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Mineralization and photodegradation of oxytetracycline by UV/H_2O_2/Fe^{2+} and UV/PS/Fe^{2+} process: quantification of radicals

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Abstract

In this study, different oxidations processes; UVA-365nm (photolysis), UV-A/H_2O_2, UV-A/H_2O_2/Fe^{2+}, UV-A/S_2O_8, and UV-A/S_2O_8/Fe^{2+} were investigated to compare removal rates efficiencies of Oxytetracycline (OTC). The role of the initial concentration of oxidants, as well as their inhibitory threshold regarding degradation and mineralization of OTC were investigated at different pH. It was found that the initial pH solution had an important role in the photolysis of OTC, since in alkaline solutions, the degradation rate was faster than in acidic solutions, but in terms of mineralization yield, it did not exceed 3%. The addition of oxidants (H_2O_2, S_2O_8) had an impact on the mineralization, which reached 50% for the UV/S_2O_8 system. To improve mineralization, ferrous ions were added to UVA/oxidants, leading to 85% mineralization.

Quantification of the main radicals involved in the oxidation process can help in the understanding of the free-radical mechanism and their respective contributions to the degradation of OTC. The ability of Dimethylsulfoxide (DMSO) to act as a free radical scavenger was considered in UV/H_2O_2 and UV/H_2O_2/Fe^{2+} systems. The hydroxyl radicals can react directly with DMSO to produce a stable intermediate, methanesulfonate. Otherwise, Isopropanol, tert-butanol and 1,4, benzoquinone were used as indirect methods to catch and to quantify the main radicals generated during UV/S_2O_8 and UV/S_2O_8/Fe^{2+}processes.

Finally, the results allowed to quantify the contributions of each radical involved in photo-oxidation for both systems, UV/H_2O_2 and UV/ S_2O_8.

Keywords: Oxytetracycline, Photo-Fenton, mineralization, photolysis, hydroxyl radical probe, sulfate radical.

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1. Introduction

Every country in the world has seen a significant increase in its population. The depletion of water resources, their scarcity, particularly in the arid and semi-arid zones of the Sahara and in the highlands, and their loss due to a lack of adequate infrastructure have resulted in an excessive need for water [1].

The water pollution is an alteration that makes it unsafe and disrupts aquatic life. It can affect surface water (rivers, lakes) and groundwater. The origins of water pollution varied and are closely related to human activities: domestic, urban, industrial and agricultural pollution. The main manifestations of surface waters pollution are of chemical or biological nature and can be pathogenic for humans[2].

Wastewater treatment remains a major challenge for the environment and the future. It is a significant issue in a policy of sustainable management of the environment.

Sewage treatment plants (STPs) receive a wide range of substances that are not fully eliminated throughout the treatment process chain. The effluent, namely a complex mixture of molecules including the metabolites, is ultimately rejected in an almost unchanged form in the receiving environment and their fate in the environment remains unknown[2][3].

Among these substances are pharmaceutical residues including antibiotics, analgesics, stimulants, and antihistamines. Tetracycline group (TCs), which include Tetracycline (TC), Oxytetracycline (OTC), Chlortetracycline (CTC), Doxycycline (DCI) and Minocycline are the most widely used antibiotic in the production and use of treatments for infections in humans and animals[4]. Most of these pharmaceutical products, coming from domestic and hospital wastewater, industrial waste and hospitals discharge, arrive in sewage treatment plants (STPs), which are not designed to handle such recalcitrant pharmaceuticals products. They are therefore not completely removed and are dismissed as contaminants into the receiving waters; they are detected at concentrations ranging from ng L^{-1} to µg L^{-1}, but their wide diversity and continuous release into the environment mean pose a severe threat to the quality of waters.

STPs is currently considered as one of the main emitters of micro-pollutants into aquatic environments[5][6], affecting the rivers worldwide. Their growth in watercourses with dramatic effects on the fauna and flora shows the need for a renewal of the complementary treatment processes of wastewater. Advanced oxidation processes (AOPs) are one of the most promising technologies for the removal of recalcitrant organic compounds in

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contaminated wastewater. They have proven to be effective treatments for the elimination of recalcitrant compounds from conventional sewage treatment plants in order to curb the growth of water pollution[7][8].

The effectiveness of these techniques (AOPs) is based on the generation of highly reactive free radicals. The main involved radicals are hydroxyl radicals ($OH^{\bullet}$)[9], which act as a powerful oxidizing agent with a high reactivity and low selectivity for the removal of organic compounds[10], and convert them into smaller fragments and finally into CO_2 and H_2O[6]. However, sulfate radicals ($SO_4^{\bullet-}$) have also been attracting significant scientific interest for the destruction of micro-pollutants such as pharmaceuticals[11] and show to be efficient for the removal of halogen-substituted pollutants; it is a strong oxidant with a redox potential of 2.5 – 3.1 V[12], namely similar to hydroxyl radical ($OH^{\bullet}$) with a redox potential of 1.8 – 2.7 V[13].

Since $OH^{\bullet}$ and $SO_4^{\bullet-}$ have been deemed to be the major active species involved in the degradation of organic pollutants in AOPs, the quantitative determination of this species in the advanced oxidation processes is very important to assess the photocatalytic activity and to understand the free-radical mechanism of different processes. Photo-oxidation by radicals, $OH^{\bullet}$ and $SO_4^{\bullet-}$, appears to be the dominant chemical degradation process of organic matter in UV/H_2O_2 and UV/ $S_2O_8^{2-}$ systems. The degree to which pollutants are oxidized depends on the quantity of generated radicals and their structure. The quantitative results can be used to estimate their respective contribution in the degradation of pollutants.

Two different kind of techniques can be used to evaluate the quantity of radicals; Electron Paramagnetic Resonance technique (EPR/ESR)[14][15] in the presence of trap agents as a direct method of free radical measurement, or indirectly by using different radical scavenging or trapping methods.

Regarding indirect methods, Coumarin (COU) is one of the trapping reagents for hydroxyl radicals, which can react directly with $OH^{\bullet}$ to produce highly fluorescent compound, the 7-hydroxycoumarin (fluorescent)[16][17]. Other compounds have been also tested as trapping agents for the hydroxyl radicals, such as terephthalic acid (non- fluorescent)which leads to 2-hydroxyl terephthalic acid (fluorescent)[18][19], Dimethyl sulfoxide (DMSO) leading to methanesulfinate (MSI^{-})[20][21], as well as 4-hydroxybenzoic acid[22], salicylic acid[23]and Atrazine [24], since their degradation can be easily followed by HPLC.

Oxytetracycline (OTC) degradation was already studied in the literature[25][26][27] and showed low mineralization yield by photo-Fenton and photo-oxidation.

Therefore, the aim of this work was firstly, to investigate some different parameters (oxidant concentration, initial pH, ferrous concentration) influencing the mineralization of OTC in water by different processes of AOPs.

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UV-A/H_2O_2, UV-A/$S_2O_8^{2-}$, UV-A/H_2O_2/Fe^{2+}, UV-A/$S_2O_8^{2-}$/Fe^{2+} were compared to better understand the degradation mechanism and to compare different processes efficiency in terms of degradation of pollutant and removal of TOC(Total Organic Carbon). On the other hand, DMSO as a chemical probe (indirect method), was used to quantify hydroxyl radical $OH^{\bullet}$ in UV/H_2O_2 and UV/H_2O_2/Fe^{2+} systems by using a high concentration of this compound to capture the maximum of radicals in solution and determine the generated radicals amount responsible for OTC mineralization in both of systems.

For further information on the degradation mechanism in the UV/ $S_2O_8^{2-}$, UV/ $S_2O_8^{2-}$/Fe^{2+} systems, inhibition studies, using scavengers, were performed to identify the main radical species. High concentrations of Isopropanol, Tert-butanol, Methanol, Benzoquinone were considered in order to determine the contribution of $OH^{\bullet}$, $SO_4^{\bullet-}$ and $HO_2^{\bullet-}$/$O_2^{\bullet-}$ radicals in the degradation of OTC at various pH.

2. Materials and methods

2.1. Chemicals and Materials

Oxytetracycline (OTC) (>99% purity), was provided by the Algerian pharmaceutical industry (SAIDAL, Medea) and was used without further purification; its chemical structure is shown in **Fig.1,** and its chemical formula is $C_{22}H_{24}N_2O_9$ with a molecular weight of 496.9 g/mol, and a maximum light absorption wavelength of 355nm.

The stock solution was prepared at a concentration of 100 $mg.L^{-1}$ by dissolving OTC in high purity water obtained from a Millipore Milli-Q system. The initial pH of OTC solutions was adjusted by the addition of sulfuric acid (1 M) or sodium hydroxide solution (0.1 M).

