



## Advanced oxidation and mineralization of 3-indole butyric acid (IBA) by Fenton and Fenton-like processes

Gökhan Ekrem Üstün<sup>a,\*</sup>, Seval Kutlu Akal Solmaz<sup>a</sup>, Tülay Morsünbül<sup>a</sup>, Hilal Safiye Azak<sup>b</sup>

<sup>a</sup> Faculty of Engineering and Architecture, Department of Environmental Engineering, Uludag University, 16059 Gorukle, Bursa, Turkey

<sup>b</sup> The Scientific and Technological Research Council of Turkey, Bursa Test and Analysis Laboratory, 16190 Bursa, Turkey

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### ABSTRACT

The degradation and mineralization of 3-indole butyric acid (IBA) in aqueous solution was examined using Fenton and Fenton-like processes. Various operating conditions were evaluated including pH and the concentrations of iron ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The highest COD removal efficiency was achieved at 0.2 mM/0.6 mM  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio and 0.2 mM/1.0 mM  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  ratio at pH 3 for Fenton and Fenton-like processes, respectively. IBA degradation and mineralization exhibited pseudo-first-order kinetics while the depletion of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  exhibited zero-order kinetics during both processes in all experiments. 97% of IBA degradation proceeded via two distinctive kinetic regimes. The initial phase of the reaction was directly attributable to the Fenton reaction wherein nearly all of the  $\text{OH}^\bullet$  radicals were generated. This was followed by a slower degradation phase, which can be thought of as a series of Fenton-like reactions within a Fenton process. In the Fenton-like process, the initial phase lasted longer than in the Fenton process because the generation of  $\text{OH}^\bullet$  radicals proceeded at slower rate; however, 98% degradation of IBA was achieved. The mineralization of IBA was 16.2% and 50% for Fenton and Fenton-like processes, respectively. After 24 h,  $\text{H}_2\text{O}_2$  was the limiting reagent for further mineralization of IBA intermediates present in the system. The results of the study showed that Fenton Process may be more useful when only removal of IBA is required and mineralization is unnecessary. But if mineralization of IBA is needed, Fenton-like process gains more important than Fenton Process due to its mineralization efficiency.

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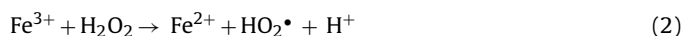
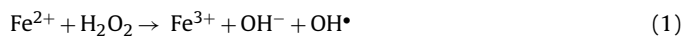
### 1. Introduction

Contamination of water resources by pesticide residues is one of the major challenges in environmental preservation and sustainability. Intensive pesticide application in worldwide modern agricultural practice to ensure production quantity and quality has resulted in a ubiquitous contamination problem. After application to the field, pesticides can leach into ground waters and run off into surface waters with rainfall and/or irrigation following some degradation pathways as biotic (microbial) and/or abiotic (photolytic and hydrolytic) processes. Consequently, there is a risk of pesticide contamination of natural waters that needs to be assessed [1,2].

The control of pesticides in water is an important measure in environmental protection. Among the many processes proposed and/or being developed to break down pesticides, biodegradation has received the greatest attention [3]. However, biological treatment may be limited in application for degradation of the complex and toxic organics as pesticide [4]. Therefore, advanced methods of

wastewater treatment based on chemical oxidation which generates powerful oxidants (hydroxyl radicals), are gaining importance [5]. These methods allow nonbiodegradable and/or inert organic compounds oxidation by free radicals and provide complete mineralization to water and carbon dioxide. The Fenton processes such as Fenton process (FP) and Fenton-like process (FLP) are capable of producing hydroxyl radicals and efficient, fast, low-cost and easy-to-operate technologies for pesticide removal [6].

Fenton reactions occurred between hydrogen peroxide and  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  according to Eqs. (1) and (2) produce highly reactive hydroxyl radicals that attack and destroy the pesticide. When  $\text{Fe}^{2+}$  used as a catalyst the reaction is referred as FP and when  $\text{Fe}^{3+}$  used as a catalyst the reaction is referred as FLP [7].



FP and FLP is involved not only in oxidation but also coagulation by forming ferrous and ferric-hydroxo complexes which act as coagulants to remove some portions of organic contaminants [8]. Because of non selective characteristic and the strong oxidation potential of hydroxyl radicals, almost all pesticides in

\* Corresponding author. Tel.: +90 224 294 0640; fax: +90 224 442 9148.

E-mail address: [gokhaneu@uludag.edu.tr](mailto:gokhaneu@uludag.edu.tr) (G.E. Üstün).

water/wastewater can be rapidly degraded and the toxicity of pesticides can be greatly reduced by these methods [9].

