Experimental study of degradation and biodegradability of oxytetracycline antibiotic in aqueous solution using Fenton process

Mustapha Zouanti[1]†, Mohamed Bezzina[1], Ramdhane Dhib[2]

[1]VSN Laboratory, Faculty of Science and Technology, University of Djilali Bounaama, Khemis Miliana, 44225, Algeria
[2]Department of Chemical Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario, Canada

ABSTRACT

The degradation of aqueous oxytetracycline (OTC) from an aqueous solution antibiotic using H_2O_2/Fe^{2+} process was studied in one 1 L batch chemical reactor. The extent of OTC degradation (20 mg/L) was investigated from a known initial pH solution, temperature and the type of catalyst (Fe^{2+}, Fe^{3+}) and for various initial concentrations of OTC, H_2O_2 and Fe^{2+}. The degradation efficiency achieved was found to be very important (90.82% and 90.63%) at initial pH solution of 3 and 4, respectively. However, the type of catalyst and the reaction temperature had a slight impact on the final degradation of OTC. The results showed that the OTC removal increased with increasing initial H_2O_2 concentration in the range of 70 to 150 mg/L and initial Fe^{2+} concentrations in the range of 2 to 5 mg/L. The highest degradation efficiency obtained at ambient temperature was 90.95% with initial concentration of OTC of 10 mg/L, H_2O_2 = 150 mg/L and Fe^{2+} = 5 mg/L. Moreover, biodegradability improved from 0.04 to 0.36 and chemical oxygen demand degradation was 78.35% after 60 min of treatment. This study proved that Fenton process can be used for pretreatment of wastewater contaminated by OTC before a biological treatment.

Keywords: Advanced oxidation processes, Chemical degradation, Fenton process, Oxytetracycline, Pharmaceutical wastewater

1. Introduction

Effluents of waste products coming from pharmaceutical industry enter environmental ecosystems through various channels such as pharmaceutical equipments, wastewater treatment plants and medical center wastes [1,2]. During the last few decades, the production and consumption of pharmaceutical products have drastically increased due to the considerable usage of medical products by the fast growing world population. Today, large quantities of medical products are produced each year for human and animal healthcare [3]. As a result, huge quantities of wastewaters are proportionally generated in pharmaceutical industries and medical centers. These relevant wastes are characterized by a high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids and toxicity. Besides, the effluents contain important amounts of toxic and persistent compounds such as organic solvents, catalyst, reactants and raw materials [4-7].

Antibiotics are among the most widely used drugs for the treatment of diseases. In particular tetracyclines (TCs) stand out as one of the most important antibiotic groups in terms of high production and worldwide distribution [8]. TCs are broad-spectrum of bacteriostatic antibiotics that are effective in treating infections caused by certain strains of Gram-negative and Gram-positive, which explains their wide use in the treatment of infectious diseases for humans and animals [9]. In fact, the most extensively used TCs are oxytetracycline (OTC), TC, chlortetracycline (CTC), and doxycycline (DC). TC is frequently used in aquaculture and veterinary [10], whereas OTC and CTC are widely administrated as growth promoters. Therefore, it is possible to find these antibiotics discharged into the environment. For instance, the concentration of TCs detected in surface water is in the range of 0.11 to 4.20 μg/L and in wastewater treatment plant (WWTP) effluents with concentrations of 46-1,300 ng/L for TC, 270-970 ng/L for CTC, and 240 ng/L for OTC [11]. Kolar et al. [12] found that OTC was

moderately toxic to organisms of activated sludge (EC_{50}17.9 mg/L). Therefore, it is necessary to develop appropriate techniques for the removal of these pollutants from contaminated wastewaters for preserving the environment.

Biological processes are quite economical for the treatment of wastewaters and they are widely studied. But, they have been proven to be ineffective in the removal of persistent or non-bio-degradable compounds [13]. For instance, biological treatment processes are not successful in effectively removing TCs antibiotics [14]. Alternatively, physico-chemical techniques such as reverse osmosis, adsorption, ultrafiltration and coagulation are also used for the treatment of wastewater, however these treatments transfer only the pollution from one phase to another, which subsequently requires further treatment [13, 15]. Therefore, it is necessary to develop more effective treatment methods such as chemical and photochemical degradation to remove completely contaminants.

For instance, advanced oxidation processes (AOPs) are proven to be very effective techniques for the degradation of a wide range of refractory pollutants in aqueous solution such as polymers [16], phenol [17], pesticides and dyes [18, 19]. These techniques are based on the generation of highly reactive radicals, such as hydroxyl radicals ($^{\bullet}OH$) and hydroperoxyl radicals ($HO_2^{\bullet}$) which can react effectively with organic pollutants and reduce intermediate re-action species to CO_2 and H_2O without producing harmful by-prod-ucts or sludges that must require further processing [3, 20].

Several researchers have studied the degradation of OTC (Fig. S1) by different AOPs methods such as ultraviolet (UV)/H_2O_2 [19, 21, 22], photo-Fenton [23], gamma radiation [11], anodic oxidation [24], pulse radiolysis [25], Ozone process [26] and photocatalysis UV/TiO_2 [27]. However, few studies focus on the mineralization and biodegradability of antibiotics using Fenton process.

In the present work, the degradation of OTC solution is inves-tigated using Fenton process in a batch chemical reactor. The main aim of this study is to analyze how the degradation process of OTC can be affected by initial concentrations of OTC, H_2O_2, Fe^{2+}, and pH as well as temperature and catalyst type. The minerali-zation and the biodegradability of antibiotic were also investigated.

