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Homogeneous modified Fenton-like oxidation using Fe^{III}-gallic acid complex for ibuprofen degradation at neutral pH

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ABSTRACT

This study aims to find a green method for the degradation of organic pollutants in water treatment. We found that chemical oxidation is an effective process in the treatment of an aqueous solution contaminated by ibuprofen (IBP). To demonstrate the application of the modified Fenton-like process under neutral pH conditions, gallic acid (GA) was used as a complexing agent to solubilize iron in a neutral aqueous solution. Our results show that 90.9% complexation was obtained by Fe^{III}:GA ratio of 1:2 and stability constant of $\log\beta = 11.66$ at pH 7. The catalytic activation of the Fe^{III}-GA complex was initiated by the addition of 5 mM of hydrogen peroxide (H_2O_2) to the neutral medium. The reduction of Fe^{III} was instantaneous and consequently, the degradation of IBP was achieved by the formation of the hydroxyl radicals ($^{\bullet}OH$) generated during the Fenton-like reaction. All experiments were performed at natural conditions of temperature with an initial IBP concentration of 0.05 and 0.1 mM of Fe^{III}-GA complex at pH 7. The effect of solution pH, temperature, dosage of H_2O_2, dosage of IBP, and dosage of Fe^{III}-GA complex on the degradation efficiency was also studied. An important degradation was obtained by choosing the initial doses of 5 mM H_2O_2 and 0.1 mM of the Fe^{III}-GA complex. IBP oxidation rates are found to be directly proportional to the increase of environmental temperature. The total organic carbon experiments showed mineralization of 88.81% of the organic carbon of IBP after 24 h of treatment in the presence of Fe^{III}-GA complex. This work enriches academic knowledge on the feasibility of degrading IBP based on the organic iron complex as a possible green technology.

Keywords: Ibuprofen; Chemical oxidation; Neutral medium; Fe^{III}-GA complex; Hydroxyl radicals

1. Introduction

Pharmaceutical products represent an emerging group of pollutants threatening our waterways and damaging our aquatic ecosystem. Several studies have been conducted by scientists raising public awareness of the presence of traces of pharmaceutical pollutants in aquatic environments. These pollutants can come from hospital waters, pharmacies, or human faeces that contains the residue of pharmaceutical products. The majority of these compounds are not biodegradable. One of the most important classes of pharmaceutical products are anti-inflammatory drugs such as ibuprofen (IBP). IBP has been proven effective in the treatment of pain disease, fever, migraine as well as rheumatic disorders [1,2]. Because of its increased consumption, this product often appears in water treatment stations as well as in surface and drinking water. For example, concentrations of 25–475 µg L^{-1} were found in treatment stations in England and Wales [3]. Other references also report concentrations ranging between 12.13 and 373.11 µg L^{-1} of IBP in wastewater in Seville, Spain [4].

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Several studies have been conducted on the eco-toxicity risks of IBP on living organisms. The results reported by Han et al. [5] show that the exposure of 10^{-4} mg L^{-1} of IBP threatens the survival of Lacy Oryzias [5]. Although no acute toxic effects of IBP on human beings have been reported, its elimination is still critical and essential in water treatment. Since wastewater treatment plants do not generally include the degradation of pharmaceutical compounds, it is necessary to find other effective processes. Advanced oxidation processes (AOPs) can be considered as powerful methods and good alternatives for the degradation of these pollutants due to their ability for removing almost all organic contaminants [6–10].

Different processes have been applied on the degradation of IBP, such as Fe^{2+}/Oxone/UV [11], PAN-MWCN, TiO_2-NH_2/UV [12], carbon/TiO_2/UV [13], BiOI-deposited TiO_2/UV [14], Fe^{3+}/H_2O_2/UV [15], Fe^{2+}/H_2O_2/UV [16], Cl_2/UV [17], Fe^{2+}/H_2O_2 [18]. The Fenton reagent Fe^{2+}/H_2O_2 has been effective in the degradation of major organic pollutants in wastewater, drinking water, industrial, agricultural rejects, surfactants, and polluted soils. The formation of hydroxyl radicals, which are responsible for the oxidation of organic pollutants, is formed by Fenton reaction in an acidic medium according to Eq. (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \quad (1)$$

Iron salts were widely used as a catalyst in Fenton's reaction because of their bioavailability in the environment. Its catalytic activity decreases with increasing pH due to the precipitation of iron above pH = 3. In order to obtain soluble iron species over a wider pH range, organic chelating agents (CA) such as nitrilotriacetic acid (NTA), and ethylenediamine-N,N′-disuccinic acid (EDDS) are generally introduced into the system producing what is called a modified Fenton-like process. However, the addition of these complexing agents may have adverse effects on the environment due to their low biodegradability [19,20].