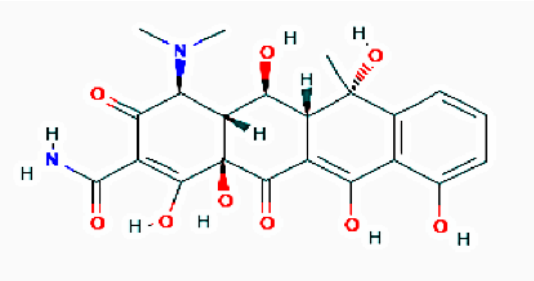

Fig.1 Chemical structure of oxytetracycline

Sodium persulfate (99% purity) and sulphuric acid (97% purity) were obtained from Merck (KGaA, Germany), hydrogen peroxide (30% w/w), iron(II) sulphate hyptahydrate ($FeSO_4$,$7H_2O$)(99.5% purity), sodium chloride (99.5% purity) were obtained from Acros Organics (Thermo Fisher Scientific, Geel, Belgium), Acetonitrile (purity 99.9%) (HPLC grade) was provided by Sigma–Aldrich (St. Quentin Fallavier, France); all solutions were prepared with ultrapure water produced from a Millipore Milli-Q system.

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2.2. Photocatalytic Procedure

Experiments were conducted in a Pyrex reactor with a double-walled cooling water jacket to maintain the temperature constant and equal to 20.0°C (±2.0°C). It involved a mercury lamp UVA (PL- L24W/10/4P, λ_{max}=365 nm; Philips, Poland) which yields an irradiation intensity of 5 $mW.cm^{-2}$ as detected with a UVA Radiometer (VLX- 3W equipped with a sensor CX 365, ALYS Technologies, Switzerland). The lamp was positioned axially inside the glass tube, which provided a maximum radiation at 365 nm. The lamp and quartz tube were immersed in the axial center of the reactor which was charged with 0.8 L of an aqueous solution containing the OTC at concentration in the range of 5–100 $mg.L^{-1}$. The solution with catalyst was continuously stirred with a magnetic bar. The pH of the sample solution was measured by pH-meter 6000 (VWR instrument). Monitoring of suspension temperature indicated no significant fluctuation (20 ± 2°C) along the experiment.

Experiments were performed in 800mL of OTC solutions of known concentrations. Then, the required volume of H_2O_2 (30% w/w) and a catalytic quantity of $FeSO_4,7H_2O$ as ferrous ion was added to the solution. 5 mL of the solution was collected and analyzed.

2.3. Analytical methods

2.3.1. High Performance Liquid Chromatography (HPLC)

The degradation of Oxytetracycline was measured by HPLC using Waters 996 system equipped with Waters 996 PDA (Photodiode Array Detector) and Waters 600LCD Pump (Waters, Guyancourt, France). The separation was achieved on Waters C 18 (4.6 × 250 mm; 5 µm) reversed-phase. The mobile phase consisted of A :0.1% formic acid in acetonitril and B : 0.1% formic acid in H_2O, with a gradient elution of 10% A for 5min then increased to 90% next 15min and back to 10% A in the next 5 min. The flow rate was 1 $mL.min^{-1}$. The detection of OTC was carried out at 355 nm and the retention time was approximately 10 min (≃ 9.90 min).

In the presence of Fe^{2+} and Fe^{3+} ions a complex between OTC and Fe^{3+} is formed which affects the detection of OTC by HPLC; to avoid the effect of complexation on detection, the pH of the sample was beforehand adjusted to acidic conditions (pH < 2) [27].

2.3.2. Total organic carbon (TOC) measurement.

The mineralization of OTC solutions was monitored by the removal of Total Organic Carbon. TOC was measured by TOC-VCPH/CPG Total Organic Analyzer Schimadzu. The catalytic combustion and conversion of

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organic carbon compounds leads to CO_2, which is identified by non-dispersive Infra-Red Detector (NDIR). Calibration was obtained with potassium hydrogen phthalate standards.

2.3.3. Radicals quantification

Hydroxyl radicals were quantified using Dimethyl sulfoxide (DMSO) as trapping agent that is characterized by its high reactivity with $OH^{\bullet}$. DMSO is first oxidized to methanesulfinic acid, that in turn reacts with $OH^{\bullet}$ leading to methanesulfonate. Two radicals $OH^{\bullet}$ are needed to form one molecule of methanesulfonate. Using ion chromatography (DIONEX DX120, Thermo Scientific, Sunnyvale, USA), methanesulfonate can be detected and quantified allowing the quantification of hydroxyl radicals. Ion chromatograph was provided with a conductivity detector. The stationary phase was constituted by an anion exchange column AS19 (4×250 mm), and the mobile phase was KOH at a concentration of 12 $mol.L^{-1}$. A gradient elution mode was adopted to accomplish the analyses, 10 $mmol.L^{-1}$ of KOH during the first 10 min; then a linear increase up to 45 $mmol.L^{-1}$ after 25 min; and this latter concentration was maintained from 25 to 35 min. The flow rate was fixed at $1mL.min^{-1}$.

2.3.4. Hydrogen peroxide quantification

Hydrogen peroxide concentration was iodometrically measured with thiosulfate as titrant. The principle of this analysis is that hydrogen peroxide reacts with excess potassium iodide (eq. 1) in the presence of an ammonium molybdate catalyst to produce diiodine, which is subsequently titrated with a standard thiosulfate solution (eq. 2).

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \quad (1)$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (2)$$

3. Results and discussion

3.1. Initial pH effect in direct photolysis of OTC

The degradation of OTC by UVA irradiation was carried out at pH 1.8, 3, 4.7, 8 and 12 as shown in **Fig.2** and **Table 1.**

The removal efficiency (R) was calculated using the following Eq.(3):

$$R(\%) = \frac{C_o - C_f}{C_f} * 100 \quad (3)$$

Where C_o and C_f are the concentration values at initial and final times (120 min) of the photodegradation, respectively.

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Table 1: OTC degradation by UV light under the influence of different pH values

pH	1.8	3	4.7	8	12
R (%)	6	8	11	43	63

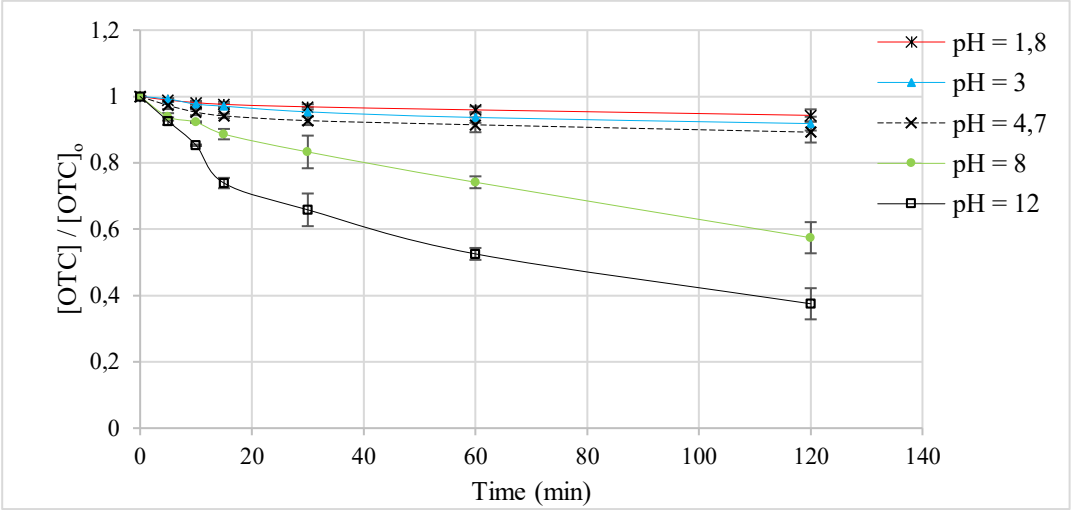

Fig.2 Degradation of OTC at different pH values under UVA light, [OTC] = 10 mg.L^{-1}

The OTC photolysis increases when the pH is increased, indicating that pH played a very important role. pH is the key factor in controlling the absorption spectrum[28]. Obviously, acidic conditions favored OTC stability, while alkaline conditions increased the OTC degradation rate. According to literature [29], when the medium pH is higher than pKa3, the dimethylammonium group might lead to the direct photolysis of OTC under UV-A **(Fig.3).** Moreover, recent kinetics studies, indicated that singlet oxygen ($^1O_2$) and superoxide anion radical ($O_2^{\bullet-}$) are both responsible for OTC degradation in water during the photolysis by UVA/B at basic pH [29][30][31].