Experiments presented in literature show that pesticide degradation ratio has been expressed in terms of COD removal efficiency as well as pesticide removal efficiency. The effects of pH, H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup> and Fe<sup>3+</sup> parameters on COD removal efficiency have been also investigated to obtain the optimal values in FP and FLP [10–12]. Triazophos degradation with FP was studied by Li et al. [10]. COD removal efficiencies were found 96.3% for industrial wastewater and 85.4% for synthesized water. Optimum values at pH 4 were 2.5 g/L of FeSO<sub>4</sub>·7H<sub>2</sub>O and 100 mL/L of 30% H<sub>2</sub>O<sub>2</sub> for synthesized water and 5.0 g/L of FeSO<sub>4</sub>·7H<sub>2</sub>O and 75 mL/L of 30% H<sub>2</sub>O<sub>2</sub> for industrial wastewater. This study has proved that the FP can degrade industrial triazophos wastewater. Lin et al. [11] also reported that the photo-FP can degrade the triazophos wastewater effectively under the optimal conditions with high COD removal efficiencies up to 95.2%. Optimal conditions are reached at 50 mM H<sub>2</sub>O<sub>2</sub>, 0.3 mM FeSO<sub>4</sub> and at a pH value of 3.0 for 10 µg/mL triazophos.

Kaichouh et al. [12] studied the degradation of imazapyr of 0.1 mM at pH 3 by FP, photo-FP and electro-FPs. COD removal efficiencies were found to 80% for FP at the optimum values for Fe<sup>2+</sup> of 1 mM and H<sub>2</sub>O<sub>2</sub> of 10 mM, 90% for photo-FP at the optimum values for Fe<sup>2+</sup> of 0.1 mM and H<sub>2</sub>O<sub>2</sub> of 1 mM and 95% for electro-FP at the optimum values for Fe<sup>2+</sup> of 0.5 mM, and I of 100 mA.

Nowadays, there is an increase also in usage of plant growth regulators as much as pesticides. A kind of biochemical pesticide named 3-indole butyric acid (IBA) is a synthetic plant hormone that enhances the growth and development of food crops and ornamental plants when applied to soil, cuttings or leaves. As pesticides, these chemical substances attract, kill and repel insects. IBA is now used commercially worldwide to root many plant species [3].

Photocatalytic oxidation for the treatment of water polluted with IBA has been investigated by Qamar and Muneer [3]. They showed that TiO<sub>2</sub> can efficiently photocatalyse the IBA in presence of light and oxygen. An aqueous solution (250 cm<sup>3</sup>) of IBA (0.18 mM) containing TiO<sub>2</sub> (1 g/L as Degussa 25) was irradiated under a 125 W medium pressure mercury lamp and 93% decomposition and 74.5% mineralization of IBA was observed.

Fenton oxidation for the treatment of water polluted with IBA has not been investigated and the information regarding the kinetic study on the degradation of IBA by FP and FLP also has not been reported in the literature. Therefore, the principal objective of this study was to investigate degradation mechanism and kinetics of IBA in aqueous solution by FP and FLP.

In this study, the effects of initial pH, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> or Fe<sup>3+</sup> concentrations on percent COD removals were first investigated. The test range of each factor was chosen according to the needs of kinetic studies. Then, a comparative kinetic evaluation between FP and FLP was carried out following the percent removal of IBA and TOC against to H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> or Fe<sup>3+</sup> depletions. Kinetic constants were also determined using the experimental data.

## 2. Materials and methods

### 2.1. Chemicals

IBA in the purest form was obtained from the Merck Chemical Company in Darmstadt. Its structure and UV spectrum is given in Fig. 1. Solutions were prepared using deionized water (*R* = 18 MΩ 1/cm, Millipore). Several other chemicals, including FeSO<sub>4</sub>·7H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> (30%), NaOH, H<sub>2</sub>SO<sub>4</sub> and HPLC-graded organic solvents as water with 0.1% trifluoroacetic acid (TFA) and acetonitrile (ACN) with 0.1% TFA were also obtained from Merck.

