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Evaluation of biodegradability and oxidation degree of hospital wastewater using photo-Fenton process as the pretreatment method

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Abstract

In this work, the photo-Fenton process was used for the pretreatment of hospital wastewater with the objective of improving its overall biodegradability and determining the degree of increased oxidation. The chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), total organic carbon (TOC) and toxicity towards the gram negative marine bioluminescent bacteria of the species *V. fischeri* were selected as the environmental sum parameters to follow the performance of this process. The enhancement of biodegradability, evaluated in terms of the BOD_5/COD ratio, increased from 0.3 to 0.52 and the oxidation degree, calculated in terms of AOS, leveled up from −1.14 to +1.58 at the optimum conditions; a dosage ratio of COD:H_2O_2:Fe(II) at 1:4:0.1, and a reaction pH of 3. The reduction in the inhibition percentage from the toxicity test indicated the safe levels for micro-organisms in degrading the residual organic substance in this method. Almost total removal percentages of COD, BOD_5, and TOC were found by a sequential activated sludge process for the pre-treated wastewater. Results obtained from this work indicated that the photo-Fenton process could be a suitable pretreatment method in reducing toxicity of pollutants and enhancing biodegradability of hospital wastewaters treated in a coupled photochemical–biological system.

Keywords: Biodegradation; Hospital wastewater; Chemical oxidation; Activated sludge; Aerobic process; Photo-Fenton

1. Introduction

Hospital wastewater contains a variety of toxic organic substances such as pharmaceuticals, radionuclides, solvents, and disinfectants for medical purposes in a wide range of concentrations due to laboratory and research activities or medicine excretion [1–5]. The contact of hospital pollutants with aquatic ecosystems leads to a risk directly related to the existence of hazardous substances, which could have potential negative effects on the biological balance of natural environments [4]. Pollution from hospital wastewaters can have effects even at low concentrations. Aquatic organisms, for instance, respond negatively to low concentrations of formaldehyde, which is a frequently found contaminant in hospital wastewater [6]. It was reported that formaldehyde in the range of 10–100 mg/L was toxic to the microbial in wastewater treatment system [7–9]. In addition, the presence of organochlorine compounds in high concentrations in hospital effluent has also been reported as toxic to aquatic life [10]. The halogenated organic compounds adsorbable on activated carbon (AOX) up to 10 mg/L were found in hospital wastewater [11].

In general, these toxic chemicals in hospital wastewater were discharged directly to wastewater treatment plants, which mostly employ biological treatment process. The failure of the wastewater treatment plant according to adverse effects of the contaminants on the community of organisms in charge of the biological decomposition of the organic matter was reported [11]. Attempts to reduce the toxicity of the chemicals in hospital were focused in many previous works [12–14]. The toxicity of formaldehyde in hospital wastewater was successfully reduced by photo-Fenton process [12]. Reverse osmosis, activated carbon, and ozonation have been shown to significantly reduce or eliminate antibiotics and pharmaceutical substances presented in the wastewater [13,14]. A submerged hollow fiber membrane bioreactor (MBR) was also proposed in treating the hospital wastewater [15]. As many treatment methods exhibit the possibility in remove the

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toxic species from wastewater effluent; however, most wastewater treatment facilities do not employ these techniques. To provide the alternative method in treating hospital wastewater, the pretreatment process to reduce the toxicity of pollutants and enhance biodegradability of the wastewater prior to discharge the waste stream to the existing biological treatment plant is proposed in this work.

The pretreatment process in this work is photo-Fenton, an emerging and very promising technology based on the oxidation of hazardous organic compounds in several wastewater types [16–18]. This process involves the use of one or more oxidizing agents, usually hydrogen peroxide and/or oxygen, and a catalyst, a metal salt or oxide (usually iron) [19–21]. This method is attractive due to the abundance and non-toxicity of iron. As reported by many previous works, the Fenton process in its unmodified form is efficient only in the acidic range and is usually most efficient at around pH 2.8 [22]. Uses of Fenton process can lead to the complete mineralization of some organic compounds, converting them to CO_2, H_2O and inorganic ions. However, the mechanism of Fenton's reactions is not yet completely cleared [21,23,24].

The prime objective of this study is to evaluate the improvement in biodegradability and oxidation degree of pollutants in hospital wastewater using the photo-Fenton process. The results are evaluated as both BOD_5/COD ratio and the increasing of the oxidation degree in terms of AOS. Additional information in toxicity reduction is also provided in this paper. The appropriate conditions for the photo-Fenton process for application to hospital wastewater are also reported for the design of the treatment process.

2. Material and methods

2.1. Wastewater source and characterization

The studied wastewater was obtained from one hospital in Bangkok, Thailand. The total volume of wastewater of this hospital is estimated at 350 m^3/day. Over a time-period of 28 days, the 24 h composite wastewater samples were taken daily due to the large variations in concentration between the different departments. The studied wastewater in this work was from analysis room (60%) and laboratory (40%). The wastewater from embalming room is not included in this work. The wastewater samples were collected from each source before entering into the entire hospital sewer network, which discharged the effluents into the biological wastewater treatment plant without pretreatment. The wastewater treatment plant failed to function for several months due to the discharging of toxic effluents from hospital activities. All the water samples were kept at 4 °C until analysis or experiments.

All reagents used in this experiment were all analytical grade and used as received without further purification. Hydrogen peroxide solution (35%, w/w), heptahydrated ferrous sulfate ($FeSO_4 \cdot 7H_2O$), and NaOH were purchased from Merck (Germany). Water used throughout was prepared with Millipore Milli-Q water.