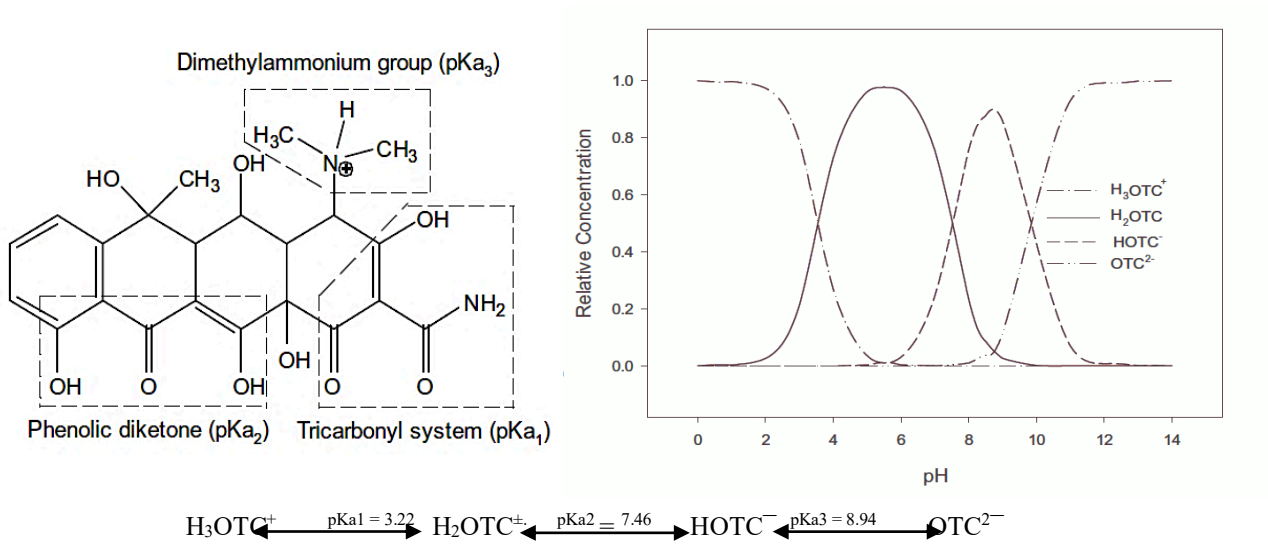

Fig.3 Structure of OTC and its distribution at different pH values[32]

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3.2. The effect of Initial oxidant concentration

The effect of the oxidant concentration on degradation was studied during two hours under UV-A radiations and in concentrations ranging from 1 mM to 10 mM for both H_2O_2 or PS (persulfate : $S_2O_8^{2-}$), the concentration of OTC was kept constant at 10 $mg.L^{-1}$.

For the three pHs (initial unadjusted pH = 4.7 ± 0.1, initial pH favorable for photo-Fenton = 3 ± 0.2 and the pH of natural water = 8.5 ± 0.2), the variation in the oxidant concentration has shown that this parameter can inhibit the photochemical reaction, above a limit concentration of H_2O_2 or PS, (**Fig.4 and Fig.5**). These compounds can become important scavengers of $OH^{\bullet}$ or $SO_4^{\bullet-}$ respectively (eq.4)(eq.5) [33][34] and in order to achieve the highest pollutant degradation, the oxidant concentration value must be optimized according to the charge of the solution.

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \quad (5)$$

In UV/H_2O_2 process, the optimal $[H_2O_2]$ value varied according to the initial pH of the solution (**Fig.4**); this may be due to the amphoteric nature of the OTC, (pKa of 3.22, 7.46 and 8.94), or to the concentration and speciation of the reactive radical which depends on the pH [26][32].

Regarding the H_2O_2 oxidant (**Fig.4**), by increasing the pH from 3 to 8.5, the mineralization rate increased from 4 up to 16%. For the different pH values, the mineralization rate increased with the increase of H_2O_2 concentration until an optimal value, followed by a decline of mineralization, most likely due to an $OH^{\bullet}$ scavenging effect by the excess of H_2O_2.

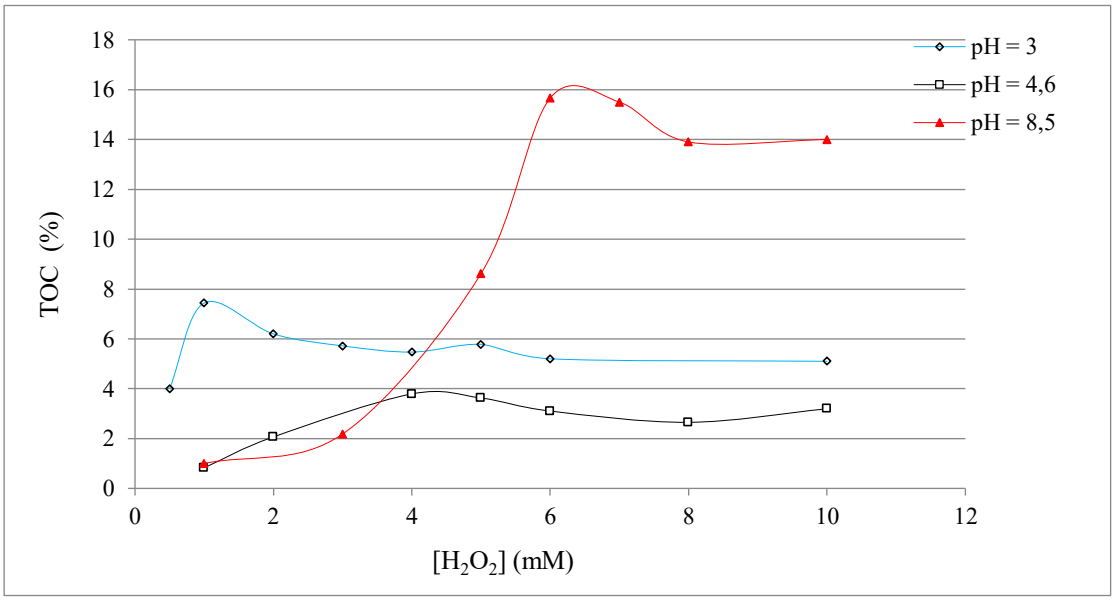

Fig.4 OTC mineralization, at different concentrations of H_2O_2, UV_{365}, [OTC] = 10 $mg.L^{-1}$, T ambient

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At pH 8.5, the form of OTC is mostly $HOTC^-$, the photochemical reactivity of OTC in alkaline conditions was much higher than in acid and neutral conditions (**Table 1**, **Fig.1**). According to Lui et al.[4], the hydroxide ion (OH^-) has a higher molar absorptivity and a higher rate constant with hydroxyl radical ($OH^\bullet$) than H_2O_2 ($k_{(OH^\bullet/HO^-)} = 7.5\times10^9\ M^{-1}s^{-1}$, $k_{(OH^\bullet/H2O2)} = 2.7\times10^7\ M^{-1}s^{-1}$). It react with hydroxyl radical ($OH^\bullet$) to produce $O^{\bullet-}$ (eq. 6)[13], and can also react with hydroperoxide anion (HO_2^-), which is a deprotonated form of H_2O_2 in alkaline conditions, consequently the two reactions have a high potential to generate radicals by UV irradiation (eqs.6, 7) and fast depletion of hydrogen peroxide. This explains the higher optimal value of H_2O_2 under alkaline pH than in an acid medium.

$$OH^\bullet + OH^- \longrightarrow O^{\bullet-} + H_2O \qquad k = 1.2\times10^{10}\ M^{-1}\ s^{-1} \qquad (6)$$

$$OH^\bullet + HO_2^- \longrightarrow H^+ + O_2^{\bullet-} + OH^- \qquad (7)$$

The hydroxyl radical is overwhelmingly in the form of $OH^\bullet$ at acidic and neutral pH (the pKa of the couple $OH^\bullet/O^{\bullet-}$ is estimated at 11.9 [35]). At more acidic pH, $OH^\bullet$ is the form of the hydroxyl radical that predominates and reacts on organic matter by electrophilic attack.

The reactivity of the OTC with $OH^\bullet$ was proved to be speedy with the second-order rate constant raising from $6.02\times10^9\ M^{-1}\ s^{-1}$ to $3.74\times10^{10}\ M^{-1}\ s^{-1}$ when pH increased from 2.0 to 11.5 [4]. It indicates the mineralization of the OTC should be much more intensive in alkaline conditions than in acid/neutral conditions. This was due to the larger quantity of $OH^\bullet$, $O^{\bullet-}$, $O_2^{\bullet-}$ and singlet oxygen ($^1O_2$), produced by photolysis under alkaline conditions, and the increase of pH would lead to the increased molar absorption coefficient of hydrogen peroxide [36].

In UV/PS process, as pH increases from 3 to 8.5, the TOC decreases from more than 50% to about 20% (**Fig.5)**. According to Liu et al., the deprotonated form of OTC has a higher reactivity with $SO_4^{\bullet-}$ than the protonated and zwitterionic forms of OTC. The reactivity between OTC and $SO_4^{\bullet-}$ produced by PS photolysis, is fast based on the high second-order rate constants which decreased from $2.22\times10^{10}\ M^{-1}\ s^{-1}$ to $6.85\times10^9\ M^{-1}s^{-1}$ when the pH decreased from 11.5 to 2.0[26]. Under alkaline conditions, more recalcitrant metabolites were formed which lead to the decrease of mineralization rate in basic medium than acidic.

Also, the results indicated that UV/PS system has optimum oxidant concentration which is highly affected by the pH. Acidic conditions have a positive effect on the mineralization rate, compared to the alkaline medium. H^+ contributes to improve removal efficiency of OTC and byproducts when PS were coupled to UV-A.