2. Experimental

2.1. Reagents

OTC hydrochloride (> 95%) was purchased from Sigma-Aldrich and was used without further purification. 50% (w/w) of hydrogen peroxide (H_2O_2) was purchased from Merck (Germany) and was used by diluting it to 35% (w/w). Analytical grade ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was purchased from Biochem (France). Ferric sulfate ($Fe_2(SO_4)_3$) with purity exceeding 90% was obtained from Prolabo (France). The pH of the solution was adjusted at the beginning with either dilute H_2SO_4 (0.5 N) and NaOH (0.1 N).

2.2. Experimental Setup and Analysis

All experiments were carried out in a double jacket 1 L stirred batch reactor as shown in Fig. 1. The reactor was covered with aluminum paper to prevent the degradation of OTC by the pho-to-Fenton system. The reactor was connected to a thermostatic

bath to maintain a constant temperature of 25℃. The reactor was also equipped with a magnetic stirrer to ensure a homogeneous reaction medium and a uniform concentration distribution in the reactor. A thermometer was placed in the reactor for temperature measurement and a port for sampling. The pH level was adjusted using a pH-meter (HANNA pH 209) at the onset of each experiment and no further pH adjustment was made during the reaction. The description and operating conditions of the reactor are given in Table 1.

For each experiment, OTC solution was prepared by dissolving 10 mg of OTC in a 500 mL flask containing distilled water. The mixture was stirred at 600 rpm for 20 min to make a homogenous stable solution. The desired concentration of Fe^{2+} was added to the solution of OTC. Specific amounts of H_2SO_4 or NaOH were injected for pH solution adjustment. The desired amount of H_2O_2 was poured into the reactor and the temperature kept constant at 25℃.

Table 1. Reactor Operating Conditions

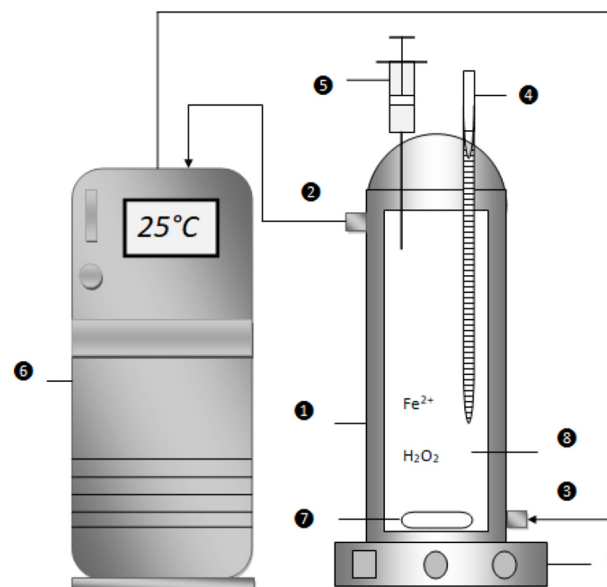| Item	Experimental operating range
Reactor volume	1 L
Temperature	25-50℃
pH	3-7
$[OTC]_0$	10-40 mg/L
$[H_2O_2]_0$	70-200 mg/L
$[Fe^{2+}]_0$	2-10 mg/L
Treated volume	500 mL
Agitation speed	600 rpm

Fig. 1. Schematic diagram of the H_2O_2/Fe^{2+} system. Legend: 1. Chemical reactor, 2. Cooling or heating water outlet, 3. Cooling or heating water inlet, 4. Thermometer, 5. Syringe, 6. Circulating water bath, 7. Magnetic bar, 8. Reaction medium, 9. Magnetic stirrer.
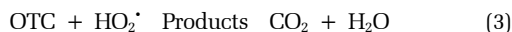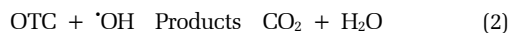
Samples were taken from the reactor at different time intervals and were immediately analyzed after being filtered in micropore disk (PES D.25 mm) of porosity of 0.45 μm. The degradation of OTC was evaluated upon measuring the absorbance of the treated solution with a spectrophotometer UV-VIS (SELECTA UV-2005). The maximum absorption wavelength is 353 nm. A calibration curve relating the absorption signal to OTC concentration was established. The UV absorption spectrum of OTC is provided in Fig. S2. The percentage of OTC removal was calculated as follows:

$$OTC\ removal = \frac{C_o - C_t}{C_o} \times 100\ \% \qquad (1)$$

Where C_0 is the initial concentration of OTC and C_t is the concentration of OTC at reaction time. COD was analyzed according to the method detailed by Thomas and Mazas [28], using a dichromate solution as oxidizer in a strong acid medium. Two (2 mL) of the test solution was mixed with dichromate reagent and digested for 2 h at 150℃. The absorbance for the color change of dichromate solution at $\lambda = 440$ mm was determined with a UV-VIS spectrophotometer. If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water [29]. A cooled incubator (VELP Scientifica, FOC 120I) with BOD sensor was used to measure the value of BOD for five days (BOD_5).

2.3. Reaction Mechanism

The mechanism of the OTC degradation in the H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} process is based on the generation of $^\bullet OH$ upon decomposition of H_2O_2 in presence of Fe^{2+} or Fe^{3+}. These $^\bullet OH$ are powerful oxidants, nonselective and highly reactive with organic matter. OTC reacts instantly with $^\bullet OH$ and produces intermediate products which sequentially react with the $^\bullet OH$ radicals and undergo a series of oxidation reactions up to total mineralization of the OTC into H_2O and CO_2 (Eq. (2)). OTC can also react with $HO_2^\bullet$ and generate other byproducts as given in Eq. (3).

$$OTC + \ ^\bullet OH \quad Products \quad CO_2 + H_2O \qquad (2)$$

$$OTC + HO_2^\bullet \quad Products \quad CO_2 + H_2O \qquad (3)$$

3. Results and Discussion

Using the experimental conditions in Table 1, several experimental tests were conducted to investigate the effect of reaction temperature and of initial concentration of the reactants on the reactor performance to degrade the organic compound considered.