2.2. Experimental method

The experimental apparatus consisted of a cylindrical quartz reactor (7841-06, Ace Glass; Vineland, NJ), a double-walled quartz cooling water jacket, and a 10 W germicide lamp with a nominal wavelength range of 254 nm. The cooling water jacket was set up inside the reactor to maintain the temperature to be within a range of 25–31 °C, preventing excessive heating of the reaction. A lamp was placed inside the cooling water jacket. The volume of aqueous solution in all conducted experiments was 1000 mL. The reaction solution was stirred with a magnetic stirrer using a constant speed at 150 rpm to maintain a well-mixed solution during the experiments. Before turning on the UV lamp, the wastewater was placed in the dark, covered with aluminum foil, and the solution was adjusted to the desired pH. The addition of adequate amounts of photocatalysts (H_2O_2 or Fe^{2+}/H_2O_2) was added to the hospital wastewater only at the beginning of irradiation process in the batch mode. Samples were retrieved from the reactor for analysis at different time intervals. Photo-Fenton was stopped instantly by adding NaOH to the reaction mixtures and quenched by adding Na_2SO_3 before analysis. The reaction period in irradiation process was 2 h for all experiments.

Changes in chemical oxygen demand (COD) were determined by means of the dichromate reflux standard method [25], biological oxygen demand (BOD_5) and pH were measured by procedures described in standard methods [25]. Soluble COD (SCOD) and soluble BOD (SBOD) were measured after filtration (0.45 mm filter paper), and used to evaluate the treatment efficiency of biological treatment process after photo-Fenton pretreatment. Initial and treated total organic carbons (TOC) were analyzed with a Shimadzu 700 TOC ANALYZER 0-1 Analytical after filtration. Hydrogen peroxide was measured by the standard iodometric titration method [26]. Experiments were done in duplicate for the same set of conditions. The variations were systematically within ±10% of the stated values.

2.3. Toxicity test procedures

The bioassay on bacteria luminescence was carried out with a LUMIStox system (Dr. Lange GmbH, Duesseldorf, Germany) following the procedure of European standard NFEN ISO 11348-3. Tests were performed using gram negative marine bioluminescent bacteria of the species *V. fischeri* NRRL-B-11177 of the *Vibrionaceae* family. Samples were filtered using a 0.45 μm pore size membrane to prevent TSS interferences on bacteria luminescence. The samples were treated with NaCl solution of 20 g/L and brought to 50 mS/cm conductivity before analysis. Starting from the concentration of the sample, eight consecutive dilutions were tested (dilution factor 1:2); the inhibition of bioluminescence was measured at a wavelength of 490 nm, with readings after 5 and 15 min of incubation at 15 °C. The EC_{50} values were calculated as reported by Bulich [27].

2.4. Biological procedure

To obtain the biodegradability information, the activated sludge system was applied in cylindrical aeration glass-vessels

Table 1
Major characteristics of hospital wastewater

Parameters	Value
pH	7.3
Conductivity (mS/cm)	14.93
Total suspended solids (mg/L)	115
Turbidity (NTU)	15
COD (mg/L)	1350
BOD_5 (mg/L)	410
TOC (mg/L)	1050
Toxicity (%)	89

with a total volume of about 500 mL. The system was aerated by using air pumps and diffusers coupled at the bottom of the reactors. The initial volume of the culture was 400 mL, which was completed to 1000 mL with substrates (hospital wastewater or glucose) at the beginning of each cycle. The mineral nutrient solution with the mixture of NH_4Cl 38.5 g, $Na_2HPO_4{\cdot}2H_2O$ 33.4 g, KH_2PO_4 8.5 g, and K_2HPO_4 21.75 g to 1 L of tap water was used to adjust the appropriate amount of nutrient corresponding the ratio of COD:N:P as 100:5:1. The activated sludge culture, obtained from Sipraya wastewater treatment plant (Bangkok, Thailand), was diluted in order to obtain a total solid concentration (TS) of 3000 mg/L. The organic solids (or total volatile solids VS) content was 76% of TS. In order to allow for microbial acclimation, all samples were incubated in the dark on a rotary shaker (150 rpm) for 28 days. During biological experiment, the pH was controlled by a probe and adjusted at 7.0 by using H_2SO_4 or NaOH. The oxygen concentration was monitored by using an O_2 probe, located at the top of the reactor. All the experiments were done in duplicate at room temperature (20–25 °C). The variations were systematically within ±5% of the stated values. COD determinations, samples (5 mL each) were taken every 12 h of incubation, after they had been centrifuged and filtered through a 0.45 μm Millipore filter. The performance of biological treatment was characterized by determining the total suspended solids (TSS), volatile suspended solids (VSS), and sludge volume index according to the procedures described by standard methods [25].

3. Results and discussion

3.1. Characteristics of hospital wastewater

To evaluate the analytical characteristics and the biological treatability, TOC, COD, BOD_5, and other parameters were measured. The values of each parameter were carried out in triplicate from the mixed wastewater and are shown in Table 1. The chemicals contaminated in wastewater from each department were listed in Table 2.

The biodegradability of organic substances is a measure of speed and completeness of its biodegradability by micro-organisms [28], and the BOD_5/COD ratio is usually determined to analyze the difficulty of organic substances to be degraded [29]. In this study the biodegradability of the raw wastewater was estimated and the initial value of the BOD_5/COD ratio was equal to 0.30. As reported by Fresenius et al. [30], the biodegradation starts immediately and runs rapidly with a ratio of BOD_5/COD in the range over or equal to 0.5. However, with a $BOD_5/COD < 0.5$, there is a possibility for chemical substances which have low biodegradability to slacken or delay the biological process. The studied hospital wastewater represented relatively low biodegradability, which is in good agreement with previous work [4]. In addition, raw hospital wastewater exhibited high toxicity to micro-organisms with the inhibition percentage of 100%.