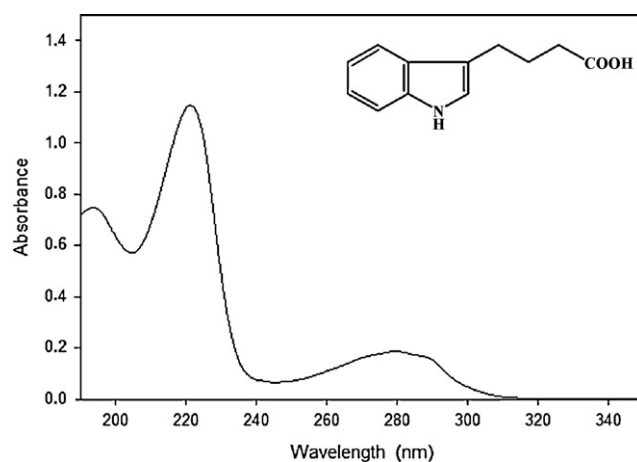


Fig. 1. Chemical structure and UV spectrum of IBA ( $\lambda_{\text{max}} = 221$  nm).

### 2.2. Experimental procedure

FP and FLP were conducted at room temperature with varying Fe<sup>2+</sup> or Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations and pH values to determine the optimum concentrations for maximum COD removal. The pH was manually adjusted to desired range (pH 2–6) using concentrated H<sub>2</sub>SO<sub>4</sub> and/or NaOH before starting the experiments. Following the pH adjustment (7.5–8) after 2 min of rapid mixing (100 rpm) and 20 min of slow mixing (30 rpm), sedimentation was performed over 2 h using a jar test set-up. COD was analyzed on samples of supernatant, which were taken 2 h after precipitation [8].

IBA degradation and mineralization tests were conducted in a 10 L reactor with mechanical stirring at 100 rpm. After the pH of the reaction solution was adjusted to 3, the required amounts of reagents (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> for FP and Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> for FLP) were added to the reactor. The reactions were initiated by adding H<sub>2</sub>O<sub>2</sub> to the reactor. Samples were taken out from the reactor periodically and the H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup> or Fe<sup>3+</sup>, IBA, COD and TOC concentrations were determined analytically.

### 2.3. Analytical methods

Since FP and FLP cannot occur at pH >10, the reaction was quenched in the collected samples by adding NaOH and MnO<sub>2</sub> powder to remove any residual H<sub>2</sub>O<sub>2</sub> [13,14]. All measurements were performed on samples that were filtered through 0.45 µm Millipore membranes (Millipore, Billerica, MA, USA) to remove Fe(OH)<sub>3</sub> and MnO<sub>2</sub>.

TOC was determined using a Shimadzu-5050ATOC analyzer. The COD was analyzed following the APHA standard method with potassium dichromate. Dissolved iron concentrations were measured by the spectrophotometric 1,10-phenanthroline method [15].

Hydrogen peroxide measurements were made spectrophotometrically (Hach DR5000 spectrophotometer) at 351 nm using the I<sub>3</sub><sup>-</sup> method [16]. Two solutions, A and B, were prepared. Solution A consisted of potassium iodide (33 g), sodium hydroxide (1 g) and ammonium molybdate tetrahydrate (0.1 g) dissolved together in 500 mL water in a volumetric flask. Solution B was potassium hydrogen phthalate (10 g) dissolved in water in a 500 mL volumetric flask. For analysis, 2.5 mL each of A and B were taken and mixed with an appropriate volume of reaction solution in a volumetric flask and diluted with deionized water. This mixture was then analyzed spectrophotometrically at 351 nm and the concentration of hydrogen peroxide was obtained from the calibration curve.

The IBA concentrations were analyzed using an Agilent 1200 Series HPLC with a diode array detector (DAD) (Agilent Technologies, CA, USA). Reverse-phase liquid chromatography (3 mL/min flow, water with 0.1 TFA and ACN with 0.1 TFA at a 78%:22% [v/v] ratio) with a C8-3.5  $\mu\text{m}$ -75 mm (L)  $\times$  4.6 mm (i.d.) ZORBAX SB column was used for separation. To detect IBA, the detector wavelength was set at  $221 \pm 20$  nm. IBA standard solutions were prepared in water in the 0.5–100 mg/L concentration range.

### 3. Results and discussion

Ferrous ion could react with hydrogen peroxide as in Eq. (1) to produce highly reactive hydroxyl radicals that attack and destroy the pesticide in FP. In this case, FP appears to be a very powerful oxidizing agent and is employed to produce sufficient quantities of  $\text{OH}^\bullet$  radicals. The generated  $\text{OH}^\bullet$  radical concentrations remain constant for all pesticide molecules at the beginning of the reaction and for a constant pesticide concentration, higher concentrations of Fenton reagents produces more  $\text{OH}^\bullet$  radicals that results kinetically faster oxidation rates and rapidly degradation [17,18].