3.1. Role of •OH Radicals in OTC Degradation

First, the results shown in Fig. 2 are very interesting and clearly exhibit the impact of H_2O_2 and Fe^{2+} in the degradation of OTC

when they are used separately or combined. The contribution of Fe^{2+} in the generation of $^\bullet OH$ radicals leads to an oxidation of 90.67% of OTC compared to 12.22% when H_2O_2 is alone. Hence, this result highlights the significant role of $^\bullet OH$ radicals in the elimination of OTC in H_2O_2/Fe^{2+} process. The degradation rate of OTC was much higher in H_2O_2/Fe^{2+} system than in H_2O_2 alone, which is probably due to the production of substantial amount of highly reactive radicals ($^\bullet OH$) that are mainly can disintegrate molecules of OTC antibiotic as $^\bullet OH$ have a high oxidation potential ($E^0 = 2.8$ V).
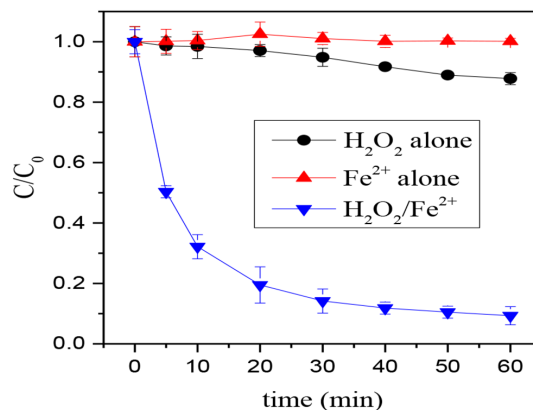

Fig. 2. Degradation of OTC by H_2O_2 or Fe^{2+} alone and H_2O_2/Fe^{2+} system, with $[OTC]_0 = 20$ mg/L, $[H_2O_2]_0 = 200$ mg/L, $[Fe^{2+}]_0 = 5$ mg/L, pH $= 3$, T $= 25℃$.

3.2. Effect of Initial H_2O_2 Concentration

Hydrogen peroxide dosage is an important factor to evaluate the performance of Fenton process. Thus, the concentration of H_2O_2 was varied from 70 mg/L to 200 mg/L for an invariant initial concentration of OTC and ferrous ion of 20 mg/L and 5 mg/L, respectively. The lowest concentration of H_2O_2 (70 mg/L) that was required to start the OTC degradation was based on the necessary stoichiometric ratios of the reaction to completely oxidize 20 mg/L of OTC according to the reaction below:

$$C_{22}H_{24}N_2O_9 + 52\ H_2O_2 \rightarrow 22\ CO_2 + 63\ H_2O + 2\ HNO_3 \quad (4)$$
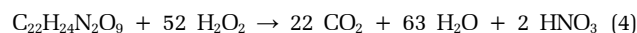
Plots in Fig. 3(a) describe the degradation of OTC at various initial concentrations of H_2O_2 and show that the rate of degradation of OTC increases with higher concentration of H_2O_2. In the presence of Fe^{2+}, hydrogen peroxide decomposes much more effectively and produces more free radicals which can immediately react with OTC. It is obvious that with higher H_2O_2 concentration, there is a higher chance to get more $^\bullet OH$ in the reacting system.

However, no enhancement was observed when the initial concentration of H_2O_2 exceeded 150 mg/L beyond a reaction time of 40 min. This result is quite interesting. It is due to an excess of hydrogen peroxide in the solution which leads to a scavenging phenomenon on $^\bullet OH$ as shown in Eq. (5).

$$H_2O_2 + \ ^\bullet OH \rightarrow HO_2^\bullet + H_2O \qquad (5)$$
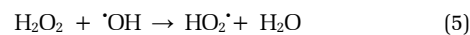
This reaction produces more $HO_2^{\bullet}$ that have an oxidation potential E^0 of 1.7 V. It is therefore less reactive than $^{\bullet}OH$ radicals and results in lowering the consumption rate of OTC. The highest consumption of H_2O_2 occurred during the first 30 min of degradation for all tests with different H_2O_2 initial concentrations. Elsewhere, Subramonian et al. [30] observed that a drop of COD removal occurred during the treatment of pulp and paper mill effluent when higher H_2O_2 was used due to the scavenging effect.

3.3. Effect of Initial Catalyst (Fe^{2+}) Concentration

Further, the presence of the catalyst in Fenton process for the generation of $^{\bullet}OH$ plays an important role as shown in the reaction below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (6)$$
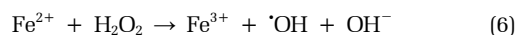
In this work, the impact of the catalyst Fe^{2+} was studied over the range of 2 to 10 mg/L. In fact, Fe^{2+} favors the generation of more $^{\bullet}OH$ radicals which therefore improves the degradation of OTC, which is confirmed by plots shown in Fig. 3(b) for higher concentration of Fe^{2+}. However, beyond 30 min of treatment, the degradation rate of OTC was lowered for Fe^{2+} initial concentration of 10 mg/L and the highest degradation efficiency achieved was 90.82% at Fe^{2+} = 5 mg/L. In fact, the reduction of OTC removal during the increase of the concentration of Fe^{2+} from 5 mg/L can be explained by the setting up of a parasitic reaction consuming the $^{\bullet}OH$ (Eq. (7)). The rate of this reaction becomes important and will compete with the degradation of the OTC. On the other hand, the Fe^{3+} ions formed at higher concentrations can react with hydrogen peroxide (Eq. (8)), and consequently reduce the degradation efficiency. Similar observations have been reported by some publications at higher concentration of Fe^{2+} [29,31,32].