3.2. Optimum conditions and biodegradability improvement of hospital wastewater by photo-Fenton process

The optimum pH for photo-Fenton treatment of hospital wastewater was found to be 3, based on BOD_5 and COD removal efficiencies which were 33% and 43%, respectively, as illustrated in Fig. 1(a). The relatively large variation in COD removal as a function of pH might have resulted from the decomposition of H_2O_2 concentrations. Normally, neutral pH leads to a gradual decomposition of H_2O_2, which prolongs the degradation reaction for a longer time. The acidic pH is much more preferable for the decomposition of H_2O_2 and the interaction between H_2O_2 and Fe(II) to generate $^{\bullet}OH$ [31].

From this study, the residual H_2O_2 concentrations were 30–80 mg/L. The concentration of H_2O_2 was the lowest at pH 3. In this work, biodegradability of the treated wastewater was slightly improved from 0.30 to 0.35 in the range of pH 2–4. The biodegradability of the solution reduced as the pH leveled up to the neutral region.

The oxidation degree of organic substances in hospital wastewater was also determined by means of average oxidation state (AOS), a gross parameter very useful for estimating the oxidation degree of mixed solutions and gives indirect information on its probability of biodegradation. This value was calculated using Eq. (1) [32]:

$$\mathrm{AOS} = \frac{4(\mathrm{TOC} - \mathrm{COD})}{\mathrm{TOC}} \quad (1)$$

Table 2
Chemicals contaminated in wastewater from each department

Department	Type of chemicals	Toxicity of wastewater (%)
Laboratory	Butanol, xylene, formaldehyde, acetone, picric acid, acetic acid, eosin and dyes, ethedium bromide	75
Analysis room	Formaldehyde, chloroform, phenol, chlorophenol, glycerol, alcohol, formic acid	90
Embalming room	Formaldehyde, glycerol, phenol	100

where TOC and COD are expressed in mmol of C L^{-1} and mmol of O_2 L^{-1}, respectively. AOS takes values between 4 for CO_2, the most oxidized state of C, and −4 for CH_4, the most reduced state of C.

It is worth noting that the original AOS value of raw wastewater was −1.14. This value was increased to the positive region to +0.5 as the pH of the reaction moved to the range of pH 2–4 (Fig. 1(b)). Beyond this point, the AOS value sharply decreased. These results suggest that organic substances in solution are well oxidized in the acidic region in the range of pH 2–4. More oxidized intermediates are expected to form in the solution.

The optimum dosage of H_2O_2 was obtained by fixing the dosage of Fe(II) at 135 mg/L and varying the dosage of H_2O_2 at pH 3. The efficiencies of the photo-Fenton process in different dosage ratios of COD:H_2O_2 are illustrated in Fig. 2(a). As observed from the results of the experiments, the BOD_5 and COD removal efficiencies of solution increase with the increase of the hydrogen peroxide concentration. The contribution of hydrogen peroxide to COD removal reached 43%, 63%, 72%, and 77% for the dosage ratios of COD:H_2O_2 as 1:1, 1:2, 1:3, and 1:4, respectively. The role of hydrogen peroxide has been pointed out in several previous works [32–34] in that the high concentration of hydrogen peroxide accelerates the photo-Fenton reaction and provides high efficiency in contaminant removal. However, the reaction rate can be inhibited with an excess of hydrogen peroxide in the system [34]. The inhibition effect was seen here as the dosage ratio of COD:H_2O_2 was 1:6; the COD removal was reduced to 48% from the initial COD. The excess of hydrogen peroxide in the system was evidence for this behavior. This was probably due to both auto-decomposition of H_2O_2 into oxygen and water (Eq. (2)), and the recombination of $^{\bullet}OH$ (Eq. (3)) as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (2)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \quad (3)$$

The excess of H_2O_2 will react with $^{\bullet}OH$ (Eq. (3)) competing with organic pollutants in hospital wastewater and consequently reducing the efficiency of the treatment.

Biodegradability of hospital wastewater was drastically improved as high concentrations of hydrogen peroxide were applied. As shown in Fig. 2(b), the values of BOD_5/COD were much higher in the photo-Fenton process than in the initial

