

# Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process

Meijuan Xu<sup>a,b,\*</sup>, Qishan Wang<sup>a</sup>, Yueli Hao<sup>a</sup>

<sup>a</sup> The College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

<sup>b</sup> The College of Mechanical and Energy Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo, Zhejiang 315100, China

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## Abstract

The bleaching wastewater effluent from a pulp and paper mill (located in Tianjin, China) was treated with solar photo-Fenton process in a lab-scale reactor (22 cm × 15 cm thermostatic dish). The mill used wastepaper as raw material and the effluent contained 332 mg L<sup>-1</sup> of total organic carbon (TOC) and 1286 mg L<sup>-1</sup> of COD. The treatment involved a constant intensity of irradiation (0.2 kW/m<sup>2</sup>) with a solar simulator of 250 W xenon lamp and various conditions of pH, temperature, and initial concentrations of H<sub>2</sub>O<sub>2</sub> and Fe(II). The better treatment conditions were searched for in the ranges of initial Fe(II) concentration from 31 to 310 mg L<sup>-1</sup> (initial pH 3.0, 30 °C), initial H<sub>2</sub>O<sub>2</sub> concentration from 0.5 to 3 Dth (1 Dth = 1883 mg L<sup>-1</sup> for TOC mineralization) (initial pH 3.0, 30 °C), initial pH from 2.0 to 6.0 (1 and 2 Dth, 10:1 of H<sub>2</sub>O<sub>2</sub>/Fe(II), 30 °C), and temperature from 30 to 50 °C (1 Dth, 10:1 of H<sub>2</sub>O<sub>2</sub>/Fe(II), initial pH 2.8). TOC removal generally showed the initial fast increase stage within the first sampling time of 15 min, followed by the gradual increase stage in the remaining sampling time of 180 min experimental time course. The highest percentage of TOC removal in the first stage was about 60% when the initial pH was either 2.8 (H<sub>2</sub>O<sub>2</sub> = 1 Dth, ratio = 10:1, temperature = 30–50 °C) or 3.5 (H<sub>2</sub>O<sub>2</sub> = 2 Dth, ratio = 10:1, temperature = 30 °C). Also under the latter condition, the value reached 82% at 120 min and was projected to reach 94% at 180 min. According to the positive effect of temperature increase on TOC removal observed in this experiment, further increase above these maximum values is possible if the temperature of the above condition were increased from 30 to 40 °C or 50 °C. Furthermore, under most of the treatment conditions, the TOC removal reached or was projected to reach over 60% toward the end of the experiments. The result indicated that the solar photo-Fenton process has a potential to effectively remove TOC from the wastepaper pulp effluent on a large scale.

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**Keywords:** Photo-Fenton process; Wastepaper pulp effluents; Advanced oxidation; Wastewater treatment; Pulp and paper industry

## 1. Introduction

Wastepaper cycling for production of pulp and paper is becoming increasingly important to reduce wood consumption and protect environments. This is particularly obvious for the areas with high population density such as the coastal areas of China where the per capita wood resource is scarce [1]. Coming with this demand is the appropriate treatment and disposal of wastewater generated from the manufacturing processes of deinking, washing, bleaching, filtration and concentration. The organic nature of the wastewater is that it contains many of

highly chlorinated and lignin compounds recalcitrant to biological treatment [2–4]. Therefore, the chemical methods that can degrade these compounds need to be identified.