The initiation of the modified Fenton-like reaction at neutral pH is similar to the initiation of the conventional Fenton-like reaction at acidic pH [21]:

$$Fe(III) + CA \rightarrow Fe(III) - CA \quad (2)$$

$$Fe(III) - CA + H_2O_2 \rightarrow Fe(II) - CA + HO_2^\bullet / O_2^{\bullet-} + H^+ \quad (3)$$

$$Fe(III) - CA + HO_2^\bullet \rightarrow Fe(II) - CA + H^+ + O_2 \quad (4)$$

$$Fe(III) - CA + O_2^{\bullet-} \rightarrow Fe(II) - CA + O_2 \quad (5)$$

$$Fe(II) - CA + H_2O_2 \rightarrow Fe(III) - CA + HO^- + HO^\bullet \quad (6)$$

In order to work under neutral pH conditions, several studies have been carried out to find other chelating ligands that are non-toxic, environmental friendly and can form soluble organic complexes [22–26]. In this work, gallic acid (GA) was used as a complexing agent, because it fulfills all of those criteria and is very abundant in natural environments [27,28]. For these reasons, GA has been applied in various AOPs. Yunfu Sun and Pignatello [29] tested the ability of GA to solubilize Fe^{III} at pH 6 and catalyze the oxidation of 0.1 mM of 2,4 dichlorophenoxyacetic acid (2,4-D) with 10 mM hydrogen peroxide in an aerated aqueous solution. The degradation of 2,4-D was found to be much faster compared with other organic acids, where 15 min was sufficient for a total degradation of 2,4-D. Dong et al. [27] studied the effect of GA on the discoloration of methyl orange (MO) by the Fenton process at pH = 4; the rate of degradation of MO in the Fe^{III}/H_2O_2 system with GA was significantly higher than that of sulfuric acid at the same pH.

In the neutral medium, recent studies introduced the organic iron complex system as a new AOP used to treat wastewater [20,30]. However, no studies have reported the use of GA as an iron-catalyzed chelating agent. This work is the first to use Fe^{III}-GA/H_2O_2 system for the treatment of a persistent pharmaceutical product (IBP) in the absence of light. The main objective of this work is to study in depth the removal of aqueous IBP by modified Fenton-like process under neutral pH conditions using non-toxic components that exist in natural aquatic environments. The effect of various factors such as pH, temperature, initial concentration of H_2O_2, initial concentration of IBP, initial concentration of Fe^{III}-GA complex and its molar ratio on the degradation of IBP induced by the Fe^{III}-GA complex was evaluated. The involvement of hydroxyl radicals as a scavenger in the Fe^{III}-GA/H_2O_2 system was also examined.

2. Materials and methods

2.1. Chemicals

All chemicals used in this work were of reagent grade. The chemicals used in the mobile phase for HPLC (acetonitrile) were obtained from CARLO ERBA Reagents, (Italy). The catalyst anhydrous iron(III) chloride ($FeCl_3$) 97% and chelating agent (gallic acid) 99.5% were obtained from Sigma-Aldrich, (Germany). Hydrogen peroxide solution (H_2O_2) 30% and auxiliary chemical for initial pH value adjustments (sodium hydroxide (NaOH)) 99% were purchased from VVWR Chemicals Prolabo, (Spain). Ibuprofen sodium (natrium) (IBP, 98%), which was used as a compound model, was sourced from SiSigma-Aldrich, (Germany)

2.2. Synthesis of Fe^{III}-GA complex

Ferric iron solution (10 mM) was prepared freshly and daily by dissolving $FeCl_3$ in 0.1 M HCl to minimize iron(III) hydrolysis and polymerization [31]. The iron chelate solution was prepared by directly mixing the ferric ion solution (10 mM) with a solution of gallic acid (5 mM) in ultrapure water. Then, after approximately 1 h of stirring, the pH of the mixture was slowly adjusted to 7 with NaOH (1 M).

2.3. Experimental setup and procedure

All experiments were performed in the absence of light. The solution was mixed using a magnetic stirrer. The reaction was initiated by adding H_2O_2, and initial concentrations of Fe^{III} (0.1 mM) and H_2O_2 (5 mM) were used. The same concentration of IBP (0.05 mM) was used to be able to compare the degradation rates of the classical

Fenton-like system at acidic pH = 3 (Fe^{III}/H_2O_2) and the modified Fenton-like at neutral pH = 7 (Fe^{III}-GA/H_2O_2).

2.4. Analytical methods

2.4.1. High-performance liquid chromatography analysis

The concentration of IBP was quantified by the high-performance liquid chromatography (HPLC) Shimadzu LC-10AT operating in isocratic mode (HPLC Shimadzu LC-10A Equipment, Japan). The HPLC column was used as an LC-18 reversed-phase column (25 cm, 4.6 mm, 5 µm), the mobile phase was composed of acetonitrile/water (60/40, v/v) with 0.01% of acetic acid. The wavelength of the UV detector was set at 222 nm and the flow rate was kept at 1.0 mL min^{-1}.