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (7)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (8)$$
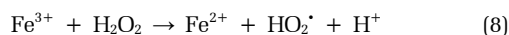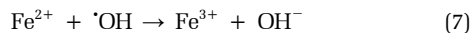
3.4. Effect of Initial OTC Concentration

The dependence of OTC degradation on its initial concentration has been investigated as well over an interval between 10 and 40 mg/L with an optimum H_2O_2 concentration of 150 mg/L and Fe^{2+} concentration of 5 mg/L.

The results in Fig. 3(c) show that the OTC degradation rate decays starting from high initial OTC concentrations. For instance, with initial OTC concentrations of 10, 20, 30 and 40 mg/L, the removal efficiency achieved after 60 min were 90.95, 90.82, 88.47 and 85.27%, respectively. Keeping the operating conditions invariant, the OTC degradation rate decreased much faster as the initial OTC concentration is augmented. However, high OTC concentrations resulted in more intermediate products which compete with OTC to react with $^{\bullet}OH$ and can also become limiting reagents. Consequently, a reduction of the rate constants was obtained.

Moreover, the reduction in degradation yield for an initial concentration of OTC can be related to a similar amount of $^{\bullet}OH$ radicals formed in all solutions considered. These results are in accordance with the data reported by Chekir et al. [33], who studied the degrada-

tion of spiramycine antibiotic by UV/TiO_2 under solar light. The degradation efficiency obtained in this study is quite similar to that of Chekir et al. [33]. In another study, Hoseini et al. [34] investigated the degradation of TC antibiotic by means of sonocatalytic system for initial concentrations of 25, 50, 75 and 100 mg/L and the removal rates reported were 70.1, 65.3, 58.3 and 50%, respectively.
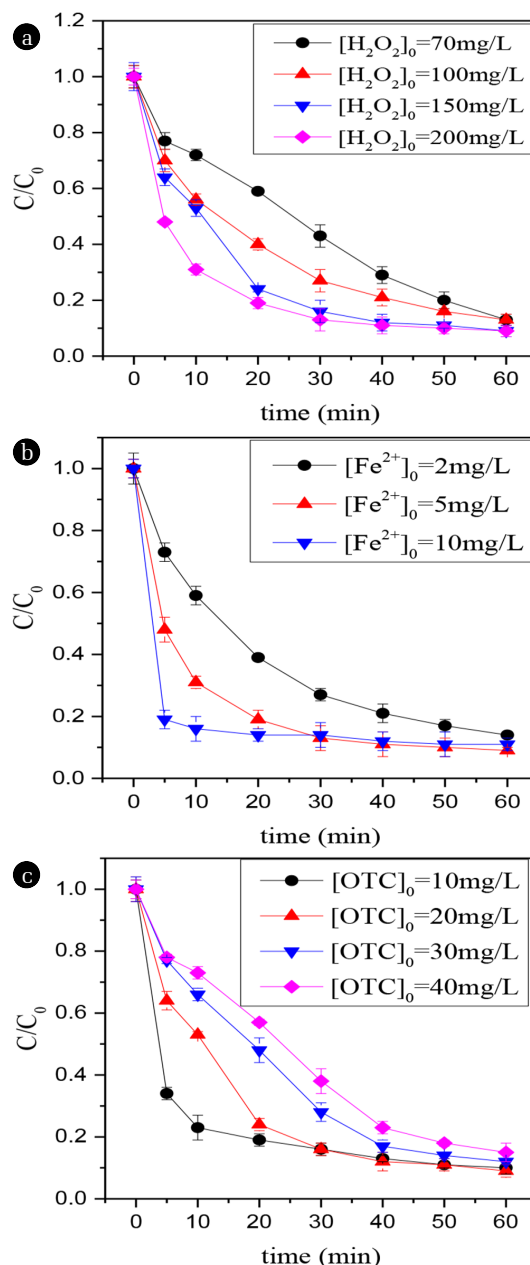

Fig. 3. Effect of different operating conditions on OTC degradation (a: initial H_2O_2 concentration with $[OTC]_0$ = 20 mg/L, $[Fe^{2+}]_0$ = 5 mg/L, b: initial Fe^{2+} concentration with $[OTC]_0$ = 20 mg/L, $[H_2O_2]_0$ = 200 mg/L, c: initial OTC concentration with $[H_2O_2]_0$ = 150 mg/L, $[Fe^{2+}]_0$ = 5 mg/L). All tests were carried out at pH = 3 and T = 25°C.

3.5. Effect of Temperature

Three experimental tests were performed at temperatures of 25, 40 and 50℃ to evaluate the reaction thermal effect on OTC degradation. Plots in Fig. 4 demonstrate that there is hardly no degradation of OTC when no H_2O_2/Fe^{2+} was utilized. Thermal energy (40 and 50℃) alone did not break OTC molecules. The tests show that OTC degradation is only effective when hydrogen peroxide H_2O_2 is mingled with ferrous iron Fe^{2+}.