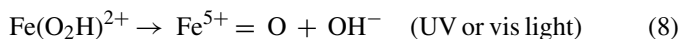
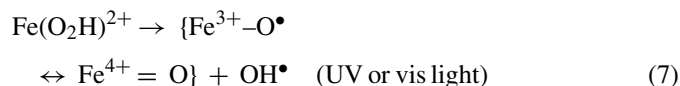
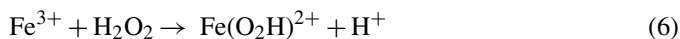
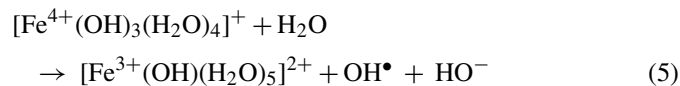
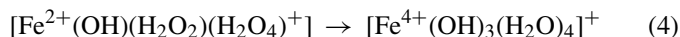
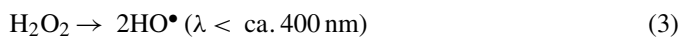
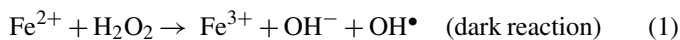
Advanced oxidation process (AOP) employs strong oxidants of H<sub>2</sub>O<sub>2</sub> and ozone to degrade organic carbon, especially under the promotion of photo irradiation, catalyst addition (TiO<sub>2</sub>, Fe(II), and Fe(III)), thermal input, and ultrasound penetration [5]. Among many AOPs, solar photo-Fenton process (combination of H<sub>2</sub>O<sub>2</sub>, Fe(II) and solar irradiation) has been approved to be rather effective in degradation and mineralization of single organic toxicants [6–11] and the mixtures of various organic wastes, including those from pulp and paper mills [12–17]. Although controversial issues exist regarding the dominant oxidizing species in the process, evidences indicated that both hydroxyl radical (OH•) and high valence Fe species (Fe<sup>3+</sup>(O<sub>2</sub>H)<sup>2+</sup>, Fe<sub>aq</sub><sup>4+</sup>, Fe<sup>4+</sup> = O, and Fe<sup>5+</sup> = O) can contribute to the strong oxidizing powers of photo-Fenton process [6,8,9,11].

\* Corresponding author at: The College of Environmental Science and Engineering, Nankai University, 94 Weijin Road, Tianjin 300071, China.

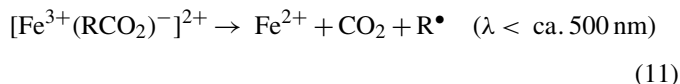
Tel.: +86 2223502972; fax: +86 2223508807.

E-mail address: [xmj80@126.com](mailto:xmj80@126.com) (M. Xu).

The reactions forming oxidizing species potentially responsible for direct attack on organic carbon can be written as follows:



The reactions leading to degradation and mineralization of organic compounds (RH) by  $\text{OH}^\bullet$  and high valence Fe can be written as:



From the above reactions, it can be seen that the advantage of involvement of Fe species in oxidation is utilization of visible light portion in the sunlight, an economical light source in waste treatment.

Many studies have shown that the effectiveness of solar photo-Fenton process in waste treatment depends on the initial concentrations of  $\text{H}_2\text{O}_2$  and Fe(II), their ratios, the initial pH, and reaction temperature [12–17]. The previous research generally showed the following facts. First, the higher initial concentration of  $\text{H}_2\text{O}_2$  increased the extent of TOC degradation, but an increased use of  $\text{H}_2\text{O}_2$  for obtaining higher extent of TOC degradation has to be justified on a case-by-case basis. Second, the optimal initial Fe(II) concentration depends on the initial  $\text{H}_2\text{O}_2$  concentration as well as waste composition. Therefore, determination of their optimal ratio is necessary for better treatment performance. Thirdly, an acidic pH was required for the solar photo-Fenton process with an optimal value often around 3.0. Fourthly, higher temperature can increase the extent and rate of TOC degradation.

The pulp and paper mill located in Tianjin (one of the biggest coastal city in China) used wastepaper as raw material and produced a large quantity of wastewater with high pollution potential (more than  $300 \text{ mg L}^{-1}$  of TOC and over  $1200 \text{ mg L}^{-1}$  of COD). The objective of this study is to determine optimal values of the above parameters for treatment of the wastewater

from the mill utilizing solar photo-Fenton process in a lab-scale reactor. The results will be the basis for scale-up treatment in the future experiment.