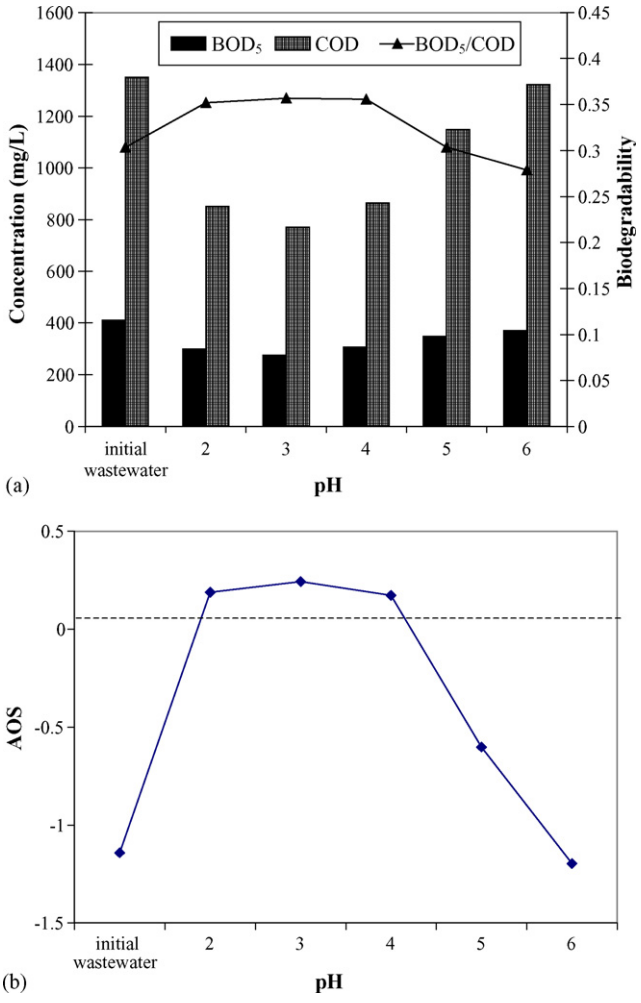

Fig. 1. Effect of pH on (a) efficiency and biodegradability of hospital wastewater using photo-Fenton process and (b) oxidation degree of organic substance. Conditions: COD:H_2O_2:Fe(II) = 1:1:0.1.

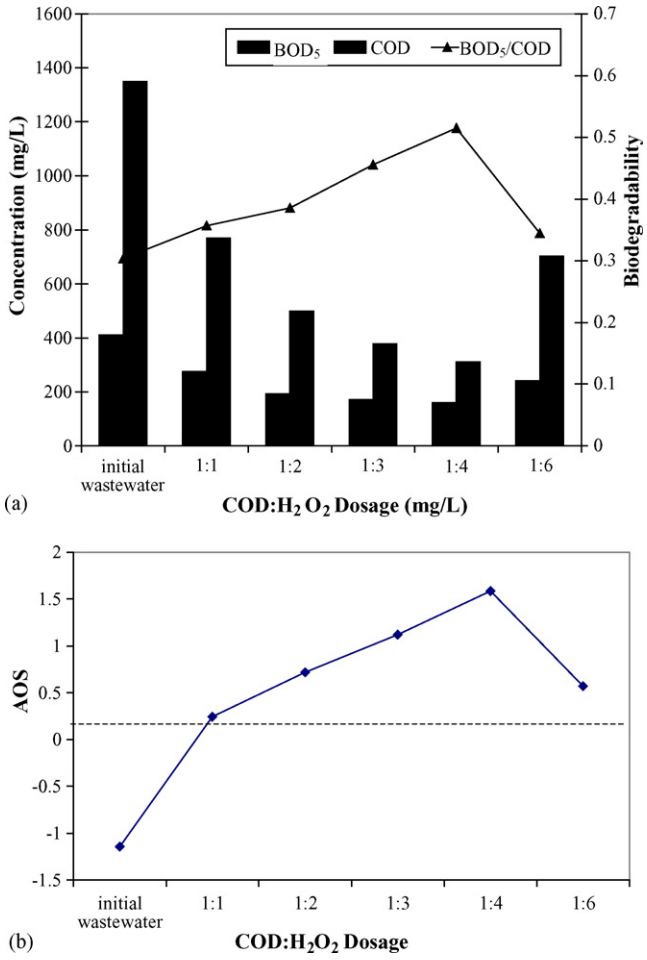

Fig. 2. Effect of H_2O_2 on (a) efficiency and biodegradability of hospital wastewater using photo-Fenton process and (b) oxidation degree of organic substance. Conditions: COD:Fe(II) = 1:0.1, Fe(II) = 135 mg/L, pH 3.

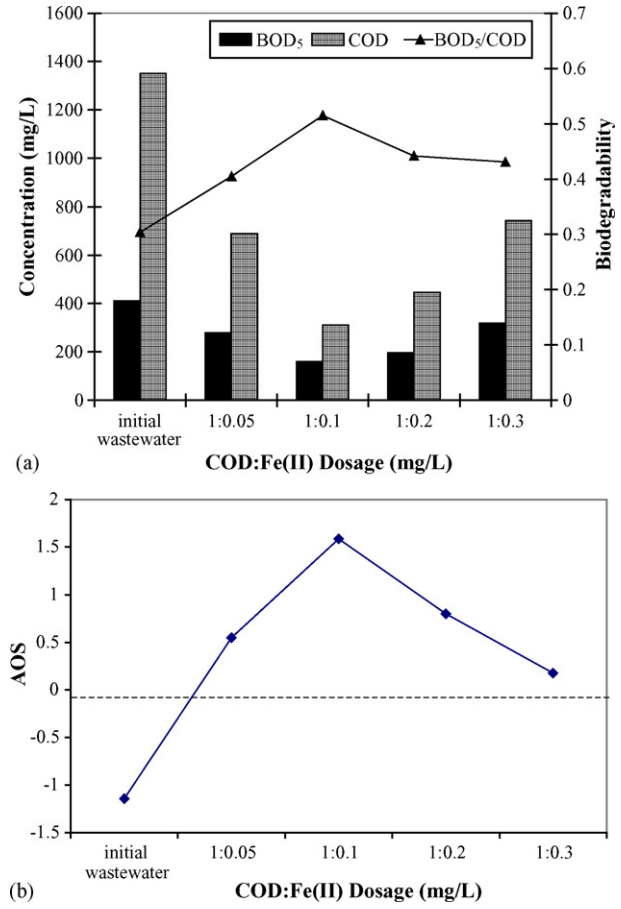

Fig. 3. Effect of Fe(II) on (a) efficiency and biodegradability of hospital wastewater using photo-Fenton process and (b) oxidation degree of organic substance. Conditions: COD:H_2O_2 = 1:4, H_2O_2 = 5400 mg/L, pH 3.