However, the decline in removal rate of OTC in alkaline conditions could be attributed to the reactions between sulfate/hydroxyl radicals ($SO_4^{\bullet-}/OH^\bullet$) and hydroxyl ions ($OH^-$) due to their increase in basic pH conditions (eqs. 9 and 10) which can lead to the production of species with lower oxidation potentials, like $O^{\bullet-}$ which are also

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produced by reaction 10[37]. The hydroxyl radicals present in alkaline media (eq.10) could be scavenged by OH^- and $SO_4^{\bullet-}$ (eqs.10 and 11), causing a reduction of contaminant removal in comparison with acidic pH values[26][35][37][38][39].

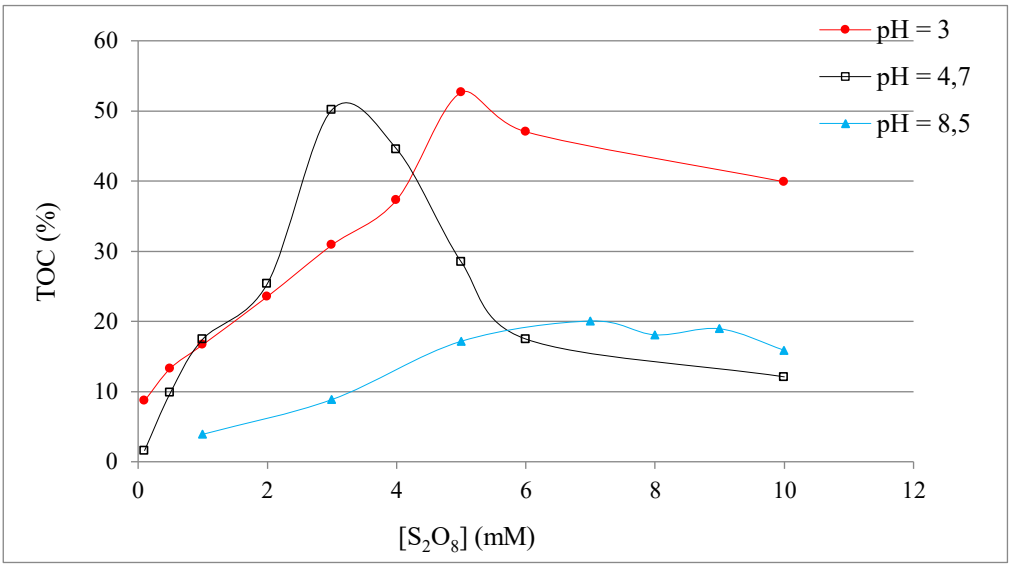

Fig.5 OTC mineralization, at different concentrations of PS, UV_{365}, [OTC] = 10 $mg.L^{-1}$, T ambient

$$SO_4^{\bullet-} + S_2O_8^{2-} \longrightarrow SO_4^{2-} + S_2O_8^{\bullet-} \qquad k = 1.2\times10^6\ M^{-1}\ s^{-1} \qquad (8)$$

$$SO_4^{\bullet-} + OH^- \longrightarrow SO_4^{2-} + OH^{\bullet} \qquad k = 7.3\times10^7\ M^{-1}\ s^{-1} \qquad (9)$$

$$OH^{\bullet} + OH^- \longrightarrow O^{\bullet-} + H_2O \qquad k = 1.2\times10^{10}\ M^{-1}\ s^{-1} \qquad (10)$$

$$SO_4^{\bullet-} + OH^{\bullet} \longrightarrow HSO_4^- + \frac{1}{2}O_2 \qquad k = 1 - 10\times10^9\ M^{-1}\ s^{-1}. \qquad (11)$$

By comparing the two systems (**Fig.4** and **Fig.5**), $HO^{\bullet}$ and $SO_4^{\bullet-}$ have different reactivity with OTC, and the difference of reactivity would lead to a different effect on degradation efficiency in $HO^{\bullet}$ and $SO_4^{\bullet-}$ based oxidation process. The mineralization of OTC by H_2O_2 and PS oxidants was clearly more efficient in the case of PS at different mediums pH. A remarkable improvement (50%) was observed in the OTC mineralization with the UV/PS system in acid pH and 20% for pH 8.5, however compared to UV/ H_2O_2 system, it has an opposite effect from 4 up to 16% of mineralization were obtained for pH 3 to 8.5 respectively, this remains a very low quantity of mineralization compared to UV/PS system. This enhancement might be related to the presence of both $OH^{\bullet}$ and $SO_4^{\bullet-}$ radicals in the solution from the efficient decomposition of PS by UV, and the highest oxidation potential of $SO_4^{\bullet-}$ radical than $OH^{\bullet}$[39], Which makes it much more effective than $OH^{\bullet}$ for the OTC removal.

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3.3. Mineralization of OTC in the different systems photo-Fenton and UV/PS/Fe^{2+}

It has been postulated that sodium persulfate ($Na_2S_2O_8$) can be activated by transition metal ions such as ferrous ion (Fe^{2+}) to produce a powerful oxidant known as the sulfate radical ($SO_4^{\bullet-}$) (eq. 12). For the photo-Fenton process, it is well known that $OH^{\bullet}$ can be generated by two techniques; (a) conventional Fenton type thermal chemistry for the Fe^{2+}/H_2O_2 system (eq. 13), (b) photosensitizing effect of $FeOH^{2+}$ and/or Fenton reaction caused by Fe^{2+} formed in situ (eqs. 14 and 15)

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{\bullet-} + Fe^{3+} + SO_4^{2} \quad (12)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \quad (13)$$

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + OH^{\bullet} \quad (14)$$

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{2+} + H^{+} + OH^{\bullet} \quad (15)$$

There was no significant mineralization of OTC by the UV irradiation alone **Fig.6** (1% mineralization); the mineralization of OTC resulted therefore only from a radical reaction, i.e., hydroxyl radical, in UV/H_2O_2 and UV/H_2O_2/Fe^{2+}(**Fig.6 (a)**) or sulfate radical, in UV/PS and UV/PS/Fe^{2+}(**Fig.6 (b)**). To improve the mineralization, the generation of radicals should be in sufficient quantity to interact with the organic compounds.

In the photo-Fenton process **(Fig.6 (a)),** the mineralization rate of OTC reached around 80%, otherwise than UV/H_2O_2 process that achieved only 7% of mineralization, owing to the limited quantity of H_2O_2. The improvement of the mineralization rate in the case of photo-Fenton was due to the presence of iron (eq.13) which increased the amount of hydroxyl radicals generated. Ferric ions Fe^{3+} can be in aqueous medium in the form of four complexes$[Fe(OH)_2]^{+}$, $[Fe_2(OH)_2]^{4+}$, $[Fe(H_2O)_6]^{3+}$ and $[Fe(OH)]^{2+}$. Several previous studies on Fe^{3+} speciation confirms that when the pH of the solution is close to a value of 3,$[Fe(OH)]^{2+}$ is the most predominant species among the four species mentioned above. Photolysis of Fe^{3+} in the form of $Fe(OH)^{2+}$ complex in a medium of a pH close to 3 leads to the formation of Fe^{2+}ions (eq.14) as well as hydroxyl radicals ($OH^{\bullet}$)(eq.15).

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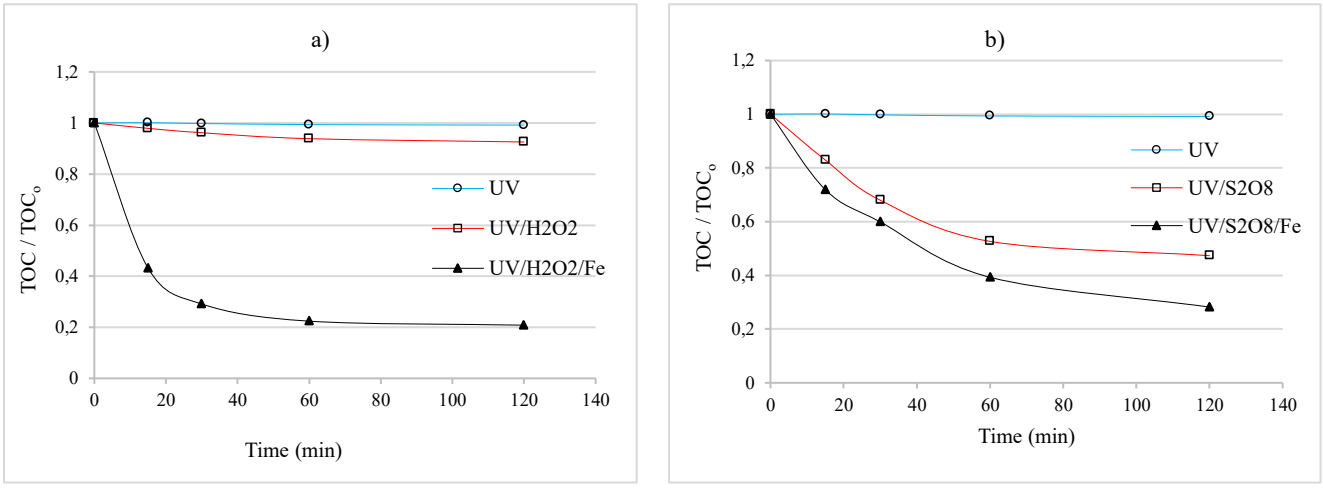

Fig.6 OTC mineralization at different processes, UV_{365}, [OTC] = 10 mg.L^{-1}, [H_2O_2] = 1 mM (a), [PS] = 5 mM (b), [Fe^{2+}] = 0.1 mM, pH = 3, T ambient

In **Fig.6.(b),** the mineralization rate of OTC between UV/PS and UV/PS/Fe^{2+}increased significantly when PS is coupled with UV and Fe^{2+} ions, reaching 72% in comparison to about 53% for the UV/PS system. This enhancement is related to the presence of both activators (Fe^{2+} and UV) which have an impact on the decomposition of PS and also the presence of both radicals $OH^{\bullet}$ and $SO_4^{\bullet-}$ in the solution[40]. The results confirm that the presence of both UV and Fe^{2+} are very effective in generation of reactive species[38].