## 2. Materials and methods

### 2.1. Methods

The waste effluent for treatment was from the bleaching process (including washing and concentration) in a pulp and paper mill located in Tianjin, China. The mill used wastepaper as raw material and  $\text{H}_2\text{O}_2$  as bleacher. The main components of the effluent were lignin and its derivatives, fibril fines and microfibrils, printing ink and drinker, and inorganic filler fragments. The suspended solid was removed by sedimentation of the effluent for 30 min. Then, the effluent was stored at  $4^\circ\text{C}$  and used within a month.

The basic characteristics of the effluent are shown in Table 1. The total organic carbon (TOC) concentration of the effluent is  $332 \text{ mg L}^{-1}$  and the chemical oxygen demand ( $\text{COD}_{\text{Cr}}$ ) is  $1286 \text{ mg L}^{-1}$ . Based on the TOC value, the theoretical demand (Dth value) of  $\text{H}_2\text{O}_2$  for mineralization of the TOC is  $1883 \text{ mg L}^{-1}$  (2 mol of  $\text{H}_2\text{O}_2$  for 1 mol of organic carbon to form  $\text{CO}_2$ ).

All chemicals used in the experiments were at least analytical grades. Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 30% hydrogen peroxide were used as Fenton reagents.

### 2.2. Procedure

The effluent of 500 mL in a beaker was first brought to the room temperature for pH adjustment with dilute sulfuric acid and sodium hydroxide solutions. Then, a desired amount of ferrous sulfate was added and pH was further adjusted. The effluent with the desired pH value was transferred into a dish reactor having the size of  $22 \text{ cm} \times 15 \text{ cm} \times 3 \text{ cm}$  and the surface area of  $330 \text{ cm}^2$  and exposed to the atmosphere. Afterwards, the dish was immersed in water bath set for the desired temperature ( $\pm 0.5^\circ\text{C}$  in precision). As soon as the effluent was warmed up to the set temperature, the experiment was initiated by adding the desired amount of  $\text{H}_2\text{O}_2$  into the dish and placing a solar simulator of 250 W xenon lamp (turned on 10 min before use) 15 cm over the dish. The constant intensity of solar irradiation was  $0.2 \text{ kW/m}^2$  as measured with an actinometer. At the same time, a peristaltic pump was started to continuously cycle the

Table 1  
Basic properties of the bleaching effluent from the pulp and paper mill

Parameter	Value
pH	8.3
$\text{COD}_{\text{Cr}}$ ( $\text{mg L}^{-1}$ )	1286
TOC ( $\text{mg L}^{-1}$ )	332
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	445
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	928
Total phenols ( $\text{mg L}^{-1}$ )	2.83
Absorbance at 218 nm ( $\text{cm}^{-1}$ )	7.25

effluent through a rubber tube (0.5 cm in diameter) in order to provide a constant mixing.

Samples were taken at 15, 30, 60, 90, and 120 min for all the experiments with some of experiments also at 150 and 180 min. The sample volume was 5 mL. Deionized water was added periodically to compensate for evaporation losses.

### 2.3. Analysis

For original effluent (after sedimentation), the following analyses were conducted. The pH was determined with a Mettler Toledo 320 pH meter. The total organic carbon was determined with a Shimadzu TOC-V CSH analyzer. The absorbance at 218 nm ( $ABS_{218}$ ) was measured with an UV–vis spectrophotometer of the model HACH DR/4000U. The anions of  $Cl^-$  and  $SO_4^{2-}$  were measured with an ICS-1500 DIONEX chromatographic instrument. The total phenols were measured with 4-aminoantipyrine colorimetric method. Chemical oxygen demand was determined by the  $KCrO_4$  method. Chemical species were identified with a gas chromatography/mass spectrometry (GC-MS, Shimadzu Polaris Q equipped with a mass selective detector) and the professional software.

For TOC and pH analysis of the samples, the same instruments were used. For TOC determination, the samples of 5 mL were first mixed with 5 mL oxidant scavenging buffer solution to stop the reactions. The solution was composed of 0.1 M KI, 0.1 M  $Na_2SO_3$ , 0.1 M  $KH_2PO_4$ , and 0.05 M NaOH [18].