wastewater. The highest value of BOD_5/COD, equal to 0.52 as obtained at the dosage ratio of COD:H_2O_2, was 1:4. Findings from this experiment suggest that the effluent, after pretreatment by the photo-Fenton process under the studied conditions can be biodegradable by biological treatment process. The enhancement of this biodegradability might be explained by the increasing oxidation degree of the organic substance as the BOD_5/COD evolution in this studied system seems to be directly correlated with the AOS evolution. A significant increase of AOS was observed from the value of −1.14 in the initial wastewater to +1.58 in the effluent in which a COD:H_2O_2 dosage ratio of 1:4 was applied. The AOS value of this point is characteristic of very oxidized compounds like organic acids [35]. The value of residual TOC supported that 52% of the organic substance underwent mineralization and the organic substance might have transformed to small molecule intermediates. The optimum Fe(II) dosage was also investigated. The residual concentration of both BOD_5 and COD as a function of the dosage ratio of COD:Fe(II), and the biodegradability plot of hospital wastewater after pretreatment in different dosage ratios of COD:Fe(II) are illustrated in Fig. 3(a). The optimum dosage of COD:Fe(II) is estimated as 1:0.1 considering the removal efficiencies of BOD_5 and COD and biodegradability after treatment. As the ferrous ion concentration increased with the dosage ratio of COD:Fe(II) from 1:0.05 to 1:0.1, the removal percentages of COD removal increased from 49% to 77%.

This behavior might be explained by the fact that Fe(II) is the main species that can catalyze hydrogen peroxide in Fenton and photo-Fenton processes. The mechanisms of these reactions are not yet completely clear and there is much disagreement in the literature on the exact intermediates that form including whether or not the hydroxyl radical itself forms [21,23,24,36]. However, recent studies have confirmed the existence of the ferryl ion ($Fe^{VI}O^{2+}$) as an intermediate and shown evidence that disfavours the hydroxyl radical as an intermediate [37,38]. As reported by several previous works [21,36], the first step in the reaction of metal complexes with H_2O_2 in most case is the formation of a transient complex of metals (or a transient ferrous peroxide complex for iron catalyst as specified by Winterbourn [39]), which may decompose to the hydroxyl radical or a higher oxidation state of the metal or it may yield an organic free radical in the presence of organic substrates. The forming of hydroxyl radicals via Fenton reaction is based on the relative rates of the decomposition reactions of metal–peroxide complex and that of its reaction with organic substrates.

Results from this work shown that, at higher ferrous concentrations with a dosage ratio of COD:Fe(II) at 1:0.2 and 1:0.3, the COD removal efficiency reduced to 67% and 45%, respectively. This result might be rationalized by the ferrous ion inhibition that occurred when too high a concentration of ferrous was presented. Ferrous ions themselves may react with hydroxyl radicals resulting in the retardation of the reaction, as shown in Eq. (4). Liou et al. [18] also indicated that the hydroxyl radical inhibition effect could occur in the photo-Fenton reaction with high ferrous concentrations:

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad (4)$$

In conjunction with the treatment efficiency, photo-Fenton with a dosage ratio of COD:Fe(II) at 1:0.1 provided the highest value of BOD_5/COD. The biodegradability of hospital wastewater was enhanced at the optimum dosage of ferrous ions. The effluent value of BOD_5/COD continually reached the unproblematic biodegradability region. The significant change of AOS as a function of the dosage of ferrous ions is illustrated in Fig. 3(b). The AOS value increased from −1.14 in the initial wastewater to +1.58 at the optimum dosage of ferrous ions applied, suggesting a significant role of ferrous ions as a pretreatment method for this hospital wastewater. However, the addition of high concentration of ferrous might cause the formation of $Fe(OH)_3$ as a brown turbidity. In this work, at the optimum conditions, small amount of sludge about 45 mg/L was observed in the treated water.

From all experiment sets, the optimum conditions of photo-Fenton treatment for hospital wastewater are summarized as follows: a dosage ratio of COD:H_2O_2:Fe(II) of 1:4:0.1, a reaction pH of 3, and a reaction time of 2 h. At these conditions, removal efficiencies of BOD_5, TOC and COD were 61%, 52% and 77%, respectively. The value of the BOD_5:COD ratio increased from 0.30 to 0.52 and the AOS increased from −1.14 to +1.58. The residual TOC after pretreatment indicated that the intermedi-

ate products produced during photo-Fenton treatment were not completely degraded.

3.3. Treatability and toxicity of hospital wastewater with high COD concentration

The optimum conditions obtained were used to treat the hospital wastewater from different hospitals with similar activities. Photo-Fenton experiments were carried out to define effectiveness of the optimized experimental conditions for different initial COD values (450, 900, 2250, 3600 and 4500 mg/L) besides 1350 mg/L. The efficiencies of the photo-Fenton process in both BOD_5 and COD removal with the ratio of BOD_5/COD are shown in Fig. 4(a). For the optimum initial concentrations of Fe^{2+} and H_2O_2 and under UV light irradiation, 95%, 82%, 61%, 59%, 55% and 50% BOD_5 removals and 98%, 92%, 77%, 70%, 64%, and 56% COD removal were obtained for the initial COD values of 450, 900, 1350, 2250, 3600 and 4500 mg/L, respectively. From this it can be derived that treatment efficiency for both BOD_5 and COD removal decreased dramatically with increasing hospital wastewater strength. The residual TOC in the wastewater of 75%, 74%, 52%, 49%, and 48% for the initial respective COD values of 450, 900, 1350, 2250, 3600 and 4500 mg/L, suggested that the photo-Fenton process cannot undergo further mineralization with high COD concentrations applied to the system.