It was found that the degradation was more efficient by UV/PS than by UV/H_2O_2(**Fig.6 (a)** and **(b)**), it is probably the result of the higher radical quantum yield of PS than H_2O_2under UV irradiation (eq.16 and eq.17) and also due to high absorption of UV, leading to higher formation of reactive radical species $SO_4^{\bullet-}$ and $OH^{\bullet}$.

$S_2O_8^{2-} + h\nu \longrightarrow 2SO_4^{\bullet-}$ ϕ = 1.4 (de-oxygenated), 1.8 (oxygen saturated) (16)

$H_2O_2 + h\nu \longrightarrow 2OH^{\bullet}$ ϕ = 1.0 (17)

However, the mineralization rate of the photo-Fenton process appeared higher than the UV/PS/Fe^{2+} process, most likely due to the higher production of $OH^{\bullet}$ by the combination of oxidant compounds (H_2O_2) and metallic catalysts(Fe^{2+}) in the presence of UV radiations.

3.3.1. Effect of the ferrous concentration

The initial iron concentration is an important parameter in the UV/H_2O_2/Fe^{2+}system; a series of experiments at pH = 3 (Recommended pH for photo-Fenton) was carried out to determine their effect and to optimize the concentration necessary to achieve better mineralization of OTC.

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Irrespective of the initial ferrous amount, a significant decrease in the TOC was quickly obtained during the first 10 minutes of the degradation process. The fast mineralization at the beginning of the reaction was attributed to the very rapid activation of oxidant by Fe^{2+}; a large number of radicals were immediately produced, and the reaction of radicals and pollutants occurred, leading to the sudden removal of the target pollutant (80 – 87% of mineralization). After the first hour, the mineralization rate decreased significantly (**Fig.7a** and 7**b**), probably due to a slower mineralization of the by-products and the reduction in the amount of oxidant.

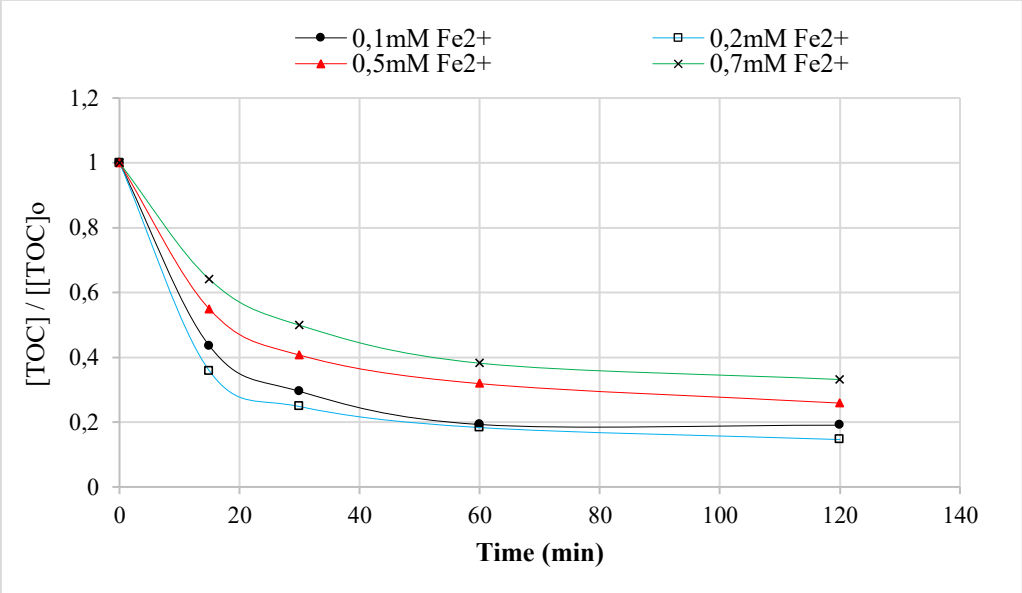

Fig.7a Effect of ferrous concentration, OTC mineralization, at different concentrations of Fe^{2+}, UV_{365}, [OTC] = 10 $mg.L^{-1}$, [H_2O_2] = 1 mM, pH = 3, T ambient

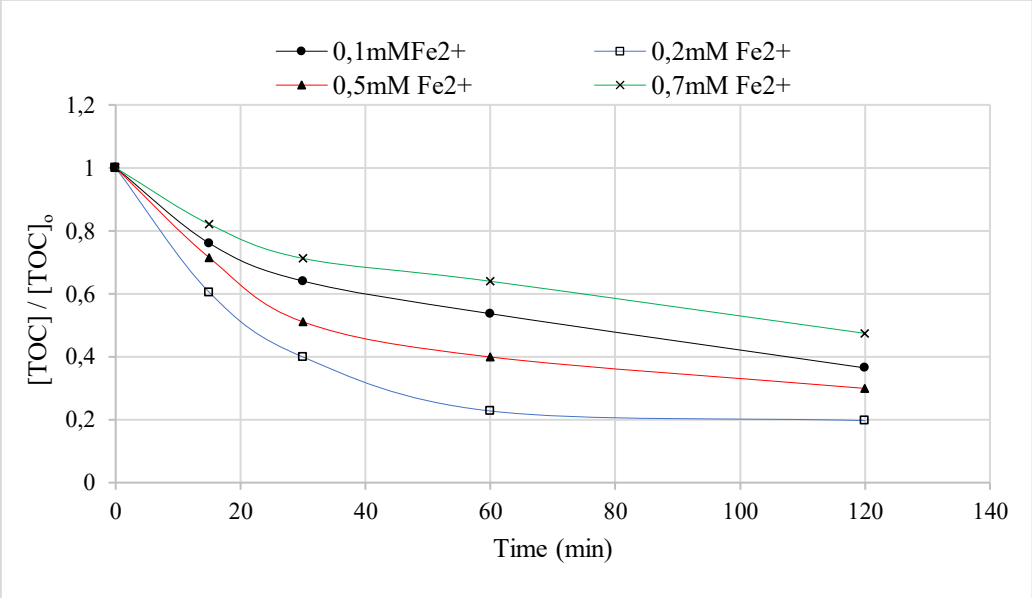

Fig.7b Effect of ferrous concentration, OTC mineralization, at different concentrations of Fe^{2+}, UV_{365}, [OTC] = 10 $mg.L^{-1}$, [PS] = 5 mM, pH = 3, T ambient

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In both systems, photo-Fenton and UV/PS/Fe^{2+}, the concentration of the Fe^{2+} catalyst accelerates the degradation kinetics until the value of $[Fe^{2+}] = 0.2$ mM, for which mineralization was optimal. Beyond this concentration, the increase in iron concentration decreased the rate of mineralization. This can be explained that the Fe^{2+} could recover radicals when the concentration of iron is in excess to give non-radical species (eq.18) and also probably due to the scavenging effect of the radicals itself (eq.19, eq.20)[12][39]. Meanwhile, the use rate of Fe^{2+} and oxidant may differ for the various target contaminants.

$$Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + HO^{-} \qquad k = 4\times10^{8}\ M^{-1}\,s^{-1} \qquad (18)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \longrightarrow S_2O_8^{2-} \qquad k = 4 - 8.1\times10^{8}\ M^{-1}\,s^{-1} \qquad (19)$$

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \qquad k = 5.3\times10^{9}\ M^{-1}\,s^{-1} \qquad (20)$$

The photo-Fenton process showed faster kinetics compared to the UV/PS/Fe^{2+} system **(Fig.7a** and **7b)**, that can be explained by the reaction rate constant of OTC with $OH^{\bullet}$ which is higher compared to the rate constant of OTC with $SO_4^{\bullet-}$ ($k_{OTC/SO4^{\bullet-}} = 6.85\times10^{9}\ M^{-1}s^{-1}$, $k_{OTC/OH^{\bullet}} = 7.18\times10^{9}\ M^{-1}s^{-1}$)[26][9]. Plus, the presence of many radicals in UV/PS/Fe^{2+}process induces the scavenging effect of radicals itself. According to Khan et al.[41], the energy of LUMO (Lower Unoccupied Molecular Orbital energy) depends on the oxidizing property of the oxidant. The lower energy of LUMO, the more easily accommodates and accepts an electron and higher will be its oxidizing property. The energy of LUMO of the PS oxidant is more than H_2O_2 (PS> H_2O_2) showing that H_2O_2 has a higher potential to oxidize organic pollutants.