For the experiments without samples taken after 120 min, the projection of TOC removal at 180 min was made through curve fit using Excel software. The coefficient of curve fitting was above 0.9.

## 3. Results and discussion

### 3.1. Organic components in the effluent

The GC–MS data indicated the following aromatic compounds in the effluent: chlorophenols (2,4-dichlorophenol and 2,4,6-trichlorophenol), chlorotoluenes (2,4-dichlorotoluene and 2,3-dichlorotoluene), methylphenols (4-chloro-2-methylphenol and 2,4-dichloro-6-methylphenol), chloroguaiacols (3,6-dichloroguaiacol and 4,5,6-trichloroguaiacol), and phenol sulphonic acids (phenol-3-sulphonic acid and phenol-4-sulphonic acid). High degree of chlorination of aromatic

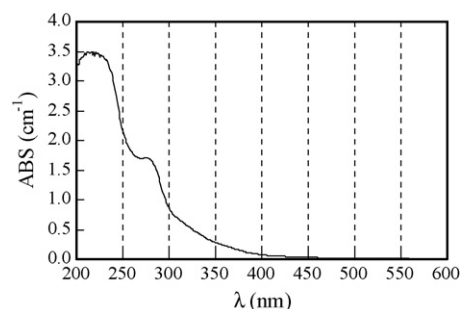


Fig. 1. The UV–vis spectrum of the diluted bleaching effluent with three volumes of water.

compounds was also reported for the regular pulp and paper mill effluents by Perez et al. [12,14].

The UV–vis spectrum of the wastewater diluted with three volumes of purified water (Fig. 1) showed the maximum absorbance at 218 nm that could be produced by  $\pi \rightarrow \pi^*$  transition of chemical functional group of minimum two conjugate C=C double bonds such as benzene ring. In fact, all the samples taken during the experiments had the maximum absorbance at 218 nm and showed rapid decrease in the value (data not shown), possibly indicating the effective destruction of aryl groups by the treatment.

### 3.2. TOC mineralization of the effluent treated with solar photo-Fenton process

In this study, five parameters were varied for obtaining a better performance in TOC removal from the effluent. These parameters include initial concentration of Fe(II), initial concentration of  $H_2O_2$ , initial concentrations of the both with their fixed ratio, initial pH, and reaction temperature. Their effects are described as follows in the above order.

#### 3.2.1. Effect of initial Fe(II) concentration

The effect was studied at the initial pH 3.0, 30 °C, under three initial  $H_2O_2$  concentrations: 1, 2, and 3 Dth. Under the experimental conditions, the percentages of TOC removal showed an initial fast increase stage within the first 15 min followed by a gradual increase stage (Fig. 2). The fast kinetics of  $OH^\bullet$  production through reaction 1 ( $k = 76.5 \text{ L mol}^{-1} \text{ s}^{-1}$ ) [10] could lead to the occurring of the first stage. The value was from 14% to 51% in the first stage and gradually reached 42–69% at the end of 180 min experiments (Table 2). The above two highest per-

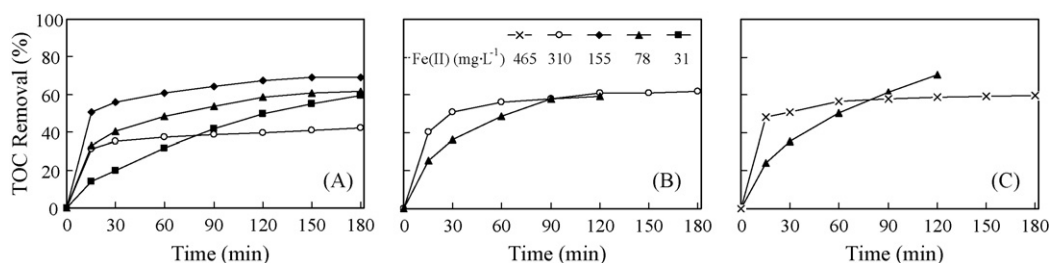


Fig. 2. The increase of TOC removal with time as affected by the initial Fe(II) concentrations at the initial pH 3.0, 30 °C. A, B, and C are for the initial  $H_2O_2$  concentrations of 1883, 3766, and 5649  $mg \text{ L}^{-1}$ , respectively.