2.4.2. Spectroscopy and pH meter equipment

The UV–visible spectra of the Fe^{III}-GA complex are recorded by a spectrophotometer (Thermo Scientific, Germany) controlled by Thermo Insight software. The solution pH was adjusted by 1.0 M of NaOH and measured using a HANNA, (Germany) 8521 type pH meter.

2.4.3. Dosage method of iron(II)

Fe^{II} contained in the samples was determined by using the 1,10-phenanthroline method. Ferrous iron forms with 1,10-phenanthroline a red-colored complex, and the absorption of this complex was measured at 510 nm by a spectrophotometer.

2.4.4. Quantification of •OH radicals

The •OH radicals generated during the IBP degradation by the modified Fenton-like process were measured quantitatively by using benzene as a scavenger. Hydroxylation of benzene at high concentrations allows detection of almost all •OH radicals due to the high reactivity of benzene with hydroxyl radicals ($k = 8 \times 10^9\ M^{-1}\ s^{-1}$) [32]. For this purpose, 7 mM of benzene was used to scavenge •OH radicals in an aqueous solution [33], quantitatively producing phenol. A HPLC Shimadzu LC-10A Equipment, (Japan) with a UV–visible detector set at 270 nm, using a mobile phase composed of water and acetonitrile 70/30 (v/v) with a flow rate of 1.0 mL min^{-1}, was used to quantify the phenol generated.

2.4.5. Total organic carbon

The follow-up of the pollutant mineralization was quantified using the total organic carbon (TOC) parameter. A Teledyne Tekmar (TOC Torch Teledyne Tekmar Analyser, USA) apparatus was used, equipped with an oxygen gas detector, an automatic sample injector and calibrated with standard solutions of potassium hydrogen phthalate.

3. Results and discussion

3.1. Spectroscopic characterization of iron(III)-gallic acid complex at neutral pH

3.1.1. UV–vis spectroscopy

To highlight the role of the iron(III)-gallic acid (Fe^{III}-GA) complex in the degradation of IBP, the UV-vis spectroscopy was used to study the basic properties of this compound. Since GA carries the galloyl group, it has been reported to have the ability to form a complex with iron with a binding constant of GA to iron was 4.78 M^{-1} [34]. In fact, similar results were observed in our UV-vis spectroscopy analysis. Fig. 1 shows that GA has an absorbance band at 260 nm in the UV range. The addition of a small volume of a concentrated Fe^{III} solution to a GA solution causes a bathochromic shift of this band; however, another wide band is formed at 550 nm. In fact, a dark blue color appears, attributing to the formation of a Fe^{III}-GA complex at free pH = 2.68. Furthermore, when the Fe^{III}-GA complex is adjusted to a neutral pH value by NaOH (1.0 M), an intense and deep purple color was observed with the appearance of a new absorbance band in the visible region. This band was absent in the case of GA alone. The UV–visible spectrum of the Fe^{III}-GA complex shown in Fig. 1 illustrates the presence of two characteristic bands indicating the formation of the Fe^{III}-GA complex at pH 7. The most intense band absorbs in the UV range with λ_{max} = 288 nm. The figure in the inset shows the UV–visible absorption spectrum of the difference [Fe^{III}-GA – Fe^{III}] of an aqueous solution containing GA and Fe^{III} at neutral pH. This difference is not identical and differs significantly from that of the acid alone for the same pH, indicating that an interaction between the metal and the ligand has occurred. Indeed, the significant change in the spectrum's shape is a clear indication for the formation of Fe^{III}-GA complex.

3.1.2. Molar ratio of the iron(III)-gallic acid complex

The stoichiometric composition of the Fe^{III}-GA complex formed by Fe^{III} and GA was carried out by the molar ratio method, which involves testing a series of iron chelates. The concentration of Fe^{III} was kept constant at 0.1 mM and the acid concentration was increased from 0 to 0.5 mM. The solution was left under agitation to allow the formation of the complex and then the pH was adjusted to neutral values

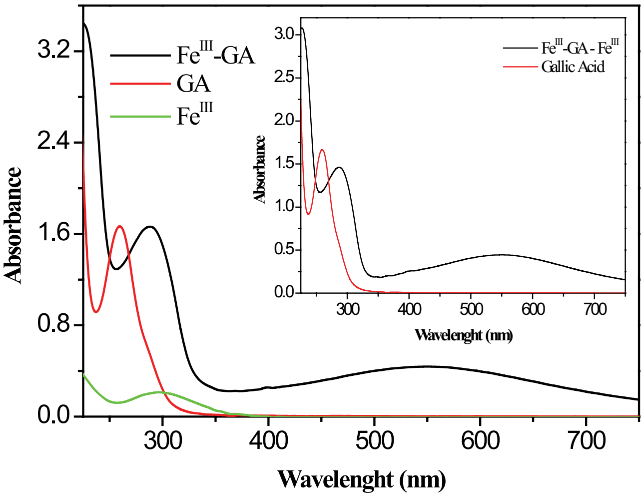

Fig. 1. UV–visible absorption spectrum: GA (0.2 mM), Fe^{III} (0.1 mM) and the Fe^{III}-GA complex (0.1 mM), pH = 7.0 ± 0.1. Insertion: UV–visible absorption spectrum of the difference [Fe^{III}-GA – Fe^{III}], pH = 7.0 ± 0.1.