3.4. Quantification of radicals

3.4.1. Hydroxyl Radicals in the presence of hydrogen peroxide as oxidant

The oxidation mechanism of Dimethyl sulfoxide DMSO by hydroxyl radicals was examined in many studies; Lee et al.[42], Bardouki et al.[20]. Two main ways can be considered, in fact, DMSO is first oxidized in methanesulfinate and in methyl radicals; the latter is in turn oxidized to formaldehyde. The methanesulfinate reacts very quickly with hydroxyl radicals (1.1 $mM.min^{-1}$ instead of 0.1 $mM.min^{-1}$ for DMSO under the same operating conditions) to produce the stable methanesulfonate intermediate. The kinetic constant for the reaction between DMSO and hydroxyl radicals is low ($0.8\times10^{7}\ M^{-1}s^{-1}$) compared to that of the methanesulfinate reaction with $OH^{\bullet}$ ($5.3\times10^{9}\ M^{-1}s^{-1}$). Monitoring the concentrations of methanesulfonate and formaldehyde during photodegradation may be a possible way to monitor $OH^{\bullet}$ concentration during the photochemical process.

In this study, hydroxyl radicals were photochemically formed from the reaction of hydrogen peroxide in presence of UV (eq.17), the reaction between hydrogen peroxide and ferrous ions (eq.13), and the reaction

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between ferrous ions and water in presence of UV (eq.15). Besides that, there are some reactions that can consume part of hydroxyl radicals, Such as, dimerization (eq.20) and oxidation of ferrous ions (eq.18).

The production of hydroxyl radicals during both UV/H_2O_2 and the photo-Fenton processes is presented in **Fig.8** and **Fig.9**. The formation of hydroxyl radicals in the photo-Fenton process (1 mM $H_2O_2 \simeq$ 2.3 mM $OH^{\bullet}$) was higher than that in the UV/H_2O_2 process (4 mM $H_2O_2 \simeq$ 0.1 mM $OH^{\bullet}$).The formation of $OH^{\bullet}$ in photo-Fenton results not only from photolysis of hydrogen peroxide (eq.17) but also from the reaction between iron and hydrogen peroxide (eq.13) and the reduction of Fe^{3+} to Fe^{2+}(eq.15) leading to a substantial amount of radicals and a complete disappearance of H_2O_2 in solution after 30min of reaction by Photo-Fenton (**Fig.10)**.

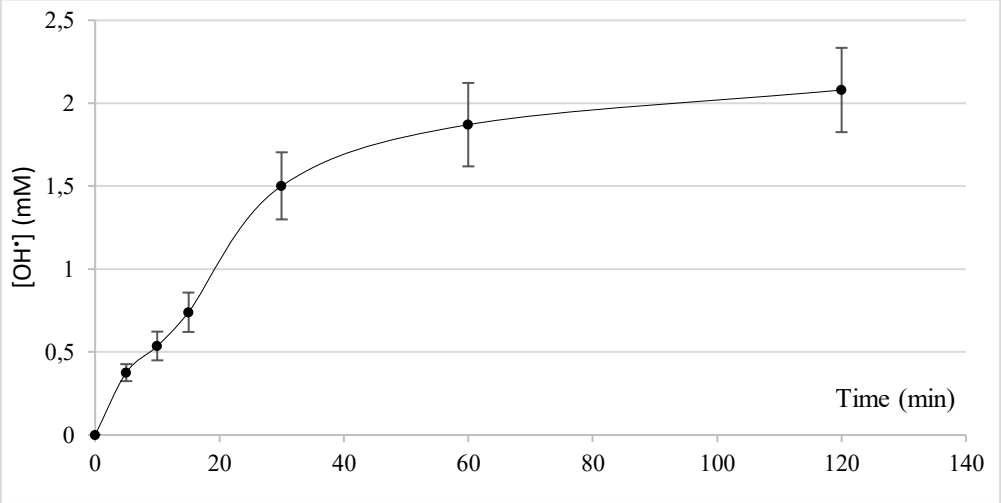

Fig.8 Evolution of production of hydroxyl radicals in photo-Fenton system, [H_2O_2] = 1 mM, [Fe^{2+}] = 0.2 mM, [OTC] = 10 mg.L^{-1}, pH = 3

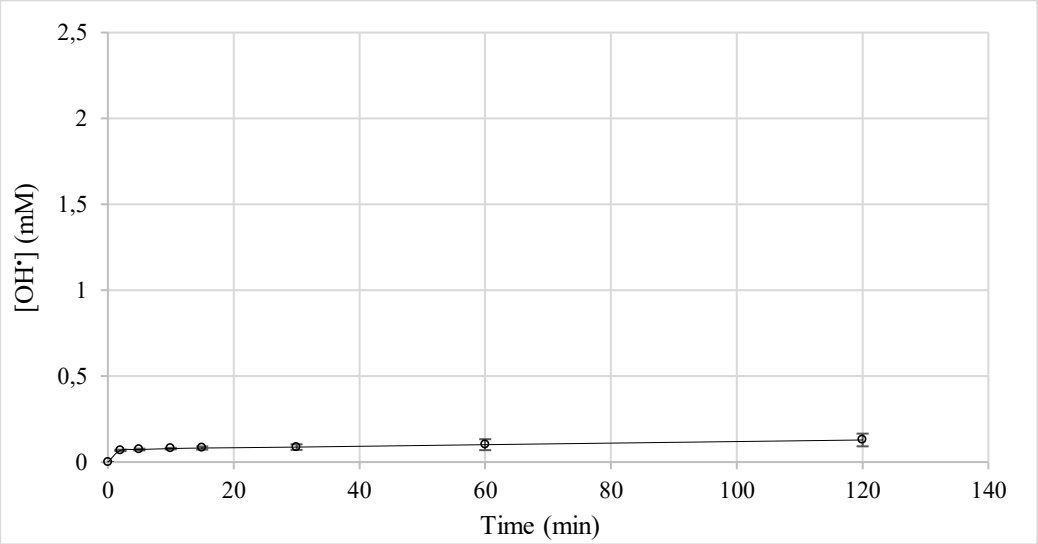

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Fig.9 Evolution of production of hydroxyl radicals in UV/H_2O_2 system, [H_2O_2] = 4 mM, [OTC] = 10 mg.L^{-1}, pH = 4.7

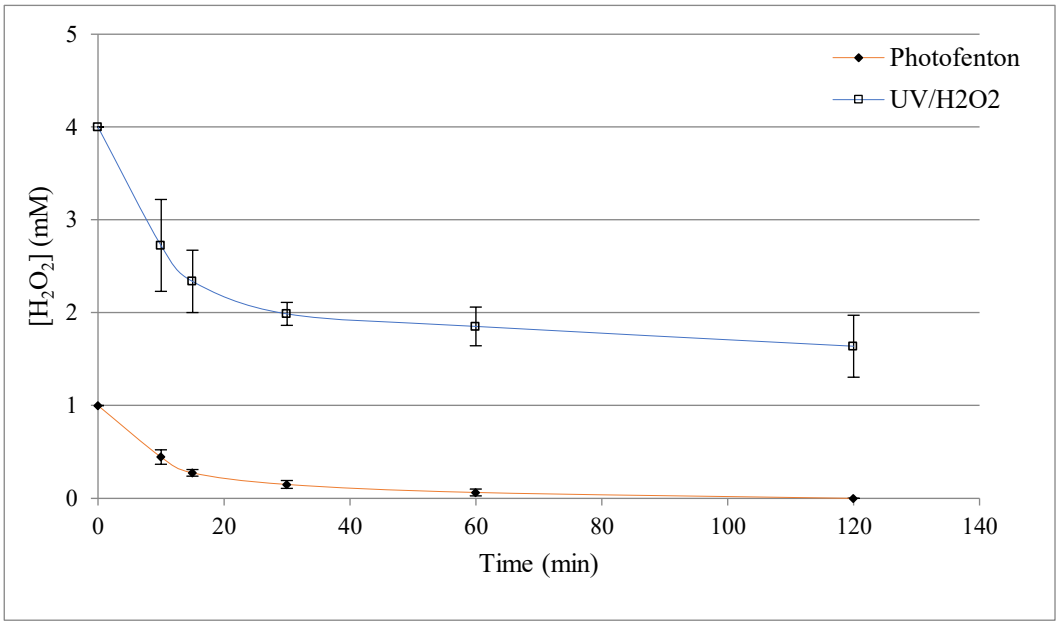

Fig.10 Evolution of hydrogen peroxide concentration during UV/H_2O_2 and photo-Fenton processes, [OTC] = 10 mg.L^{-1}

3.4.2. Radicals by Sodium persulfate process

To obtain more information on the degradation mechanism, inhibition studies using probes were carried out to identify the main radical species involved in the UV/PS and UV/PS/Fe^{2+} systems. Experiments were performed with a fixed initial concentration of 100 mM isopropanol, Tert-butanol and 1,4 Benzoquinone (BQ) to determine the contributions of $SO_4^{\bullet-}$, $OH^{\bullet}$ and $HO_2^{\bullet-}$/ $O_2^{\bullet-}$in the degradation of OTC at different pH values.