Table 2  
Comparison of TOC removal between various initial concentrations of H<sub>2</sub>O<sub>2</sub>, Fe(II), and Fenton reagent dose, at the initial (15 min) and final (120 or 180 min) sampling time points (the numbers in parenthesis obtained from curve fitting)

Treatment condition			TOC removal (%)		
H <sub>2</sub> O <sub>2</sub> (mg L <sup>-1</sup> )	Fe(II) (mg L <sup>-1</sup> )	H <sub>2</sub> O <sub>2</sub> /Fe(II)	15 min	120 min	180 min
Effect of initial Fe(II) concentration					
1883	310	5:1	31	40	42
1883	155	10:1	51	67	69
1883	78	20:1	33	59	62
1883	31	50:1	14	50	60
3766	310	10:1	41	60	62
3766	78	40:1	26	61	(68)
5649	78	60:1	24	70	(89)
5649	465	10:1	48	59	60
Effect of initial H <sub>2</sub> O <sub>2</sub> concentration					
942	78	10:1	36	51	54
1883	78	20:1	33	59	62
3766	78	40:1	26	61	(68)
5649	78	60:1	24	70	(89)
1883	310	5:1	31	40	42
3766	310	10:1	41	60	62
Effect of initial Fenton reagent dose					
942	78	10:1	36	51	52
1883	155	10:1	51	67	69
3766	310	10:1	41	60	62
5649	465	10:1	48	59	60

centage values were obtained with 155 mg L<sup>-1</sup> of initial Fe(II) concentration and 1 Dth of initial H<sub>2</sub>O<sub>2</sub> concentration.

Higher initial Fe(II) concentration generally increased the rate (especially indicated by 15 min data) and the extent (maximum or close to maximum as indicated by 180 min data) of TOC removal (Table 2, Fig. 2). The only exception was observed with an increase from 155 to 310 mg L<sup>-1</sup> for 1 Dth of initial H<sub>2</sub>O<sub>2</sub> concentration. This might be due to the reverse of reaction (2) in which Fe(II) scavenges OH• and consumes H<sub>2</sub>O<sub>2</sub>. It was also found that the higher removal rates for all three initial H<sub>2</sub>O<sub>2</sub> concentrations were obtained when the initial Fe(II) concentration was kept at the ratio of H<sub>2</sub>O<sub>2</sub>/Fe(II) 10:1. However, the better ratio might be found for 2 and 3 Dth of initial H<sub>2</sub>O<sub>2</sub> concentrations if the higher initial Fe(II) concentrations were examined.

Although the amount of TOC removal with the lowest initial Fe(II) concentration (31 mg L<sup>-1</sup>) was the least (14%) during the first 15 min, the amount was more than that of the highest initial

Fe(II) concentration (310 mg L<sup>-1</sup>) after 90 min and only 9% less than the highest value at 180 min (Table 2, Fig. 2). As a catalyst, iron salt would not be consumed in the reaction and thus lower initial Fe(II) concentration would mean less amount of iron salt ending up in the final waste, which can be beneficial for the environments. Therefore, when treatment is allowed for a few hours, sacrifice of initial fast removal rate might be worth in order to use less iron salt.

### 3.2.2. Effect of initial H<sub>2</sub>O<sub>2</sub> concentration

The two-stage kinetics of TOC mineralization as described above also occurred for the different initial H<sub>2</sub>O<sub>2</sub> concentrations (0.5–3 Dth or 942–5649 mg L<sup>-1</sup>) under the conditions of the initial Fe(II) concentration of 78 and 310 mg L<sup>-1</sup>, initial pH 3.0, and 30 °C (Fig. 3). The percentage of TOC removal was from 24% to 41% in the first stage, from 49% to 60% at 120 min, and reached or was projected (through curve fit) to reach 42–70% at 180 min (Table 2). The above highest values