Besides, plots in Fig. 4 show also that the degradation rate of OTC is favored by increasing the temperature. In the first stage, the degradation efficiency after 20 min of reaction increases from 76 to 89% for a temperature of 25 to 50℃. The oxidation reaction of the OTC by the $^{\bullet}OH$ is therefore favored by an addition of thermal energy. In fact, the solution temperature influences the electron transfer and the mass transfer rates, which in turn influences the rate of generation of $^{\bullet}OH$ and their reactivity with OTC. In the second stage (up to 20 min), the degradation rate slowed down due to a lower production rate of Fe^{2+} from Fe^{3+} [35] and the degradation efficiency slightly improved. The final degradation efficiency achieved after 60 min were 90.82, 92.23 and 92.88 % for the temperature of 25, 40 and 50℃, respectively. However, because of the rise in operating cost for a low gain achieved by increasing the temperature from 25 to 50℃, ambient temperature seems the best setting to apply to an OTC system. Similar observations were reported by Aygun et al. [36] in the first and the second stage of treatment using Fenton process.
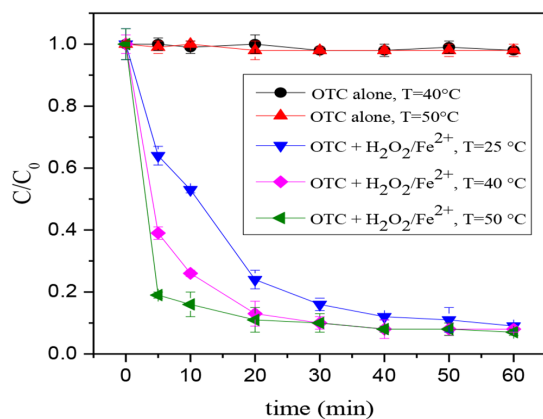

Fig. 4. OTC degradation versus time for different reaction temperatures, with $[OTC]_0 = 20$ mg/L, $[H_2O_2]_0 = 150$ mg/L, $[Fe^{2+}]_0 = 5$ mg/L, pH = 3.

The apparent rate constants (k_{app}) of the degradation of OTC obtained in the first OTC degradation stage at 25, 40 and 50℃ were 0.068, 0.145 and 0.213 min^{-1}, respectively. Accordingly, the apparent activation energy (E_{app}) of the OTC degradation reaction in a Fenton process was determined using the Arrhenius equation as follows:

$$\ln k_{app} = \ln A - \left(\frac{E_{app}}{RT}\right) \quad (9)$$

Where A is the frequency factor, E_{app} is the apparent activation

energy, R is the gas constant and T is the temperature. Fig. S3 shows a linear plot of ln k_{app} versus 1/T with a determination coefficient greater than 0.99. The apparent activation energy E_{app}, obtained from the Arrhenius plot (Fig. S3) is 36.58 kJ/mol. This result indicates that the degradation of an aqueous solution of OTC by Fenton process requires low activation energy and therefore it can be easily achieved. In this context, the results reported by Karatas et al. [37] are in accordance with the data obtained in this study.

3.6. Effect of Initial pH Solution

Several AOPs studies [16] which were conducted on wastewater treatment concluded that the determination of pH of a solution being treated is a key variable to investigate. In particular, the degradation of organic compounds by Fenton process is generally carried out in an acidic pH medium to preserve the aqueous Fe^{2+} ions in the solution.

In fact, solutions with initial pH between 1 and 7 were made to investigate the acidity effect on OTC degradation in a Fenton process. Each solution consists of OTC, H_2O_2 and Fe^{2+} which initial respective concentrations are 20 mg/L, 150 mg/L and 5 mg/L.

Plots in Fig. 5 show that for solutions with a pH values from 1 to 7, the OTC degradation yield in the Fenton process are 68.72, 77.37, 90.82, 90.63, 80.75, 68.62 and 46.26%, respectively. The experimental tests demonstrate that the OTC degradation rate increases for solutions which pH is less below a threshold of about 3.5 which can characterized as an optimum pH for solutions to be treated in the Fenton process. For pH values below 3, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing the reduction in hydroxyl radicals production. At pH 1 and 2, the low degradation may be due to the •OH scavenging of H^+ ions (Eq. (10)) [38]. Moreover, the H_2O_2 gets solvated in the presence of high concentration of H^+ ion to form stable oxonium ion $H_3O_2^+$. An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [39]. On the other hand, the drop in OTC degradation efficiency at pH > 4 may be due to the precipitation of dissolved
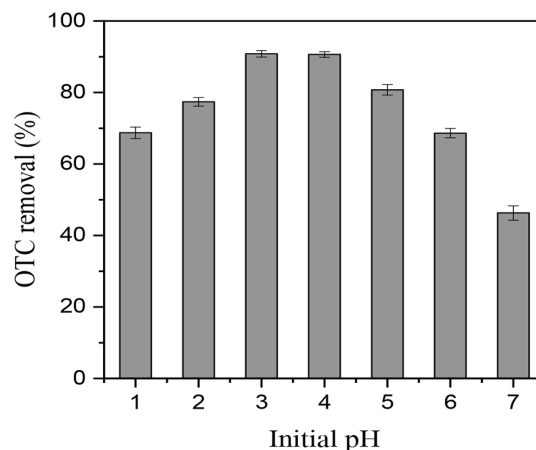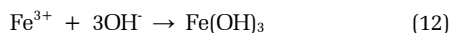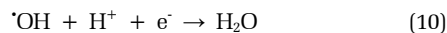