The initial IBA concentration (0.5 mM) was selected to be high enough to determine by HPLC but IBA was disappeared in 1–2 min of the reaction at high concentrations of iron ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) and  $\text{H}_2\text{O}_2$ . Therefore a relatively low amount of iron ions (0.05–0.8 mM) and  $\text{H}_2\text{O}_2$  (0.2–1.5 mM) were used in the optimization experiments which enables to obtain slower kinetics and provide favourable conditions for the determination of reaction rates. The test range of parameters ( $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) was chosen according to the needs of kinetic studies presented in literature [18,19].

#### 3.1. Effect of initial pH on removal efficiency

The pH value has a decisive effect on the oxidation potential of  $\text{OH}^\bullet$  radicals because of the reciprocal relationship between the oxidation potential and the pH value ( $E^0 = 2.8$  V and  $E^{14} = 1.95$  V) [6].  $\text{OH}^\bullet$  radicals generation occurs in acidic condition. At pH values within the range 3–7, the iron ions react with hydroxide ions to form ferrous and ferric hydroxide complexes which accounts for the coagulation capability of Fenton's reagent and iron tends to precipitate as hydroxide [20].

At pH values within the range 1–2, the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  (Eq. (1)) is seriously affected causing the reduction in  $\text{OH}^\bullet$  radical production due to  $\text{OH}^\bullet$  scavenging by  $\text{H}^+$  ions according to Eq. (3) [18,19];



Therefore, pH is an important parameter in FP and FLP. Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations [7,9,18–21].

In this study, the effect of pH on COD removal was studied in the range of 2–6 at the experiment condition of  $[\text{IBA}] = 0.5$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{H}_2\text{O}_2] = 0.6$  mM in FP and  $[\text{Fe}^{3+}] = 0.2$  mM,  $[\text{H}_2\text{O}_2] = 1.0$  mM in FLP. COD removal efficiencies at different pH values by FP and FLP are illustrated in Fig. 2. In all this pH range, COD removal efficiency achieved by FP was higher than FLP although similar impression was shown for the two systems. An optimum pH to achieve the highest COD removal efficiency was found at around pH 3 for both FP and FLP. These results are in agreement with those reported in previous studies [9,18,20,22,23].

At low pH values (<3), COD removal efficiency were low due to scavenging effect of  $\text{H}^+$  ions that explained in Eq. (3). By increasing the pH to 3, the highest COD removal rate is obtained for the two systems. At pH values between 3 and 5, COD removal efficiency decreased slightly with increasing pH due to  $\text{H}_2\text{O}_2$  was stable in this pH range, but the decomposition rate of  $\text{H}_2\text{O}_2$  rapidly

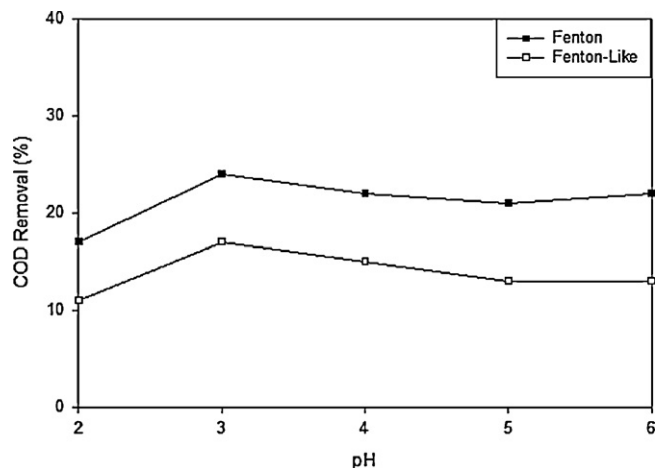


Fig. 2. Effect of initial pH value on COD removal from IBA-containing wastewater (conditions:  $[\text{IBA}] = 0.5$  mM,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 0.2$  mM/0.6 mM,  $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2] = 0.2$  mM/1.0 mM).

increased with increasing pH above 5 [24] and COD removal efficiency remained almost stable. The presumed reasons are that slower decomposition of  $\text{H}_2\text{O}_2$ , [18,25], the deactivation of the ferrous catalyst by the formation of ferric hydroxyl complexes and the coagulation effect of Fenton's reagent [19,20].

#### 3.2. Effect of initial $\text{H}_2\text{O}_2$ concentration on removal efficiency

The effect of initial  $\text{H}_2\text{O}_2$  concentration on COD removal was performed by varying  $[\text{H}_2\text{O}_2]$  from 0.2 to 1.5 mM and at the experiment condition of  $[\text{IBA}] = 0.5$  mM, pH 3,  $[\text{Fe}^{2+}]$  and  $[\text{Fe}^{3+}]$  at 0.2 mM in FP and FLP.