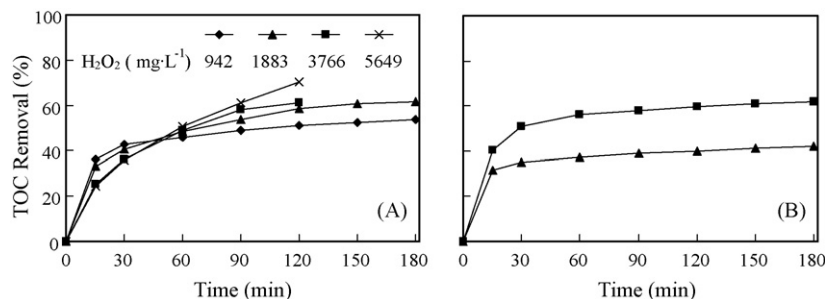


Fig. 3. The increase of TOC removal with time as affected by the initial H<sub>2</sub>O<sub>2</sub> concentrations at the initial pH 3.0, 30 °C. A and B are for the initial Fe(II) concentrations of 78 and 310 mg L<sup>-1</sup>, respectively.

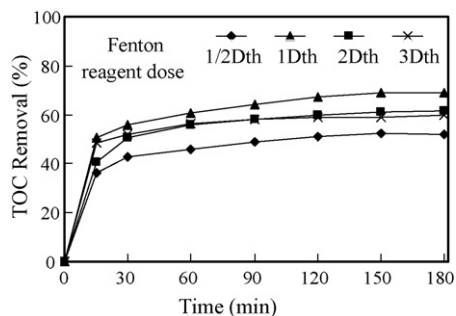
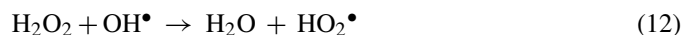


Fig. 4. The increase of TOC removal with time as affected by the initial Fenton reagent doses (1 Dth = 1883 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> and 155 mg L<sup>-1</sup> Fe(II)) at the initial pH 3.0, 30 °C.

for 15 and 120 min were obtained with 2 Dth of initial H<sub>2</sub>O<sub>2</sub> concentration and 310 mg L<sup>-1</sup> of initial Fe(II) concentration. Whereas, the highest value for 180 min was obtained with 3 Dth and 78 mg L<sup>-1</sup>.

In the first 15 min, the TOC removal rate increased with decreasing initial H<sub>2</sub>O<sub>2</sub> concentration for the initial Fe(II) concentration of 78 mg L<sup>-1</sup>, whereas, the opposite occurred for 310 mg L<sup>-1</sup> (Table 2). This can be explained by the competition of the following reaction with the OH<sup>•</sup> radical production reactions described above



in which excess H<sub>2</sub>O<sub>2</sub> (high ratio of H<sub>2</sub>O<sub>2</sub>/Fe(II)) scavenges OH<sup>•</sup> and consumes itself by the formation of HO<sub>2</sub><sup>•</sup> of low oxidation potential [10].

### 3.2.3. Effect of both initial H<sub>2</sub>O<sub>2</sub> and Fe(II) concentrations with their fixed ratio of 10:1

Because the initial ratio 10:1 of H<sub>2</sub>O<sub>2</sub>/Fe(II) showed a better performance in TOC removal, this ratio was selected for studying the effect of total Fenton reagent dose on TOC removal. Under this ratio and the initial pH 3.0, 30 °C, the percentages of TOC removal with the four doses of Fenton reagent were from 36% to 51% in 15 min, from 51% to 67% in 120 min, and from 53% to 69% at 180 min (Table 2, Fig. 4). The highest values were obtained with 1 Dth dose of Fenton reagent.