(pH = 7). Fig. 2 shows the UV–visible absorption spectra of mixtures of GA and Fe^{III} in neutral aqueous solutions.

The 550 nm band was chosen as the characteristic absorbance band of the Fe^{III}-GA complex. The organic fraction no longer absorbs at this wavelength, and Fe^{III} is found in the form of a precipitate Fe(OH)$_3$ at pH 7. The evolution of absorbance at 550 nm has increased with increasing GA concentration; however, the absorbance has become stable when the concentration of GA reaches 0.2 mM, as shown in Fig. 3. It can be concluded that Fe^{III} was completely complexed with a stoichiometric ratio of 1:2. These results are in agreement with those mentioned in the literature [35–37].

Iron is generally found in two forms in solutions characterized by the molar ratio Fe:L. The soluble chelated form is present in significant amounts, while the uncomplexed free iron is present as a precipitate. The soluble chelated form can be measured by the phenanthroline spectrophotometric method. Measurements of the ferrous iron content were carried out after filtration using filter syringes with a pore size of 0.45 µm in order to avoid errors in the measurement of the precipitate fraction.

The total iron content was measured after the addition of ascorbic acid (0.15 mM), which was used as a reducing agent to ensure the total reduction of ferric iron. This concentration was determined after testing several values ranging from 0.025 to 0.5 mM by which the total reduction of ferric iron was obtained. The experimental results presented in Fig. 4 confirmed that the stoichiometric ratio Fe^{III}:GA 1:2 is sufficient to obtain 90.9% Fe^{III} chelated.

3.1.3. Stability of Fe^{III}-GA complex

Monitoring the stability of the complex is important to ensure its formation when competing ions are present during the degradation reaction of the pollutant. While studying the stability of Fe^{III}-GA solution stored in the dark and at 4°C temperature for 1 week, no evolution was observed in the absorption spectra. The stability constant of the Fe^{III}-GA complex was calculated, using the relationship [38]:

$$\log \frac{A_i}{A_{\max} - A_i} = \log \beta + n \log C_L \tag{7}$$

where A_i is the corresponding absorbance for the molar ratios tested, $A_{\max}$ is the maximum absorbance of the complex Fe^{III}-GA at 550 nm, β is the stability constant, and C_L is the concentration of the ligand (GA) corresponding to each A_i. The results are obtained from Fig. 5 and grouped in Table 1.

3.2. Comparison of degradation of IBP by Fe^{III}/H$_2$O$_2$ (pH 3) and Fe^{III}-GA/H$_2$O$_2$ (pH 7)

Ferrous species play a key role in the overall rate of H$_2$O$_2$ decomposition and degradation of organic pollutants, which are present in the aquatic media by Fenton-type reactions because the decomposition of H$_2$O$_2$ by Fe^{II}/

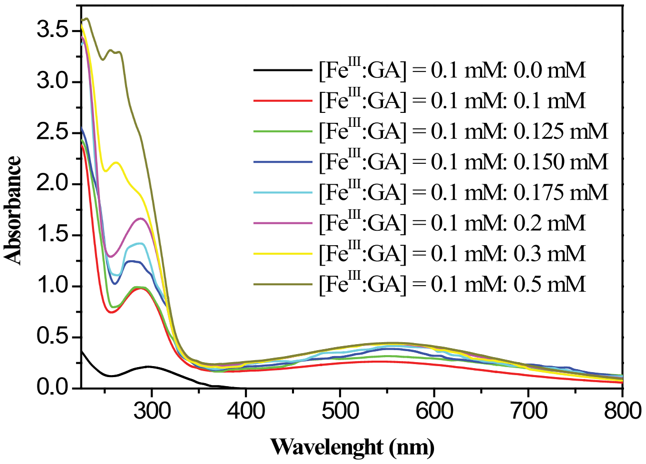

Fig. 2. UV-visible spectra of GA and Fe^{III} mixtures in aqueous solution at pH = 7.0 ± 0.1.