The results shown in Fig. 3 indicate that the COD removal efficiency increased with increasing  $\text{H}_2\text{O}_2$  concentration in the range of 0.2–0.6 mM in FP and 0.2–1.0 mM in FLP due to the increment of  $\text{OH}^\bullet$  radical produced through the decomposition of increasing  $\text{H}_2\text{O}_2$  [18,19,26,27]. However, COD removal efficiency decreased with increasing  $\text{H}_2\text{O}_2$  concentration in the range of 0.6–1.5 mM in FP and 1.0–1.5 mM in FLP. This may be due to recombination of  $\text{OH}^\bullet$  radicals, scavenging of  $\text{OH}^\bullet$  by  $\text{H}_2\text{O}_2$  and incremental generation of  $\text{HO}_2^\bullet$  also consumed  $\text{OH}^\bullet$  (Eqs. (4)–(6)) [18,19,26].

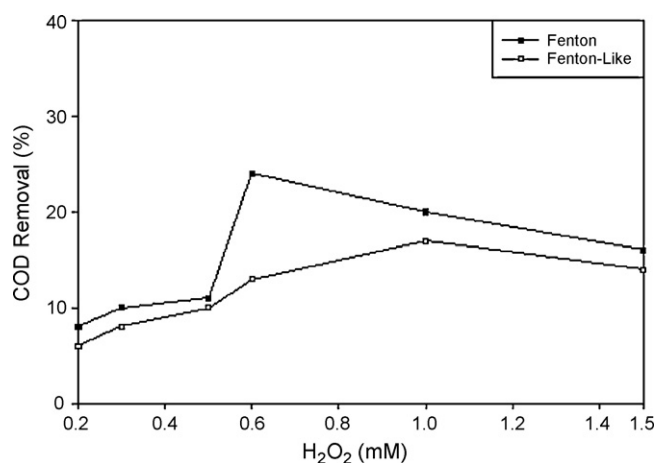
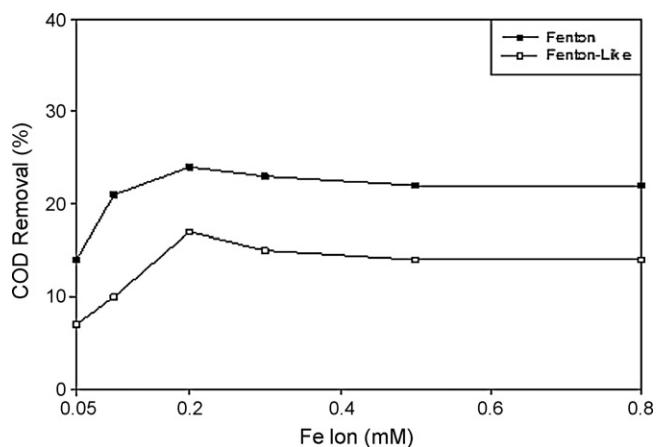


Fig. 3. Effect of initial  $\text{H}_2\text{O}_2$  concentration on COD removal from IBA-containing wastewater (conditions:  $[\text{IBA}] = 0.5$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Fe}^{3+}] = 0.2$  mM, pH 3).



**Fig. 4.** Effect of Fe ions on COD removal from IBA-containing wastewater (conditions: [IBA] = 0.5 mM, [H<sub>2</sub>O<sub>2</sub>] = 0.6 mM for FP, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM for FLP, pH 3).



FLP (Eq. (2)) occurred between Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> produces much less reactive hydroperoxyl radicals (HO<sub>2</sub><sup>•</sup>) and these radicals do not contribute to oxidative degradation of organic substance efficiently [18,20,28]. Therefore, COD removal efficiency achieved by FP was higher than FLP in all H<sub>2</sub>O<sub>2</sub> range. It can be inferred that the optimum H<sub>2</sub>O<sub>2</sub> concentrations were found as 0.6 mM and 1.0 mM, coinciding with the highest COD removal efficiencies as 24% and 17% in FP and FLP, respectively.

In this experimental study, different impressions on COD removal were observed between two systems with increasing H<sub>2</sub>O<sub>2</sub> concentration especially in the ranging from 0.5 to 1.5 mM. For the highest COD removal, required optimum amount of H<sub>2</sub>O<sub>2</sub> in FP was smaller than required in FLP. The generation of the radicals by Fenton reagents involves a complex reaction sequence in an aqueous solution and additional HO<sub>2</sub><sup>•</sup> produced via Eq. (2) can participate in propagating radical chain reactions [20]. For a greater extent oxidation of organic compounds, this may be result in larger consumption of H<sub>2</sub>O<sub>2</sub> in FLP than FP.