The lower amounts of TOC removal with 2 and 3 Dth of Fenton reagent doses compared with those of 1 Dth could be explained by the factor of the initial ratio of reagent dose to organic carbon load in the effluent. When the reagent dose was

Table 3

Comparison of TOC removal between various initial pH values at the initial (15 min) and final (120 or 180 min) sampling time points (the numbers in parenthesis obtained from curve fitting)

pH	TOC removal (%)		
	15 min	120 min	180 min
Initial concentration of H <sub>2</sub> O <sub>2</sub> 1883 mg L <sup>-1</sup> and Fe(II) 155 mg L <sup>-1</sup>			
2.0	38	58	(67)
2.5	56	70	76
2.8	57	69	(72)
3.0	51	67	69
3.5	52	69	(76)
4.0	47	67	(76)
6.0	43	61	(69)
Initial concentration of H <sub>2</sub> O <sub>2</sub> 3766 mg L <sup>-1</sup> and Fe(II) 310 mg L <sup>-1</sup>			
3.0	41	60	62
3.2	46	70	71
3.5	58	82	(94)

in excess versus the amount of organic carbon in the effluent, the OH<sup>•</sup> radical scavenging reactions could divert a large amount of H<sub>2</sub>O<sub>2</sub> from organic carbon oxidation. Although this explanation can be rather attempting, the results indicate the necessity to determine the possible optimal dose of Fenton reagent in reaching higher TOC removal.

### 3.2.4. Effect of initial pH

The rate of TOC removal was greatly affected by the initial pH level, especially in the first 15 min of the initial rapid mineralization stage (Table 3, Fig. 5). The range of the values was from 38% to 58% in 15 min, from 58% to 82% in 120 min, and from 62% to 94% in 180 min. The three highest values were reached with the initial pH 3.5 under the condition of 2 Dth dose of 10:1 ratio Fenton reagents, 30 °C. Because the initial pH 3.5 was the highest among the three levels tested, it is possible to remove more TOC if the initial pH was further increased.

Table 3 shows that for 1 Dth dose of 10:1 ratio Fenton reagent, the values of TOC removal at the initial pH 2.5 were always among the highest in 15 min (56%), 120 min (70%), and 180 min (76%). However, the effect of initial pH on TOC removal under the condition of 1 Dth dose and 30 °C became less with treatment time (Fig. 5). The differences in TOC removal percentage values among different initial pHs were no more than 12% in 120 min and 9% in 180 min (Table 3). Such phenomenon

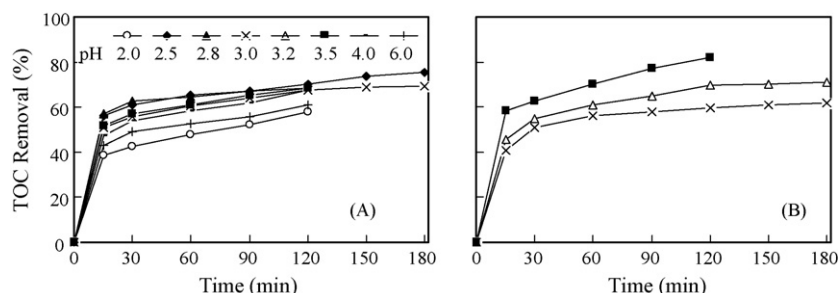


Fig. 5. The increase of TOC removal with time as affected by the initial pH values at 30 °C. A and B are for the initial Fenton reagent doses of 1 Dth and 2 Dth (H<sub>2</sub>O<sub>2</sub> = 1883 and 3766 mg L<sup>-1</sup>, Fe(II) = 155 and 310 mg L<sup>-1</sup>).



Table 4

Comparison of TOC removal between various treatment temperature at the initial (15 min) and final (120 or 180 min) sampling time points (the numbers in parenthesis obtained from curve fitting)

Temperature (°C)	TOC removal (%)		
	15 min	120 min	180 min
30	57	69	(72)
40	59	70	(72)
50	65	77	(79)

was not observed for 2 Dth dose of 10:1 ratio Fenton reagent (Table 3).

It should be noticed that the percentage of TOC mineralization with the initial pH 6.0 was not too much less than the highest value (9% less in 120 min and 7% less in 180 min) even though much iron will precipitate under this pH. Because the initial pH was adjusted after addition of iron salt, high initial pH such as 6.0 would mean that most of Fe(II) was oxidized to Fe(III) when the experiment started.