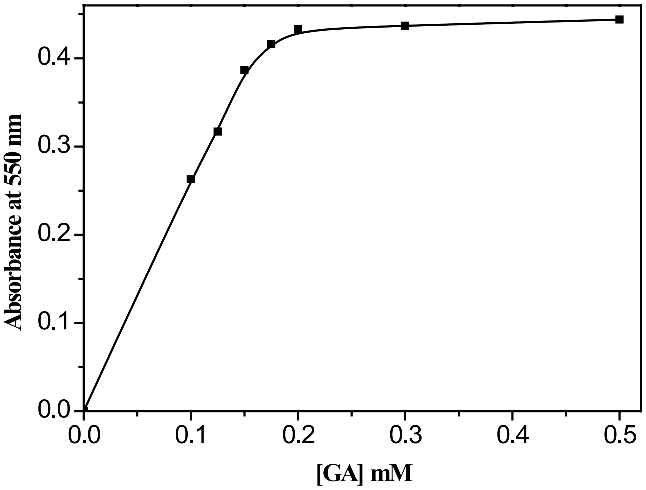

Fig. 3. Evolution of the absorbance at 550 nm as a function of the GA concentration.

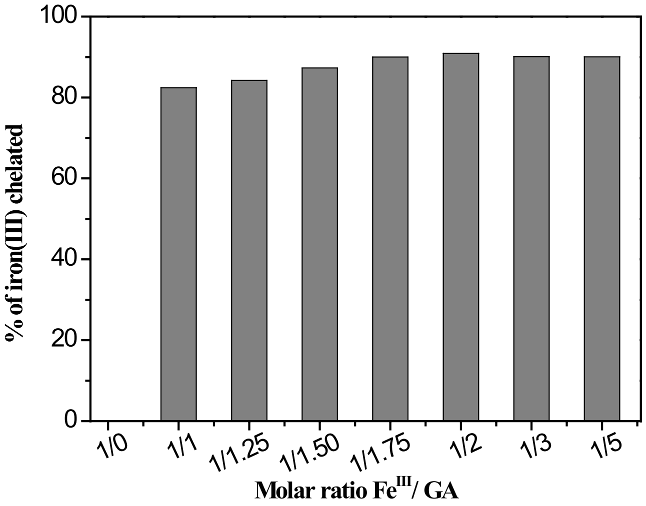

Fig. 4. Percentage of iron chelates formed with several Fe^{III}:GA molar ratio tested.

Fe^{III} represents the unique source of hydroxyl radicals $HO^\bullet$. Given the greater complexing capacity of GA, it is necessary to clarify its role in the Fenton-like system. Fig. 6a presents a comparison between two different systems of IBP degradation using the Fe^{III}/H_2O_2 process in the presence and absence of GA in neutral and acidic media (pH 7 and pH 3), respectively. It turns out that the reaction kinetics in the classical Fenton-like system with 0.1 mM Fe^{III} at acidic pH is different from that of the modified Fenton-like with 0.1 mM Fe^{III}-GA complex at pH 7. In the classical Fenton-like process, IBP degrades rapidly in the early times reaching a maximum removal of 84.68% after 1 h of reaction, and then it slows down in the second phase. However, in the presence of Fe^{III}-GA complex, higher efficiency with disappearance of 95.96% was obtained after 5 h of reaction.

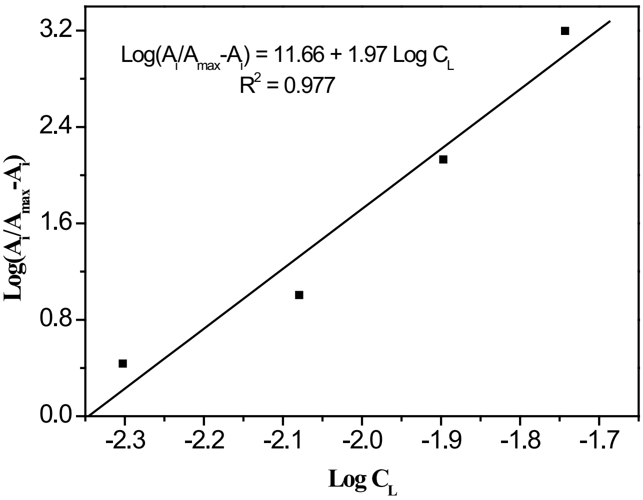

Fig. 5. Stability constant of the complex Fe^{III}-GA (0.1 mM) formation at pH = 7.0 ± 0.1.