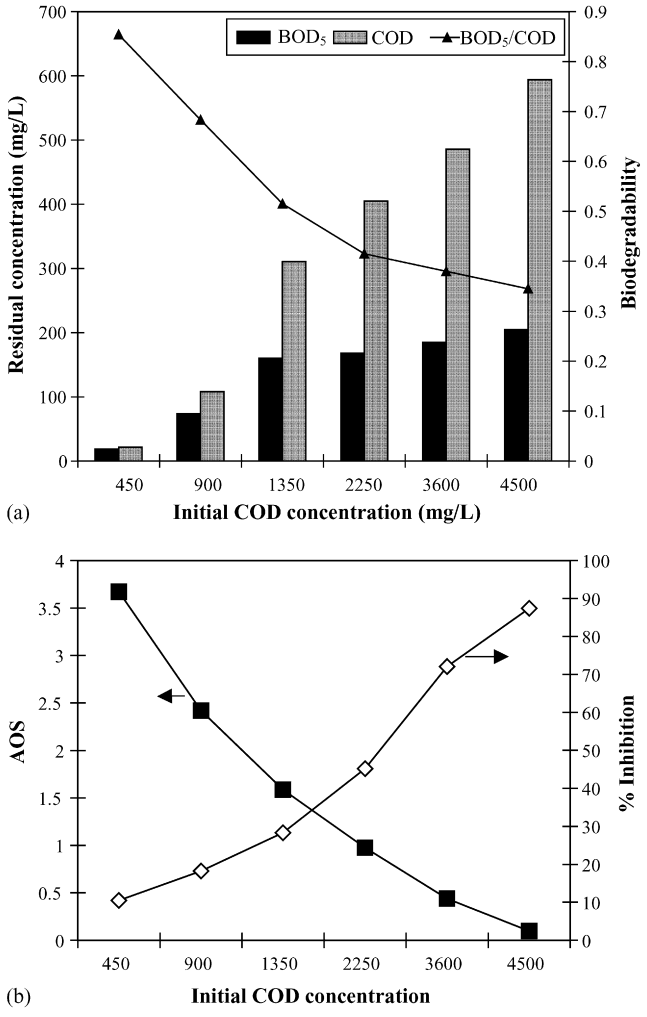

Fig. 4. Effect of initial COD concentration on (a) efficiency and biodegradability of hospital wastewater using photo-Fenton process and (b) oxidation degree of organic substance and percentage of inhibition in toxicity test. Conditions: COD:H_2O_2:Fe(II) = 1:1:0.1, pH 3.

The biodegradability characterized by the BOD_5/COD value also decreased with the increase of the initial COD concentration of hospital wastewater. The BOD_5/COD value sharply decreased from 0.85 for 450 mg/L of initial COD concentration to 0.35 for 4500 mg/L of initial COD concentration.

The decreasing treatability of the photo-Fenton process with high strength hospital wastewater can be clearly seen in Fig. 4(b). The AOS for all conditions was calculated and, in addition, the toxicity of treated effluent from photo-Fenton process was measured. The high value of AOS of +3.68 at 450 mg/L initial COD concentration falls to +2.41, +1.58, +0.97, + 0.44, and +0.09 for the initial respective COD values of 900, 1350, 2250, 3600 and 4500 mg/L. On the contrary, the inhibition percentage rises from 10.51% at 450 mg/L initial COD concentration to 18.25%, 28.3% and 45.2% for the initial respective COD values of 900, 1350, and 2250 mg/L. An inhibition percentage of higher than 50% was found for the rest of the conditions. Based on the toxicity test results presented here, hospital wastewater with an initial COD concentration of up to 2250 mg/L is the most suitable for pretreatment by the photo-Fenton process at the obtained optimum conditions. The optimum reaction conditions have to be re-established for higher initial COD values.

3.4. Biological treatability of hospital wastewater with and without photo-Fenton pretreatment

Initially, the biodegradability of the hospital wastewater was evaluated through the evolution of the BOD_5/COD ratio. For untreated samples of 1350 mg/L initial COD concentration, this parameter attains values of about 0.30 while photo-Fenton treatments of 2 h permit its enhancement up to values near 0.52, which represent considerable biodegradability according to the findings of Marco et al. [40] and Esplugas et al. [41]. This result indicates that the photo-Fenton process can break down or rearrange molecular structures of organic matter and convert the non-biodegradable organics to more biodegradable forms. This is a fact of remarkable importance for the application of photochemical–biological integrated systems to wastewater treatment [42]. Photochemical processes can transform organic recalcitrant compounds into easily biodegradable products, improving the efficiency and reducing the cost of further biological steps.

In this part the biological treatment process was studied to determine the treatability of pretreatment hospital wastewater in comparison with raw wastewater. Raw and pre-treated effluent was submitted to a biological degradation process using activated sludge in a batch experiment. The evolution of COD during the biological treatment for both types of wastewater is illustrated in Fig. 5. Results from this experiment confirm the low biodegradability of raw hospital wastewater, which attains a maximal COD removal of about 30% after a 72 h treatment

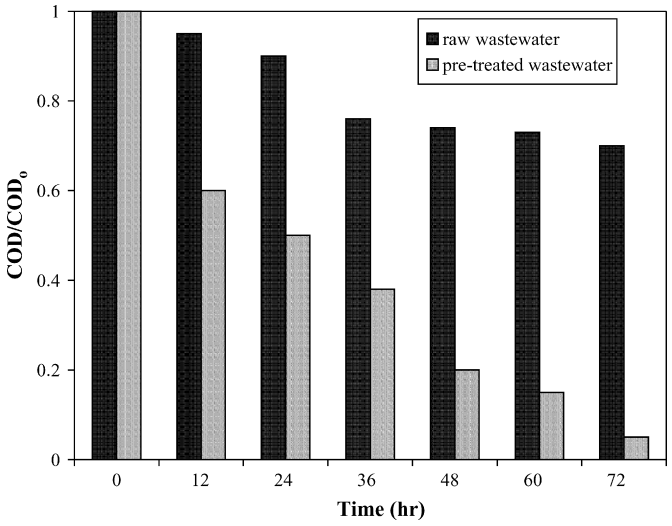

Fig. 5. COD removal during 72 h biodegradation experiments for raw hospital wastewater and pre-treated wastewater by photo-Fenton process.