Therefore, for the initial pH 6.0, the treatment process was actually Fenton-like reaction ( $H_2O_2$  plus Fe(III)) instead of Fenton reaction. Furthermore, because the initial pH of the effluent was 8.3, its treatment with higher initial pH would be an advantage in consideration of the cost associated with pH adjustment (Tables 4 and 5).

### 3.2.5. Effect of treatment temperature

The two-stage kinetics of TOC removal as described previously also occurred at the higher temperatures of 40 and 50 °C (Fig. 6). The TOC mineralization was always faster at higher temperatures and reached 65% in 15 min, 77% in 120 min, and was projected to reach 79% in 180 min at the reaction temperature 50 °C.

The positive effect of temperature increase up to 50 °C on TOC removal was also found in the other studies [12,17]. The effect would indicate that the maximum value of TOC removal reached in this experiment with 2 Dth  $H_2O_2$ , initial pH 3.5, 30 °C, can be further increased if higher temperatures were examined.

Because the effluent temperature is normally between 40 and 50 °C, no energy input is required for treatment operation at high temperatures. Therefore, efficient TOC removal is highly possible under the conditions of the real treatment operation.

Table 5

Comparison of pH values (ranges at 15 min and final time point for the initial pH 2.8, 3.0 and 3.5 for inclusion of the values obtained under various experimental conditions) at three different time points

0 mm	15 mm	120 or 180 mm
2.0	2.1	2.0
2.5	2.5	2.6
2.8	2.6–2.8	2.5–2.9
3.0	2.6–2.9	2.5–3.0
3.5	2.7–2.9	2.5–2.9
4.0	2.9	2.8
6.0	3.5	3.4

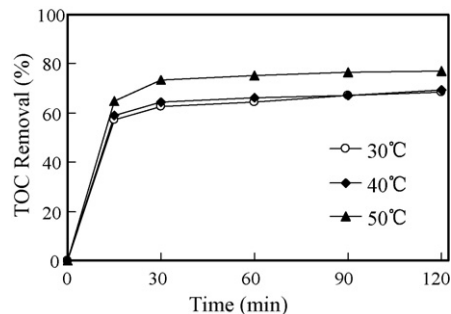


Fig. 6. The increase of TOC removal with time as affected by the treatment temperatures at the initial pH 2.8 and the Fenton reagent dose of 1 Dth ( $H_2O_2 = 1883 \text{ mg L}^{-1}$  and  $Fe(II) = 155 \text{ mg L}^{-1}$ ).

### 3.3. Change of effluent pH with time of treatment

Under all experimental conditions, there was a rapid drop in pH in the first 15 or 30 min (data not shown). Then, the pH gradually either decreased, or increased, or stabilized. The highest final pH at the end of the experiments occurred with the highest initial pH of 6.0 and was 0.5–1.5 units higher than those of the treatments with lower initial pHs. This would illustrate the advantages of not only treatment of original effluent but also disposal of treated effluent with higher initial pH (more Fenton-like reactions) due to the detrimental effect of acidic pH on the environments.

Many reactions could have contributed to the observed pH changes. Among those reactions, the dominant ones in causing pH decrease can include hydrolysis of Fe(III) ions (transformed from Fe(II)) and formation of organic acids from organic carbon degradation. The dominant reactions in causing pH increase can include mineralization of organic acid, the reaction that could be responsible for the slight increases in pH in the second stage of some conditions.

## 4. Conclusions

From the results obtained in this experiment, the following conclusions can be made:

- (1) Solar photo-Fenton process is highly efficient in treatment of the wastepaper pulp effluent under the selected experimental conditions. Generally, over 60% of TOC can be removed within a few hours and over 90% removal in the same time scale can be expected under the fine-tuned conditions, especially under high temperatures.
- (2) The large-scale use of the process has a strong potential to efficiently remove TOC from the effluent. This potential can be realized by use of an economical irradiation source of solar light and the high temperature of the original effluent.
- (3) More treatment conditions need to be tested, especially under high temperatures and in conjugation with use of biological treatment methods, in order to obtain higher efficiency of treatment.

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