First, isopropanol was supposed to effectively capture $SO_4^{\bullet-}$ sulfate radicals and hydroxyl radicals $OH^{\bullet}$ by considering second-order rate constants[26][43]($k_{Isopr,SO4^{\bullet-}}$ = 7.42 x10^7 $M^{-1}.s^{-1}$, $k_{Isopr,OH^{\bullet}}$ = 1.9 x10^9 $M^{-1}s^{-1}$), while Tert-butanol is considered more selective towards hydroxyl radicals $OH^{\bullet}$, than sulfate radicals $SO_4^{\bullet-}$ [44][43] ($k_{Tert\text{-}b,\ OH^{\bullet}}$ = 6.0 x 10^8 $M^{-1}s^{-1}$, $k_{Tert\text{-}b,SO4^{\bullet-}}$ = 8.31 x 10^5 $M^{-1}s^{-1}$). Then, it is possible to estimate the percentage of radical scavenging by using the aqueous chemical concentration and the reactivity of the radicals with OTC (very high trapper concentration (100 mM)), except that the reaction of hydroxyl radicals with OTC was faster than with tert-butanol; so methanol was chosen for the trapping of $OH^{\bullet}$ radicals, ($k_{méthanol,OH^{\bullet}}$ = 1 x 10^9 $M^{-1}s^{-1}$)[43]. Also, the addition of 1.4 benzoquinone (that have two forms) caused inhibition by reaction with superoxide ($k_{BQ,HO2^{\bullet}/O2^{\bullet}}$ = 9.6 x 10^8 $M^{-1}s^{-1}$(eq.21))[45].

$$O_2^{\bullet-} + H^+ \longleftrightarrow HO_2^{\bullet} \qquad (pKa = 4.8) \qquad (21)$$

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In this work, the photo-oxidation reactions were performed at pH of 4.7 ± 0.2(initial unadjusted pH) for UV/PS and at pH 3 ± 0.05 for UV/PS/Fe^{2+}.

In the UV/PS system, $OH^{\bullet}$ and $SO_4^{\bullet-}$ are the main radicals formed in the solution. These radicals could be directly generated from the PS promoted by UVA irradiation (eq.16). **Fig.11** shows similar kinetics between the absence of a scavenger and the presence of benzoquinone (BQ), 23% of the degradation of OTC, was obtained. It can be consequently deduced that under UV, the persulfate oxidation does not produce $O_2^{-\bullet}$or $HO_2^{\bullet}$ radicals. Benzoquinone should not be used as a chemical probe in UV/PS system. In the presence of isopropanol, about 98% of OTC remained in the solution. A decrease in pH caused by UV irradiation of persulfate was remarked during the experiments (from 4.7 to 2.3); it could result in the transformation of $SO_4^{\bullet-}$ to $OH^{\bullet}$ (eq.22 and eq.9) and the release of H^+ ions. The very low OTC degradation observed could confirm that the $HO^{\bullet}$ and $SO_4^{\bullet-}$ generated, in acidic solution were trapped by isopropanol and methanol.

$$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + OH^{\bullet} + H^+ \qquad (22)$$

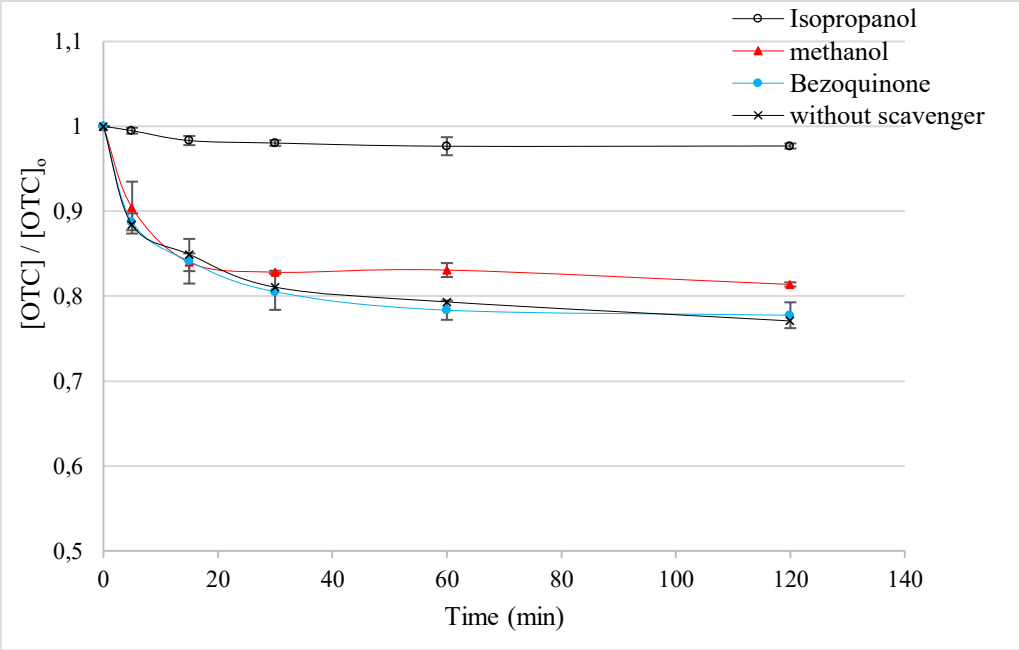

Fig.11 Kinetic removals of OTC at various conditions; isopropanol, Benzoquinone, methanol, pH = 4.7 ± 0.2, $[OTC]_o = 100\ mg.L^{-1}$; $[PS]_o = 3\ mM$

With methanol, 17% degradation was observed. So, it can be assumed that the difference observed in OTC degradation when trapping agents were used separately, should correspond to the contribution of $SO_4^{\bullet-}$ by 17% and 6% $OH^{\bullet}$, these were estimated at 74% and 26% respectively (**Fig.12**).

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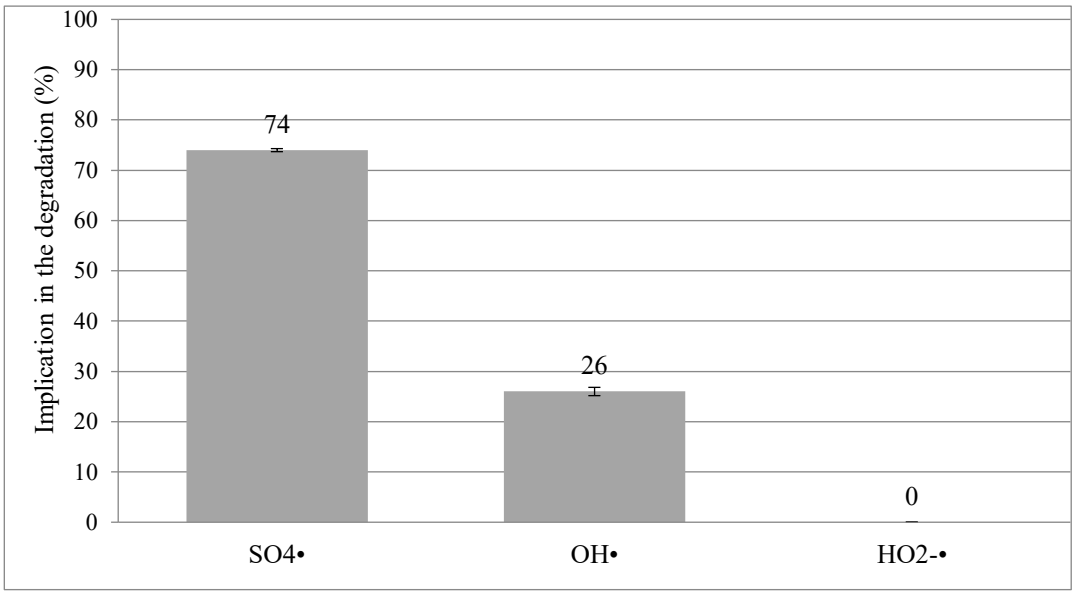

Fig.12 Effect of Isopr. Tert-butanol and Benzoquinone on system and distribution of different radicals at pH = 4.6 ± 0.2; $[OTC]_o$ = 100 mg.L^{-1}, $[PS]_o$ = 3 mM

Theoretically, the predominant radical species in UV/PS/Fe^{2+}system are $HO_2^{\bullet-}$, $SO_4^{\bullet-}$ and $OH^{\bullet}$. Scavenging studies using the same radical probes (in UV/PS system) were carried out. The benzoquinone is a good candidate as a probe to react with $HO_2^{\bullet-}$ radical. The detection and the role of $HO_2^{\bullet-}$ were estimated by comparing the difference between the photodegradation efficiency of OTC without scavenger and after adding excess BQ. The addition of an excess of BQ(100 mM) reduced the degradation of OTC by 30% compared to the system without free radical scavenger (**Fig.13**); this percent represents the contribution of $HO_2^{\bullet-}$ radical to OTC oxidation. The $HO_2^{-\bullet}$ radical, could be formed by the following reaction (eq.23)[46].

$$Fe^{2+} + HO_2 \longrightarrow Fe^{3+} + HO_2^{\bullet-} \qquad (23)$$

Adding to the reaction (eq.16) the superoxide anion radical leads to the formation of $SO_4^{\bullet-}$ and $OH^{\bullet}$ through the following reactions;

$$S_2O_8^{2-} + HO_2^{\bullet-} \longrightarrow SO_4^{\bullet-} + HO_2 + SO_4^{2-} \qquad (24)$$

Also, In the presence of iron, the formation of sulfate radicals increases by interaction with persulfate ion.