Table 3
Major characteristics of raw hospital wastewater, pre-treated wastewater by photo-Fenton process, and final effluent after biological treatment

	Raw wastewater	Pre-treated wastewater	Final effluent
COD (mg/L)	1350	310	67.5
BOD (mg/L)	410	159	8
TSS (mg/L)	115	45	35
VSS (mg/L)	65	25	10
Cl^- (mg/L)	300	47	30
NH_4^+–N (mg/L as N)	80	20	13
NO_2^-–N (mg/L as N)	<0.0005	<0.0005	<0.0005
NO_3^-–N (mg/L as N)	0.50	0.35	0.20

time. In contrast, the COD of pre-treated hospital wastewater by the photo-Fenton process fades progressively, attaining a COD removal of higher than 90% at the end of a 72 h treatment time. In addition, the SVI value for the sludge in the biological treatment was 75 mL/g SS, which indicated a good settleability of the sludge in the biological system [43]. The characteristics of raw wastewater, pretreatment wastewater by photo-Fenton process, and the treated effluent after biological treatment are shown in Table 3. The obtained results are clearly demonstrated that photo-Fenton process can be the effective pretreatment process to enhance the biodegradability of the hospital wastewater. To help assess the economic viability of the process, an economic analysis was performed. From our study, the operating cost, which concerned only with the electricity cost was around US$ 0.52/m^3 wastewater. The chemical costs for $FeSO_4 \cdot 7H_2O$ and H_2O_2 were US$ 0.01/m^3 and 0.93/m^3, respectively.

4. Conclusions

Hospital wastewater contains several organic substances that are resistant to biological degradation with low biodegradability ratios ($BOD_5/COD = 0.3$). These complex matrixes show a resistance toward conventional activated sludge biological treatment process. In this work, the photo-Fenton process was initiated as a pretreatment method to increase biodegradability and reduce toxicity of wastewater prior to the biological treatment process. A significant enhancement of biodegradability was found at the optimum conditions as follows: a dosage ratio of COD:H_2O_2:Fe(II) of 1:4:0.1 and a reaction pH of 3. At these conditions, the value of the BOD_5:COD ratio increased from 0.30 in raw wastewater to 0.52 for treated wastewater and the oxidation degree of the organic substance, measured as AOS, increased from −1.14 to +1.58. The toxicity of the wastewater drastically reduced with this process. The coupled photochemical–biological systems in this work represent a suitable solution for the treatment of hospital wastewater samples with an efficient remediation of the major characteristics (BOD_5, COD, TOC) of the wastewater.

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References

[1] B. Erlandsson, S. Matsson, Medically used radionuclides in sewage sludge, Water Air Soil Pollut. 2 (1978) 199–206.
[2] M.L. Rischardson, J.M. Bowron, The fate of pharmaceutical chemicals in the aquatic, Pharmacology 37 (1985) 1–12.
[3] K. Kűmmerer, Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources—a review, Chemosphere 45 (2001) 957–969.
[4] E. Emmanuel, Y. Perrodin, G. Keck, J.-M. Blanchard, P. Vermande, Ecotoxicological risk assessment of hospital wastewater: a proposed framework for raw effluents discharging into urban sewer network, J. Hazard. Mater. A 117 (2005) 1–11.
[5] B.H. Sørensen, N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lützhøft, S.E. Jørgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393.
[6] A.P. Murphy, W.J. Boegll, K.V. Price, C.D. Moody, A Fenton-like reaction to neutralize formaldehyde waste solutions, Environ. Sci. Technol. 23 (1989) 166–169.
[7] Z. Lu, W. Hegemann, Anaerobic toxicity and biodegradation of formaldehyde in batch cultures, Water Res. 32 (1998) 209–215.
[8] M. Qu, S.K. Bhattacharya, Toxicity and biodegradation of formaldehyde in anaerobic methanogenic culture, Biotechnol. Bioeng. 55 (1997) 727–736.
[9] R.F. Hickey, J. Vanderwilen, M.S. Switzerbaum, The effects of organic toxicants on methane production and hydrogen gas levels during the anaerobic digestion of waste activated sludge, Water Res. 21 (1987) 1417–1427.
[10] P. Leprat, Les rejets liquides hospitaliers, quels agents et quelles solutions techniques, Revue Techniques hospitalières 632 (1998) 49–52.
[11] St. Gartiser, L. Brinkler, T. Erbe, K. Kummerer, R. Willmund, Contamination of hospital wastewater with hazardous compounds as defined §7a WHG, Acta Hydrochim. Hydrobiol. 2 (1996) 90–97.
[12] P. Kajitvichyanukul, M.C. Lu, C.H. Liao, W. Wirojanagud, T. Koottatep, Degradation and detoxification of formaline wastewater by advanced oxidation processes, J. Hazard. Mater. 135 (2006) 337–343.
[13] D.L. Sedlak, K.E. Pinkston, Factors affecting the concentrations of pharmaceuticals released to the aquatic environment, Water Resour. Update 120 (2001) 56–64.
[14] C.H. Huang, J.E. Renew, K.L. Smeby, K. Pinkerston, D.L. Sedlak, Assessment of potential antibiotic contaminants in water and preliminary occurrence analysis, Water Resour. Update 120 (2001) 30–40.