Fig. 5. OTC degradation efficiency versus initial pH solution, with $[OTC]_0 = 20$ mg/L, $[H_2O_2]_0 = 150$ mg/L, $[Fe^{2+}]_0 = 5$ mg/L, T = 25℃.

iron in presence of high concentration of OH⁻ ions (Eq. (11) and (12)), and a decrease of H_2O_2 decomposition into hydroxyl radicals. In addition, another study [38] reported that higher pH in solutions caused the oxidation potential of hydroxyl radical to decrease.

$$\cdot OH + H^+ + e^- \rightarrow H_2O \qquad (10)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (11)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (12)$$

3.7. Effect of Type of Catalyst (Fe^{2+}, Fe^{3+})

Fig. 6 shows a comparison between two systems of degradation, Fenton system (H_2O_2/Fe^{2+}) and Fenton-like system (H_2O_2/Fe^{3+}) that were operated using identical operating conditions (OTC = 20 mg/L, H_2O_2 = 150 mg/L, Fe^{2+} = Fe^{3+} = 5 mg/L). The degradation yield achieved was 90.82% and 88.20% in Fenton and Fenton-like systems, respectively. But, in the first 30 min, the degradation rate in the Fenton process was much faster than that in the Fenton-like process. This can be related to OTC oxidation having much more affinity for $\cdot OH$ radicals in the Fenton process according to Eq. (3) which has a rate constant of 70 Lmol⁻¹s⁻¹. However, the oxidation in the Fenton-like process is much more favored with $HO_2\cdot$ which has less power of oxidation than $\cdot OH$ radicals. Moreover, the rate constant (0.02 Lmol⁻¹s⁻¹) of production of $HO_2\cdot$ is very slow as defined in Eq. (8).

From 30 min onwards to the reaction end, the rate of OTC degradation is almost the same in both processes. Similar observations were reported by Wang et al. [40] who studied the decolourisation of wastewater from an azo dye in Fenton and Fenton-like processes.
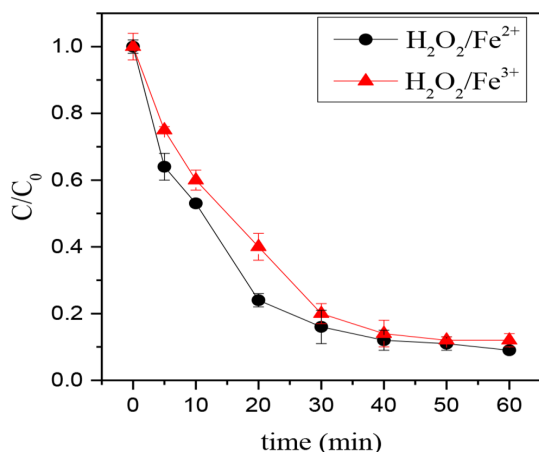
tration on the COD reduction was studied by considering initial OTC concentration of 20, 40, 60 and 80 mg/L which correspond to initial COD of 31.70, 63.25, 90.56 and 125.29 mg/L, respectively. The percent of COD reduction achieved after 60 min of treatment were found to be 78.35, 70.13, 63.80 and 51.27% (figure not shown). These results show that COD removal decreases with higher initial COD, which can be explained by the increasing of byproducts that slow down the mineralization. In the other hand, the effect of initial pH solution was also examined in the range of 2 to 5 for initial OTC concentration of 20 mg/L. The highest CODs removal percent obtained were 78.35 and 76.62% for initial pH of 3 and 4, respectively. As plotted in Fig. S4, the COD removal decreases progressively when the initial pH is higher than 3, this is may be due to a lower dissolved iron that can be responsible for the decomposition of H_2O_2 into hydroxyl radicals. These results confirm an optimum pH of 3 for the Fenton process.

As shown in Fig. 7, the rate of COD reduction was quite fast in the first 20 min (65.37% of COD removed) and then slows down gradually until the end of the reaction. This trend may be due to a rapid consumption of Fe^{2+} at the reaction beginning and the generation of large amount of hydroxyl radicals which are mainly responsible on disintegrating the organic compound. Then, the OTC degradation rate remained slow because of a decrease in hydroxyl radicals and the mineralization was achieved with other species radicals such as the hydroperoxyl radical which has a low oxidation power than hydroxyl radical. Fig. 7 also shows that the ratio of BOD_5/COD increased significantly from 0.04 to 0.36. This increment demonstrates clearly that the treated OTC product has a higher biodegradability compared to OTC before mineralization. The ratio of biodegradability BOD_5/COD is 0.36 and it is considered adequate for biological treatment as wastewater is considered biodegradable if this ratio is 0.4 [41].

Fig. 6. Performance of Fenton and Fenton-like processes for OTC degradation, with $[OTC]_0$ = 20 mg/L, $[H_2O_2]_0$ = 150 mg/L, $[Fe^{2+}]_0$ = 5 mg/L, $[Fe^{3+}]_0$ = 5 mg/L, pH = 3, T = 25℃.
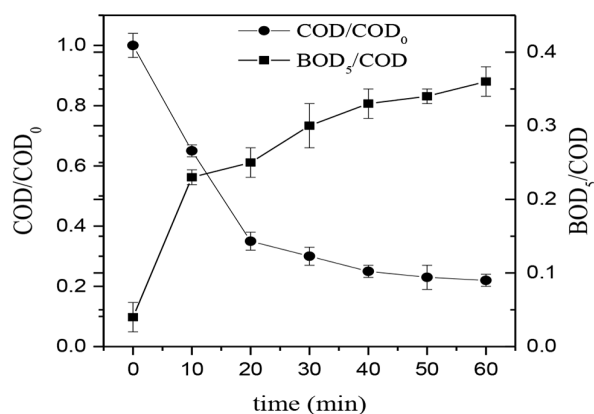
Fig. 7. Mineralization and biodegradability of treated OTC solution with $[OTC]_0$ = 20 mg/L, $[H_2O_2]_0$ = 150 mg/L, $[Fe^{2+}]_0$ = 5 mg/L, pH = 3, T = 25℃.