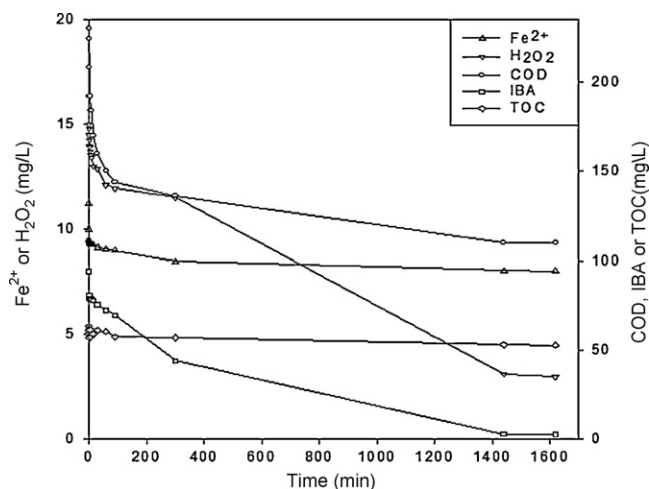
### 3.3. Effect of initial Fe ion concentration on removal efficiency

The effect of initial Fe ion (Fe<sup>2+</sup> or Fe<sup>3+</sup>) concentration on COD removal was performed by varying [Fe<sup>2+</sup>] and [Fe<sup>3+</sup>] from 0.05 to 0.8 mM and at the experiment condition of [IBA] = 0.5 mM, pH 3, [H<sub>2</sub>O<sub>2</sub>] = 0.6 mM in FP and [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM in FLP.

The results shown in Fig. 4 indicate that the COD removal efficiency increased with increasing Fe ion concentration due to catalytic decomposition effect on H<sub>2</sub>O<sub>2</sub> induced by the initial Fe ion. Fe<sup>2+</sup> or Fe<sup>3+</sup> plays a very important role in initiating the decomposition of H<sub>2</sub>O<sub>2</sub> to generate the very reactive OH<sup>•</sup> radicals in FP and FLP. When the initial Fe ion concentration increased, the catalytic effect also accordingly increased [18–20,26,29,30]. However, addition of the iron salt above 0.2 mM did not effect the percent COD removal in FP and FLP.

When higher concentration of Fe<sup>2+</sup> or Fe<sup>3+</sup> was used as a catalyst, a great amount of Fe<sup>3+</sup> in FLP or comes from the process of H<sub>2</sub>O<sub>2</sub> decomposition by Fe<sup>2+</sup> in FP (see Eq. (1)) was easy to exit in the form of Fe(OH)<sup>2+</sup> in acidic environment [18]. Hence, it is desirable that the initial Fe ion (Fe<sup>2+</sup> or Fe<sup>3+</sup>) concentration should be as small as possible, so that the sludge production from iron complex can be reduced [19,26].

As seen in Fig. 4, Fe<sup>2+</sup> or Fe<sup>3+</sup> of 0.2 mM can be used as an optimum concentration for both the processes. Observed COD removal efficiency at the optimum concentration by FP was higher than FLP.



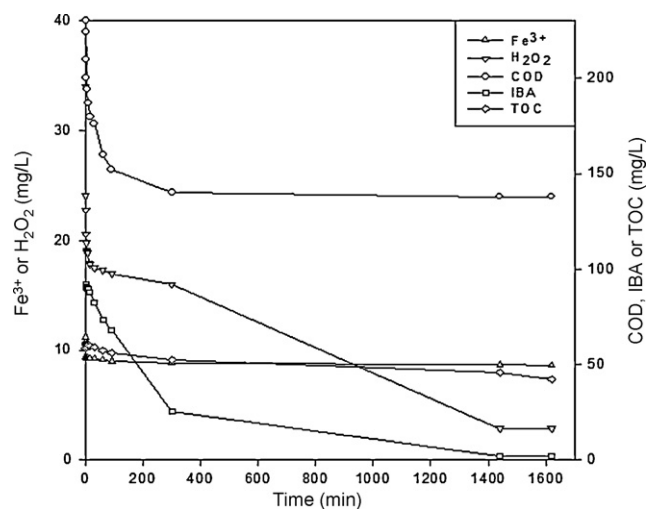
**Fig. 5.** Time-dependent IBA, TOC, COD, Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations for FP ([IBA] = 0.5 mM; Opt. [Fe<sup>2+</sup>] = 0.2 mM; Opt. [H<sub>2</sub>O<sub>2</sub>] = 0.6 mM; Opt. pH 3).

### 3.4. IBA degradation kinetics for FP and FLP

To observe the degradation kinetics of the system, the optimized Fe<sup>2+</sup>, Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations were employed at pH 3 to degrade 0.5 mM [IBA] during 24 h period in aqueous solution. The results from these experiments are presented in Figs. 5 and 6 for FP and FLP, respectively.

