a coagulant dose of 5000 mg l<sup>-1</sup> at pH 11, or alternatively an ozone dose of 2300 mg l<sup>-1</sup> at pH 3, or 500 mg l<sup>-1</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O addition at pH 3 in case of the catalytic ozonation process, were sufficient. The positive influence of chemical treatment methods on the biodegradability of textile effluents was more pronounced in the case of the originally extremely non-biocompatible disperse dye-bath components as compared with previous investigations conducted with raw, coagulated and biologically treated textile industry wastewater [45] and dyehouse effluents simulating wastewater from the reactive dyeing and rinsing process stages [46].

## 4. Conclusion

The present experimental work intended to treat a simulated disperse dye-bath effluent via coagulation, ozonation and catalytic ozonation. It was confirmed that in particular the Fe<sup>2+</sup>/O<sub>3</sub> process is fairly appropriate to remove color and COD of the dye-bath. This

combined treatment system can be applied at its natural acidic pH and at appreciably lower  $\text{Fe}^{2+}$ -ion concentrations as compared to conventional ferrous sulfate doses applied for the coagulation procedure at pH 11. The kinetic ozonation studies also confirmed that during the  $\text{Fe}^{2+} + \text{O}_3$  process color and COD removal occurred not only due to the coagulating effect of ferrous iron but also as a consequence of the enhanced oxidative reaction of the disperse dye-bath effluent via ozone. The preliminary biodegradability study also revealed that all three investigated alternative chemical processes are promising pre-treatment methods to improve the overall efficiency and reduce inhibitory levels of a proceeding biochemical oxidation technique for the thorough re-remediation of textile industry wastewater. Owing to the vast number of commercial dyes used and the chemical complexity of dyehouse effluents, more detailed research is needed to optimize ozone treatment of several dye classes individually, in different combinations and ultimately in their real background matrices.

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