3.8. Mineralization and Biodegradability of Treated OTC Solution

To evaluate the effectiveness of mineralization of OTC using Fenton process, COD was investigated at optimal operating conditions found for OTC degradation. The effect of initial antibiotic concen-

4. Conclusions

Oxidation and molecular degradation of OTC were investigated under different operating conditions in Fenton and Fenton-like

processes for 60 min of reaction. An OTC degradation efficiency of 12.22% was obtained when H_2O_2 was used alone in the Fenton process. However, the degradation rate of OTC in the Fenton process (H_2O_2/Fe^{2+}) and Fenton-like process (H_2O_2/Fe^{3+}) was much higher, with a removal efficiency of 90.82% and 88.20%, respectively. An increase of OTC initial concentration lowered the degradation efficiency and an excess of H_2O_2 can also impede removal efficiency of OTC. Besides, the initial pH is an important parameter in the degradation of OTC. A high degradation rate was obtained for a pH of 3 confirming the optimum pH value for Fenton process. The highest value of 90.95% removal efficiency was achieved in the Fenton process operated with a ratio H_2O_2/OTC of 15, Fe^{2+} concentration of 5 mg/L and pH value of 3 at an ambient temperature of 25°C. Under the same operating conditions, the highest percent of COD removal achieved was 78.35%. A remarkable enhancement in OTC biodegradability from 0.04 to 0.36 was also achieved in 60 min reaction time. This study indicated that Fenton process can be used for pretreatment of wastewater contaminated by OTC before a biological treatment.

Acknowledgments

Nomenclature

E_{app}	Apparent activation energy (kJ/mol)
k_{app}	Apparent rate constants (min-1)
A	Frequency factor
E^0	Oxidation potential (V)
OTC	OTC antibiotic
pH	Hydrogen potential of the solution
R	Gas constant (8,314 J mol-1 K-1)
T	Temperature of the solution (°C)
TCs	Tetracycline antibiotics group

References

1. Khetan SK, Collins TJ. Human pharmaceuticals in the aquatic environment: A challenge to green chemistry. *Chem. Rev.* 2007;107:2319-2364.

2. Lillenberg M, Yurchenko S, Kipper K, et al. Presence of fluoroquinolones and sulfonamides in urban sewage sludge and their degradation as a result of composting. *Int. J. Environ. Sci. Technol.* 2010;7:307-312.

3. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* 2009;35:402-417.

4. Laera G, Cassano D, Lopez A, et al. Removal of organics and degradation products from industrial wastewater by a membrane bioreactor integrated with ozone or UV/H_2O_2 treatment. *Environ. Sci. Technol.* 2011;46:1010-1018.

5. Gupta SK, Gupta SK, Hung Y-T. Treatment of pharmaceutical wastes. In: Wang LK, Hung YT, Howard HL, Yapijakis C, eds. Waste treatment in the process industries. CRC Taylor and Francis; 2006. p. 167-233.

6. Schröder HF. Substance-specific detection and pursuit of non-eliminable compounds during biological treatment of waste water from the pharmaceutical industry. *Waste Manage.* 1999;19:111-123.

7. Sreekanth D, Sivaramakrishna D, Himabindu V, Anjaneyulu Y. Thermophilic treatment of bulk drug pharmaceutical industrial wastewaters by using hybrid up flow anaerobic sludge blanket reactor. *Bioresour. Technol.* 2009;100:2534-2539.

8. Figueroa RA, Leonard A, MacKay AA. Modeling tetracycline antibiotic sorption to clays. *Environ. Sci. Technol.* 2004;38:476-483.

9. López-Peñalver JJ, Sánchez-Polo M, Gómez-Pacheco CV, Rivera-Utrilla J. Photodegradation of tetracyclines in aqueous solution by using UV and UV/H_2O_2 oxidation processes. *J. Chem. Technol. Biotechnol.* 2010;85:1325-1333.

10. Palominos RA, Mondaca MA, Giraldo A, Peñuela G, Pérez-Moya M, Mansilla HD. Photocatalytic oxidation of the antibiotic tetracycline on TiO_2 and ZnO suspensions. *Catal. Today* 2009;144:100-105.

11. López Peñalver JJ, Gómez Pacheco CV, Sánchez Polo M, Rivera Utrilla J. Degradation of tetracyclines in different water matrices by advanced oxidation/reduction processes based on gamma radiation. *J. Chem. Technol. Biotechnol.* 2013;88:1096-1108.

12. Kolar B, Arnuš L, Jeretin B, Gutmaher A, Drobne D, Durjava MK. The toxic effect of oxytetracycline and trimethoprim in the aquatic environment. *Chemosphere* 2014;115:75-80.

13. Feng L, van Hullebusch ED, Rodrigo MA, Esposito G, Oturan MA. Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review. *Chem. Eng. J.* 2013;228:944-964.

14. Mboula VM, Hequet V, Gru Y, Colin R, Andres Y. Assessment of the efficiency of photocatalysis on tetracycline biodegradation. *J. Hazard. Mater.* 2012;209:355-364.