In the presence of Isopropanol, about 56% of OTC degradation was still observed; 23% inhibition was observed with methanol, therefore the contribution of radicals to OTC degradation was estimated to be 44%, 23% and 30% for $SO_4^{\bullet-}$,$OH^{\bullet}$, and $HO_2^{\bullet-}$ respectively (**Fig.14**).

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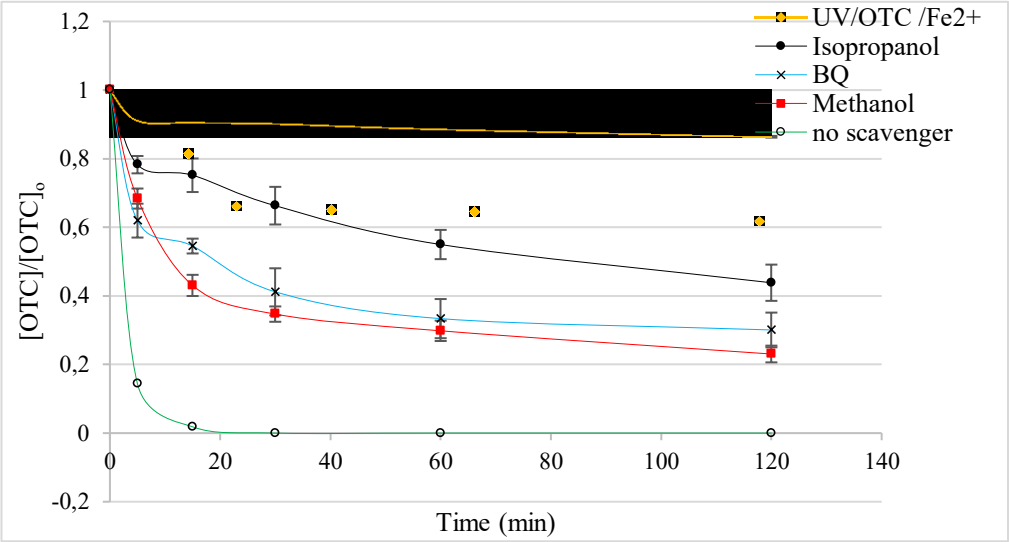

Fig.13 Kinetic removal of OTC at various conditions; pH = 3 ± 0.2, $[OTC]_o$ = 100 mg.L^{-1}; $[PS]_o$ = 5 mM , $[Fe^{2+}]$ = 0.2 mM

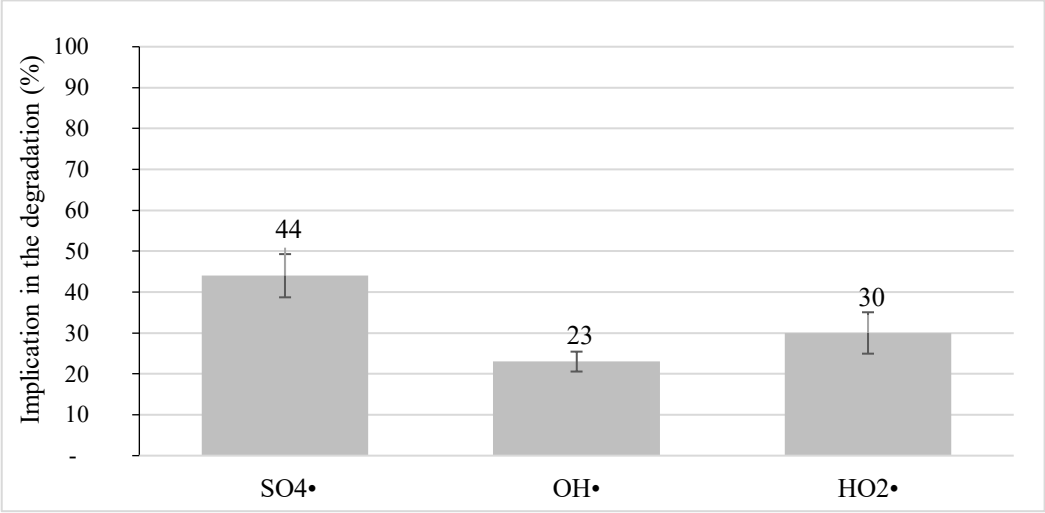

Fig.14

Effect of Isopr. Tert-butanol and Benzoquinone on system and distribution of different radicals at pH = 3 ± 0.2, $[OTC]_o$ = 100 mg.L^{-1}; $[PS]_o$ = 3 mM, $[Fe^{2+}]$ = 0.2 mM

4. Conclusion

In this study, different oxidants (H_2O_2, PS), activated by UVA irradiation, were tested to degrade the OTC antibiotic in aqueous solution, under specific pH conditions. The mineralization rate increased with the increasing initial oxidant concentration; beyond the optimal amount, an inhibition effect was observed. In the presence of H_2O_2, the mineralization rate increased with the pH, while it decreased for increasing pH in the presence of PS oxidant.

In the UV/H_2O_2 process under UVA radiations, the degradation and the mineralization of OTC were very weak. DMSO was used as a molecular probe in order to quantify the hydroxyl radicals, generated by H_2O_2 under UVA

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irradiation in the presence or absence of Fe, and elucidate their contribution in the OTC mineralization during the photochemical treatment. In photo-Fenton, $OH^{\bullet}$ are formed through two pathways: from photolysis of hydrogen peroxide and from the reaction between iron and hydrogen peroxide.

In photo-Fenton process, the maximum quantity of hydroxyl radicals was generate at 120 min under UV radiations with a large quantity of 2.3 mM of $OH^{\bullet}$; unlike in the UV/H_2O_2 process, where the amount of hydroxyl radicals was very low (0.025 mM of $OH^{\bullet}$) for even higher concentration of H_2O_2.

In the persulfate oxidation system, the mineralization was improved to 55%. It was shown that isopropanol, as an indirect technique, can be used in free radicals quantification and detection in photo-oxidation systems. The absence of superoxide radical $HO_2^{\bullet-}$ should be underlined and the radicals $SO_4^{\bullet-}$/$HO^{\bullet}$ are present simultaneously with respective contributions of 81% and 19%.

The reactions implied in UV/PS process can strongly be affected by the hydroxide anions which react with sulfate radicals (high oxidation potential) to obtain other radicals with lower oxidation potential.

Based on the comparison of UV/oxidant processes, it was suggested that UV/PS would be used under all pH conditions for destructing OTC.

By adding Fe^{2+} to UV/H_2O_2 and UV/PS systems, a significant increase of OTC mineralization rate and kinetic was observed. In photo-Fenton, the process was faster than in UV/PS/Fe^{2+}system.

The results show that $SO_4^{\bullet-}$ was the most involved radical in OTC mineralization in the different PS systems, with the following contributions: 44%, 30% and 23% for $SO_4^{\bullet-}$, $HO_2^{\bullet-}$ and $OH^{\bullet}$ in UV/PS/Fe^{2+} system, respectively. It was also observed that iron can be one of the inhibiting factors of OTC mineralization, if it exceeds the optimal concentration (0.2 mM) which is related to the amount of the pollutant and oxidant.

To summarize, the efficiencies of the various tested processes in OTC degradation and mineralization are as follows: UV/H_2O_2/Fe^{2+} > UV/PS/Fe^{2+}> UV/PS >UV/H_2O_2.

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Declarations

Conflict of interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by El khir Ouahiba, Chabani Malika, Amrane Abdeltif and Fourcade Florence. Paper editing& supervision by Assadi Aymen Amin. The first draft of the manuscript was written by ELkhir Ouahiba, Chabani Malika and Bouafia Souad and all authors commented on previous versions of the manuscript.

Consent for publication

All authors read and approved the final manuscript

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Availability of data and materials

Not applicable

Authors' information (optional)

Not applicable

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