[15] X. Wen, H. Ding, X. Huang, R. Liu, Treatment of hospital wastewater using a submerged membrane bioreactor, Process Biochem. 39 (2004) 1427–1431.
[16] J. Araña, E.T. Rendón, J.M.D. Rodríguez, J.A.H. Melián, O.G. Díaz, J.P. Peña, Highly concentration phenolic wastewater treatment by the photo-Fenton reaction, mechanism study by FTIR-ATR, Chemosphere 44 (2001) 1017–1023.
[17] B. Utset, J. Garcia, J. Casado, X. Doménech, J. Peral, Replacement of H_2O_2 by O_2 in Fenton and photo-Fenton reactions, Chemosphere 41 (2000) 1187–1192.
[18] M.-J. Liou, M.C. Lu, J.N. Chen, Oxidation of explosives by Fenton and photo-Fenton processes, Water Res. 37 (2003) 3172–3179.
[19] S. Wadley, T.D. Waite, Fenton processes, in: S. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London, 2004, pp. 111–117.
[20] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.
[21] S. Goldstein, D. Meyerstein, G. Czapski, The Fenton reagents, Free Radic. Biol. Med. 15 (1993) 435–445.
[22] J.J. Pignatello, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.
[23] M.L. Kremer, Mechanism of the Fenton reaction, evidence for a new intermediate, Phys. Chem. Chem. Phys. 1 (1999) 3595–3605.
[24] H.B. Dunford, Oxidations of iron (II)/(III) by hydrogen peroxide: from aquo to enzyme, Coordin. Chem. Rev. 233–234 (2002) 311–318.
[25] APHA, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1992.
[26] G.O. MuÈller, Lehrbuch der Angewandten Chemie, Band III, Hirtzel Verlag, S. Leipzig, 1981.
[27] A.A. Bulich, Use of luminescent bacteria for determining toxicity Aquatic Toxicity, vol. 667, ASTM STP, Philadelphia, 1979.
[28] D.T. Sponza, Application of toxicity tests into discharges of the pulp–paper industry in Turkey, Ecotoxicol. Environ. Safety 54 (2003) 74–86.
[29] M. Seiss, A. Gahr, R. Niessner, Improved AOX degradation in UV oxidative wastewater treatment by dialysis with nanofiltration membrane, Water Res. 13 (2003) 3242–3248.
[30] W. Fresenius, W. Schneider, B. Böhnke, K. Pöppinghaus, Technologie des eaux résiduaires—Production, collecte traitement et analyse des eaux résiduaires, Springer-Verlag, Berlin, 1990, p. 1137.
[31] J. De Laat, E. Tace, M. Dore, Degradation of chloroethanes in dilute aqueous solution by H_2O_2/UV, Water Res. 28 (1994) 2507–2519.
[32] J.P. Scott, D.F. Ollis, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, Environ. Prog. 14 (1995) 88–103.
[33] S. Rahhal, H.W. Richter, Reduction of hydrogen peroxide by the ferrous iron chelate of diethylenetriamine-*N*,*N*,*N*',*N*,*N*'-pentaacetate, J. Am. Chem. Soc. 110 (1988) 3126–3133.
[34] D.K. Moon, T. Maruyama, K. Osakada, T. Yamamoto, Chemical oxidation of polyaniline by radical generating reagent, Chem. Lett. (1991) 1633–1636.
[35] V. Sarria, S. Parra, N. Adler, P. Péringer, N. Benitez, C. Pulgarin, Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, Catal. Today 76 (2002) 301–315.
[36] M. Masarwa, H. Cohen, D. Meyerstein, D.L. Hickman, A. Bakac, J.H. Espenson, Reactions of low-valent transition-metal complexes with hydrogen peroxide. Are they 'Fenton-like" or not? I. The case of Cu_{aq}^{+} and Cr_{aq}^{2+}, J. Am. Chem. Soc. 110 (1988) 4293–4297.
[37] F. Buda, B. Ensing, M.C.M. Gribnau, E.J. Baerends, DFT study of the active intermediate in the Fenton reaction, Chem. Eur. J. 7 (2001) 2775–2783.
[38] B. Ensing, F. Buda, F.E. Blochl, E.J. Baerends, A Car-Parrinello study of the formation of oxidizing intermediates from Fenton's reagent in aqueous solution, Phys. Chem. Chem. Phys. 4 (2002) 3619–3627.
[39] C.C. Winterbourn, Toxicity of iron and hydrogen peroxide: the Fenton reaction, Toxicol. Lett. 82–83 (1995) 969–974.
[40] A. Marco, S. Esplugas, G. Saum, How and why to combine and biological processes for wastewater treatment, Water Sci. Technol. 35 (1997) 321–327.
[41] S. Esplugas, S. Contreras, D.F. Ollis, Engineering aspects of the integration of chemical and biological oxidation: simple mechanistic models for the oxidation treatment, J. Environ. Eng. 130 (2004) 967–974.
[42] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, S. Malato, J.V. Weber, Solar photocatalytic degradation of humic acids as a model of organic compounds of landfill leachate in pilot-plant experiments: influence of inorganic salts, Appl. Catal. B 53 (2004) 127–137.
[43] K. Andreasen, L. Sigvardsen, Experiences with sludge settleability in different process alternatives, Water Sci. Technol. 33 (1996) 136–146.