15. Oller I, Malato S, Sánchez-Pérez J. Combination of advanced oxidation processes and biological treatments for wastewater decontamination – A review. *Sci. Total Environ.* 2011;409:4141-4166.

16. Hamad D, Mehrvar M, Dhib R. Experimental study of polyvinyl alcohol degradation in aqueous solution by UV/H_2O_2 process. *Polym. Degrad. Stab.* 2014;103:75-82.

17. Maleki A, Mahvi A, Mesdaghinia A, Naddafi K. Degradation and toxicity reduction of phenol by ultrasound waves. *Bull. Chem. Soc. Ethiop.* 2007;21:33-38.

18. Stock NL, Peller J, Vinodgopal K, Kamat PV. Combinative sonolysis and photocatalysis for textile dye degradation. *Environ. Sci. Technol.* 2000;34:1747-1750.

19. Low FCF, Wu TY, Teh CY, Juan JC, Balasubramanian N. Investigation into photocatalytic decolorisation of CI Reactive Black 5 using titanium dioxide nanopowder. *Color. Technol.* 2012;128:44-50.

20. He X, Mezyk SP, Michael I, Fatta-Kassinos D, Dionysiou DD. Degradation kinetics and mechanism of β-lactam antibiotics by the activation of H_2O_2 and $Na_2S_2O_8$ under UV-254 nm

irradiation. *J. Hazard. Mater.* 2014;279:375-383.

21. Liu Y, He X, Fu Y, Dionysiou DD. Degradation kinetics and mechanism of oxytetracycline by hydroxyl radical-based advanced oxidation processes. *Chem. Eng. J.* 2016;284:1317-1327.

22. Yuan F, Hu C, Hu X, Wei D, Chen Y, Qu J. Photodegradation and toxicity changes of antibiotics in UV and UV/H_2O_2 process. *J. Hazard. Mater.* 2011;185:1256-1263.

23. Pereira JH, Queirós DB, Reis AC, et al. Process enhancement at near neutral pH of a homogeneous photo-Fenton reaction using ferricarboxylate complexes: Application to oxytetracycline degradation. *Chem. Eng. J.* 2014;253:217-228.

24. Fernandes A, Oliveira C, Pacheco MJ, Ciríaco L, Lopes A. Anodic oxidation of oxytetracycline: Influence of the experimental conditions on the degradation rate and mechanism. *J. Electrochem. Sci. Eng.* 2014;4:203-213.

25. Jeong J, Song W, Cooper WJ, Jung J, Greaves J. Degradation of tetracycline antibiotics: Mechanisms and kinetic studies for advanced oxidation/reduction processes. *Chemosphere* 2010;78:533-540.

26. Li K, Yediler A, Yang M, Schulte-Hostede S, Wong MH. Ozonation of oxytetracycline and toxicological assessment of its oxidation by-products. *Chemosphere* 2008;72:473-478.

27. Pereira JH, Vilar VJ, Borges MT, González O, Esplugas S, Boaventura RA. Photocatalytic degradation of oxytetracycline using TiO_2 under natural and simulated solar radiation. *Sol. Energy* 2011;85:2732-2740.

28. Thomas O, Mazas N. La mesure de la demande chimique en oxygène dans les milieux faiblement pollués. *Analusis* 1986;14:300-302.

29. Elmolla E, Chaudhuri M. Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution. *J. Hazard. Mater.* 2009;170:666-672.

30. Subramonian W, Wu TY, Chai S-P. Photocatalytic degradation of industrial pulp and paper mill effluent using synthesized magnetic Fe_2O_3-TiO_2: Treatment efficiency and characterizations of reused photocatalyst. *J. Environ. Manage.* 2017;187:298-310.

31. Mansour D, Fourcade F, Bellakhal N, Dachraoui M, Hauchard D, Amrane A. Biodegradability improvement of sulfamethazine solutions by means of an electro-Fenton process. *Water Air Soil Pollut.* 2012;223:2023-2034.

32. Perez M, Torrades F, Domenech X, Peral J. Fenton and photo-Fenton oxidation of textile effluents. *Water Res.* 2002;36:2703-2710.

33. Chekir N, Laoufi NA, Bentahar F. Spiramycin photocatalysis under artificial UV radiation and natural sunlight. *Desalin. Water Treat.* 2014;52:6832-6839.

34. Hoseini M, Safari GH, Kamani H, Jaafari J, Ghanbarain M, Mahvi AH. Sonocatalytic degradation of tetracycline antibiotic in aqueous solution by sonocatalysis. *Toxicol. Environ. Chem.* 2013;95:1680-1689.

35. Ramirez JH, Costa CA, Madeira LM. Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. *Catal. Today* 2005;107:68-76.

36. Aygun A, Yilmaz T, Nas B, Berktay A. Effect of temperature on Fenton oxidation of young landfill leachate: Kinetic assessment and sludge properties. *Global Nest J.* 2012;14:487-495.

37. Karatas M, Argun YA, Argun ME. Decolorization of antraquinonic dye, Reactive Blue 114 from synthetic wastewater by Fenton process: Kinetics and thermodynamics. *J. Ind. Eng. Chem.* 2012;18:1058-1062.

38. Lucas MS, Peres JA. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes Pigm.* 2006;71:236-244.

39. Kwon BG, Lee DS, Kang N, Yoon J. Characteristics of p-chlorophenol oxidation by Fenton's reagent. *Water Res.* 1999;33:2110-2118.

40. Wang S. A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. *Dyes Pigm.* 2008;76:714-720.

41. Tekin H, Bilkay O, Ataberk SS, et al. Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *J. Hazard. Mater.* 2006;136:258-265.