Table 1
Molar ratio, percentage of iron chelated and stability constants of Fe^{III}-GA complex

Complex	Fe^{III}-GA
Stoichiometry	1:2
% Iron chelated	90.9%
logβ (this work)	11.66
logβ (literature)	11.4 ± 0.1 [39]

The difference in oxidation rates between the two processes can be explained by the high reactivity of the ferrous species at pH 3. Furthermore, in the case of a modified Fenton-like system, hydroxyl radicals play a double role by oxidizing GA in the complex and IBP together. The reaction rate constants of these species and the hydroxyl radicals were estimated to be $k_{HO^\bullet/GA} = 11 \times 10^9\ M^{-1}\ s^{-1}$ and $k_{HO^\bullet/IBP} = 3.11 \times 10^9\ M^{-1}\ s^{-1}$ [40,41]. This is in line with results reported by Christoforidis et al. [42] indicating that the intermediate products of the oxidation of GA in the complex with the Fenton system improve the degradation efficiency of the pollutant. Additionally, Fig. 6b indicates that the formation of hydroxyl radicals in the classical Fenton-like system was carried out in two phases in which the $HO^\bullet$ forms rapidly at the beginning of the reaction reaching a maximum of 0.77 mM after 2 h of reaction. In the second phase, the $HO^\bullet$ concentration is approximately constant; this is due to the decomposition of hydrogen peroxide by the Fenton reagent leading to the reduction of Fe^{III} [Eq. (1)]. Although the rate of $HO^\bullet$ formation is slow using the modified Fenton-like process, $HO^\bullet$ radicals continue to form significantly during the IBP removal and reach a maximum of 0.81 mM after 5 h of reaction. As mentioned above in reaction rate constants, the GA alone does not only form complex with Fe^{III} and prevent its precipitation, but also accelerates the reduction of Fe^{III} to promote the formation of $HO^\bullet$ [27]. This experiment confirms that iron(III) organic complexes offer the possibility for the Fenton-like reaction to operate at pH levels suitable for the environment.

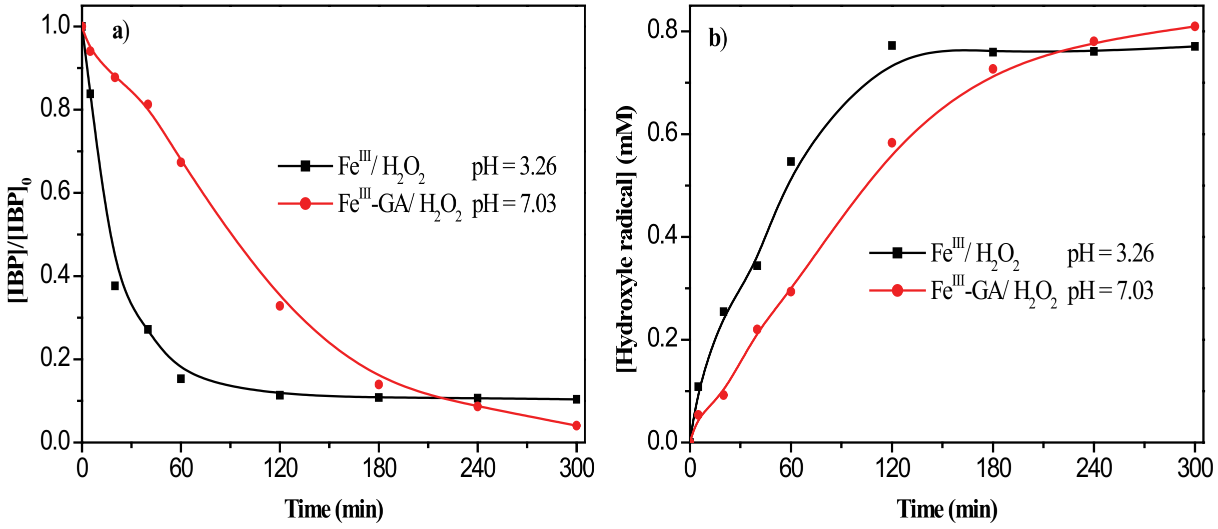

Fig. 6. (a) Comparative study between classical Fenton-like and modified Fenton-like for the degradation of IBP (0.05 mM), H_2O_2 (5 mM), T = 25°C and (b) hydroxyl radicals formation.

3.3. Effect of H_2O_2 concentration on IBP degradation

In order to clarify the influence of H_2O_2 concentration on the degradation of IBP; experiments were performed at pH 7 and room temperature 25°C using increasing concentrations ranging from 1 to 50 mM in the presence of 0.1 mM Fe^{III}-GA. According to the results obtained in Fig. 7, in the case of the absence of H_2O_2, no elimination of IBP was observed. However, in the presence of H_2O_2, the oxidation rate of IBP is proportional to the increase in hydrogen peroxide concentration. Indeed, the degradation efficiency of IBP increased quickly from 55.48% to 99.78% with the increase in H_2O_2 concentration from 1 to 50 mM after 2 h of reaction time. In addition, the rate constant k was estimated to be from 6.65×10^{-3} to 5.35×10^{-2} min^{-1} in the studied range from 1 to 50 mM during the same reaction times. The reaction constant obtained at 50 mM was eight times higher than that obtained at 1 mM. Moreover, the increase in the rate of IBP removal is due to the important consumption of $^{\bullet}OH$ radicals generated while increasing H_2O_2 concentration in the studied range. These results can be explained by the fact that hydroxyl radicals react more positively with IBP than with hydrogen peroxide. In fact, the reaction rate constant of IBP and $^{\bullet}OH$ was higher to that obtained between $^{\bullet}OH$ and H_2O_2 and was estimated at $k_{HO^{\bullet}/IBP} = 3.11 \times 10^9$ M^{-1} s^{-1} and $k_{HO^{\bullet}/H_2O_2} = 2.7 \times 10^7$ M^{-1} s^{-1} [20,41]. Therefore, the use of high concentrations of H_2O_2 increases the rate of IBP elimination and consequently the production of hydroxyl radicals responsible for pollutant destruction.