The IBA concentration decreases exponentially until the end of the 24 h period, when nearly 97% and 98% of IBA is degraded by FP and FLP, respectively. IBA degradation and mineralization exhibit pseudo-first-order kinetics while H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> or Fe<sup>3+</sup> depletion exhibit zero-order kinetics during both processes in all experiments. Reaction rates are given numerically in Table 1.

Although H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> or Fe<sup>3+</sup> depletion proceeds very rapidly in the first 5 min of the reaction, the OH<sup>•</sup> radical generation is not enough to extensively decompose IBA. IBA degradation proceeds very slowly because of the low reagent dosages (Fe<sup>2+</sup> or Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub>) under the present experimental conditions. After 5 min of reaction time, Fe<sup>2+</sup> or Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> depletion decreases and the reagents reach steady-state depletion rates where these compounds continue to degrade IBA for 24 h, but at a very low rate (Table 1). This is due to a drop in the OH<sup>•</sup> radicals availability and lack of an additional continuous OH<sup>•</sup> radical generation source such



**Fig. 6.** Time-dependent IBA, TOC, COD, Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations for FLP ([IBA] = 0.5 mM; Opt. [Fe<sup>3+</sup>] = 0.2 mM; Opt. [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM; Opt. pH 3).

**Table 1**  
Reaction rates with efficiencies (%) of the IBA degradation and mineralization mechanism.

	H <sub>2</sub> O <sub>2</sub> (mg/L·min)		Fe (mg/L·min)		IBA (1/min)		COD (1/min)		TOC (1/min)	
	FP	FLP	FP	FLP	FP	FLP	FP	FLP	FP	FLP
<i>t</i> = 0–5 min										
<i>k</i>	0.2785	1.0867	0.0292	0.0244	0.0058	0.0032	0.0399	0.0371	0.0015	0.0107
<i>r</i> <sup>2</sup>	0.999	0.979	0.992	0.996	1.000	0.997	0.986	0.998	1.000	0.992
%	33	44	17	17	16	2.2	17	16	3.5	8
<i>t</i> = 5 min to 24 h										
<i>k</i>	0.0071	0.0107	0.0007	0.0004	0.0023	0.0026	0.0004	0.0002	0.0001	0.0002
<i>r</i> <sup>2</sup>	0.995	0.993	0.994	0.997	0.999	1.000	0.996	0.996	0.990	0.995
%	52	47	12	6	81	96	36	24	12.7	42
<i>t</i> = 0–24 h										
<i>k</i>	0.0071	0.0107	0.0007	0.0004	0.0023	0.0026	0.0004	0.0002	0.0001	0.0002
<i>r</i> <sup>2</sup>	0.995	0.993	0.994	0.997	0.999	1.000	0.996	0.996	0.990	0.995
%	85	91	29	23	97	98	53	40	16.2	50

as UV in photocatalytic FP. For these reasons, the reaction results in a very low steady-state concentration of OH• radicals [31].

During the first 5 min of reaction, the initial phase is directly attributable to FP. Degradation rate of IBA in FP was almost 2-fold higher than occurred in FLP. Almost all of the OH• radicals are generated and most of the H<sub>2</sub>O<sub>2</sub> (40% and 50% of total consumption for FP and FLP, respectively) and Fe<sup>2+</sup> or Fe<sup>3+</sup> (60% and 75% of total consumption for FP and FLP, respectively) are consumed. At the beginning of the process, depletions of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> corresponding the usage of H<sub>2</sub>O<sub>2</sub> was higher in FLP although degradation of IBA was low. This is supposed that the generated free radicals involved in a complex reaction sequence [20].

After the initial phase, IBA showed a slower degradation in FP. This is caused by the rapidly oxidation of a large fraction of Fe<sup>2+</sup> to Fe<sup>3+</sup> in the first 1–2 min of reaction time and the presence of any amount of Fe<sup>3+</sup> in this system at the beginning of the reaction slows system kinetics regardless of the concentrations of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> [31]. After the first 5 min of reaction until 24 h, this second phase can be considered as a series of FLP reactions due to Fe<sup>3+</sup> was the predominant for the two systems [9,32]. The degradation rates of IBA demonstrated similar results as 0.0023 1/min and 0.0026 1/min in FP and FLP, respectively. The massive OH• radicals generated in the first stage of FP could account for the initial IBA oxidation, which was much slower in FLP due to the fact that the generation of OH• radicals proceeded at slower rate [33]. However, after 30 min of reaction time, a considerable increase in IBA degradation was observed due to the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, thus making FP possible again and generating additional OH• radicals during FLP [9]. After 90 min of reaction time, the IBA degradation ratio reached the same value in both FP and FLP. As shown in Figs. 5 and 6, similar concentrations were observed between FP and FLP during the experiments.