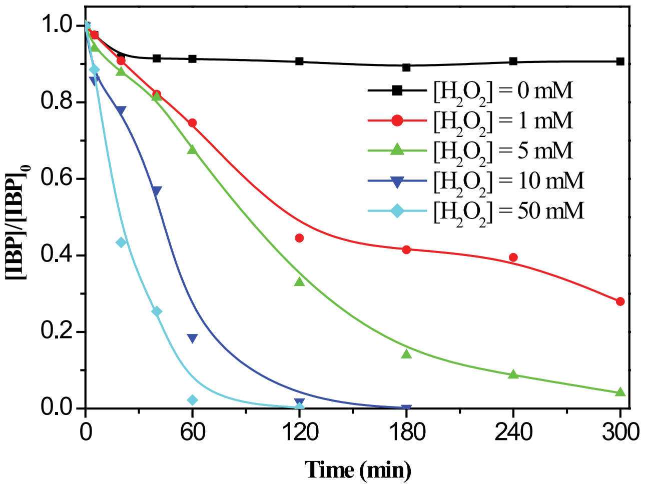

Fig. 7. Effect of H_2O_2 concentrations on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system (0.1 mM), pH = 7.0 ± 0.1, T = 25°C.

3.4. Effect of Fe^{III}-GA complex concentration

To evaluate the role of the iron(III)-gallic acid complex, the effect of its concentration on 0.05 mM IBP degradation was examined at different doses from 0 at 0.5 mM, using 5 mM of H_2O_2 at neutral medium and room temperature 25°C. In accordance with the results shown in Fig. 8a, no disappearance of the pollutant was observed in the absence of the Fe^{III}-GA complex, and this is because IBP does not undergo any complexing and/or oxidation with hydrogen peroxide. However, a great correlation was observed between IBP destruction and the presence of the Fe^{III}-GA complex in the concentration range studied from 0.05 to 0.1 mM. Indeed, the removal of IBP with 0.05 mM Fe^{III}-GA reached 80.99% after 300 min of reaction, while 95.96% was obtained with 0.1 mM; however, a slowdown in the degradation process for the higher doses was observed.

On the other hand, according to the results shown in Fig. 8b, the ferrous iron formed acts similarly to the removal reaction of IBP. Indeed, the formation of Fe^{II} is rapid and important whatever the starting concentration of the complex. It is characterized by the presence of an induction phase where significant concentrations were observed at the beginning of the reaction, which is probably due to the redox cycle of iron. A second phase