When considered the overall degradation kinetic of IBA, it was observed that FP was more efficient than FLP at the initial phase but after that the degradation reaction was not changed between FP and FLP. This indicates that FP plays a more important role than FLP only at the beginning of the process, at a time when only FP reagents and the substrate are present [31]. Shortly after the OH• radicals are produced, the parallel mechanisms described between FP and FLP proceed. From these experimental results, it can be concluded that FP degrades the IBA faster than FLP and may be more useful when only removal of IBA is required and mineralization is unnecessary. These results are in agreement with those reported in previous studies [9,32].

### 3.5. Mineralization study

The Fe<sup>2+</sup> or Fe<sup>3+</sup> concentrations are higher than H<sub>2</sub>O<sub>2</sub> at the end of the 24 h, suggesting that H<sub>2</sub>O<sub>2</sub> is the limiting reagent for further

degradation and mineralization of the IBA intermediates present in the system. Total IBA mineralization is unattainable by either FP or FLP under the present experimental conditions in this study.

As can be seen in Figs. 5 and 6, 16.2% of IBA mineralization arose within 24 h against 97% IBA degradation during FP, and 50% of IBA mineralization arose against 98% IBA degradation during FLP. IBA degradation was much higher than TOC removal. The great difference between degradation and mineralization efficiencies also implies that the products of IBA oxidation mostly stayed at the intermediate stage under the present experimental conditions [18].

During the initial phase, almost no TOC removal efficiency was observed (3.5% and 8% for FP and FLP, respectively). However, the mineralization rates of IBA were 15-fold and 50-fold higher in the initial phase than the second phase. In the second phase, IBA mineralization and TOC removal efficiency slowly increase. This slow mineralization occurred during both processes, and may be attributed to lower OH• radical generation compared to the initial phase as well as competitive effects with IBA intermediates. At the end of the 24 h, H<sub>2</sub>O<sub>2</sub> was almost depleted so that IBA was not mineralized completely [22].

The COD/TOC ratio initially had a value of 3.60 and decreased to 2.47 at the end of FLP. This suggests a relatively important presence of low-chain length organic acids, including dicarboxylic acids [23,33]. On the other hand, the initial COD/TOC value was 3.42 and decreased to 2.0 at the end of FP. This shows the lower degree of mineralization attained compared to FLP. Mineralization rate of IBA in FLP was almost 7-fold and 2-fold higher than occurred in FP in the initial phase and second phase, respectively.

When considered the overall mineralization of IBA, it was observed that FLP was more efficient than FP. This indicates that FLP was the predominant system for the mineralization of IBA. The same conclusion had been reported by Doong and Chang [32] for photocatalytic degradation of organophosphorous pesticides.

## 4. Conclusions

The results reported above show that the optimum conditions for 0.5 mM of [IBA] were obtained at pH 3 as [Fe<sup>2+</sup>]/[H<sub>2</sub>O<sub>2</sub>] ratio of 0.2 mM/0.6 mM in FP and [Fe<sup>3+</sup>]/[H<sub>2</sub>O<sub>2</sub>] ratio of 0.2 mM/1.0 mM in FLP. IBA degradation and mineralization exhibited pseudo-first-order kinetics while H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> or Fe<sup>3+</sup> depletion exhibited zero-order kinetics during both processes in all experiments. In FP, 16.2% of IBA was mineralized and 97% was degraded; these figures were 50% and 98% for FLP. These results show that the mineralization rate of FLP is higher than FP, while FP and FLP demonstrate similar IBA degradation rates. This is because after the initial phase, FP converts to a series of FLP reactions and parallel mechanisms proceed between FP and FLP in IBA degradation. It can be considered that the great difference between mineraliza-

tion efficiency of FP and FLP comes from the different optimization ratios of the reagents as  $[Fe]/[H_2O_2]$ .  $H_2O_2$  is the limiting reagent for further mineralization, and IBA and its oxidation products mostly stayed at the intermediate product stage. Total IBA mineralization is unattainable either FP or FLP. It is concluded that FP may be more useful when only removal of IBA is required and mineralization is unnecessary. But if mineralization of IBA is needed, FLP gains more important than FP due to its mineralization efficiency. The observations related to this study indicates that obtained high IBA degradation and mineralization rates make Fenton processes practically applicable for the treatment of water contaminated with IBA.

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