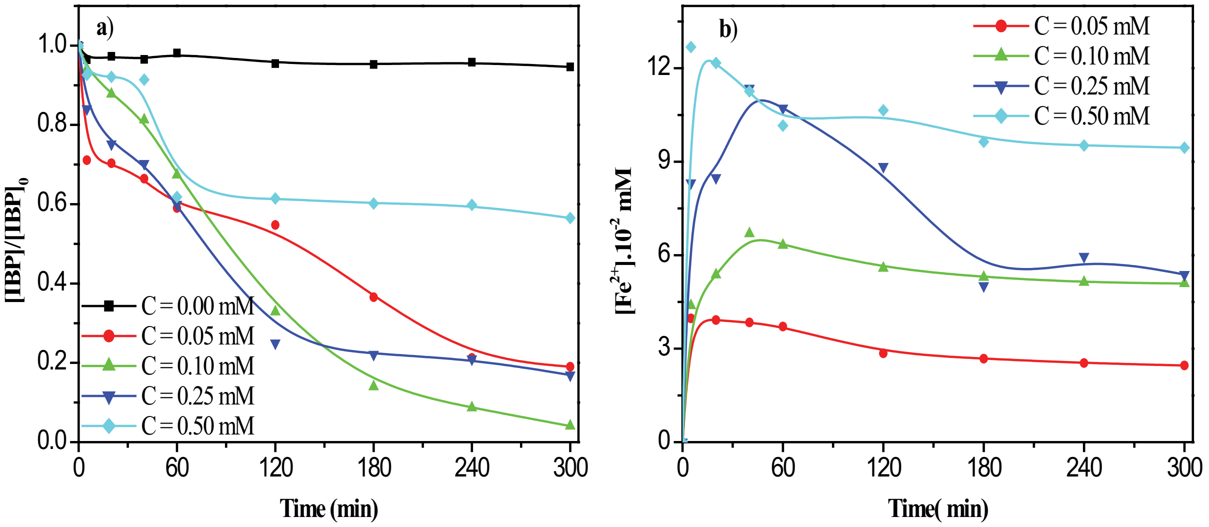

Fig. 8. (a) Effect of Fe^{III}-GA complex concentration on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system (0.1 and 5 mM), pH = 7.0 ± 0.1, T = 25°C and (b) Fe^{II} formation.

is characterized by a slight decrease in the Fe^{II} content when the complex concentration is in the values of 0.25 to 0.50 mM as mentioned in Fig. 8b. Also, the concentration in the plateau is higher with respect to the concentration of the complex. In oxidation processes, the use of high complex concentrations generates low molecular weight organic intermediates. Moreover, the organic species produced also consume hydroxyl radicals and the competition is more intense in concentrated solutions.

3.5. Effect of Fe^{III}:GA molar ratio on IBP degradation

Fe^{III} and GA are essential components in the IBP degradation process. Therefore, the study of their molar ratio (metal: ligand) is necessary. Experiments have been carried out in which the concentration of 5 mM of H_2O_2 and 0.1 mM Fe^{III} ions in the presence of GA with initial doses varying from 0.1 to 0.3 mM at fixed pH 7 and T = 25°C. Fig. 9a shows that the degradation of IBP was dependent on Fe^{III}:GA molar ratio, and that the optimal ratio Fe^{III}:GA was estimated to be 1:2. Furthermore, the removal efficiency of IBP increases from 82.27% to 95.96% after 5 h of reaction when the Fe^{III}:GA molar ratio changes from 1:1 to 1:2. Nevertheless, a slowdown in the oxidation process was observed for the Fe^{III}:GA molar ratio at 1:3. In addition, the formation of Fe^{II} was rapid at the beginning of the reaction for all molar ratios tested, and the kinetics was proportional to the IBP removal reactions as shown in Fig. 9b.

Jovanovic et al. [43] have found that the molar ratio Fe^{III}:GA in the formation of iron complex with GA at pH 7 was shown to be 1:2. In general, iron complexes with GA promote the production of hydroxyl radicals at low concentrations Fe:GA < 1:2 due to the reduction of Fe^{3+} to Fe^{2+}, and the chelation of iron becomes the dominant factor. Therefore, the removal of the pollutant was more intense for the 1:1 and 1:2 ratios. However, the use of excess GA leads to inhibition in the degradation process as it acts as an $^{\bullet}OH$ radical scavenger in the absence of iron [37,44].

3.6. Effect of IBP concentration

Optimal oxidation of the substrate can be achieved by the consumption of hydroxyl radicals produced by the reagents themselves, that is, H_2O_2 and the Fe^{III}-GA complex. Based on this, IBP degradation was monitored for fixed concentrations of 5 mM H_2O_2 and 0.1 mM iron(III) complex, as well as for IBP initial variable concentrations from 0.01 to 0.10 mM with the same molar ratio (Fe^{III}:GA 1:2) at pH 7 under a temperature of T = 25°C.

According to the kinetics obtained from Fig. 10, it can be seen that the most efficient degradation of IBP was achieved when using the lowest IBP concentration. Moreover, the oxidation rate decreases with the increase of IBP initial concentration, and the kinetic constant was found to be from 2.74×10^{-2} to 4.03×10^{-3} min^{-1} as shown in Table 2.

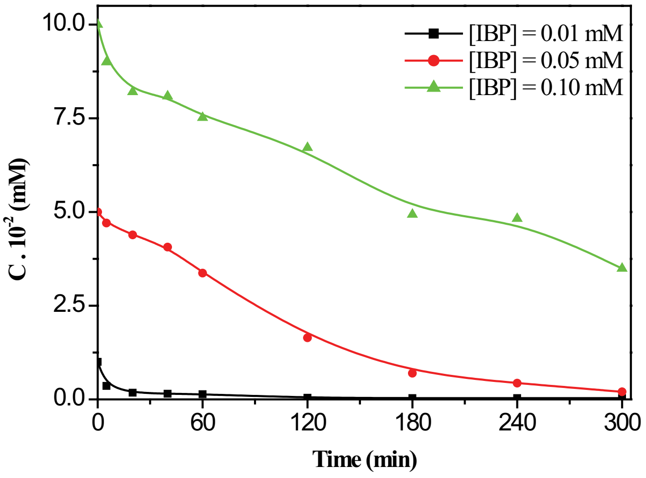

Fig. 10. Effect of the initial concentration of the IBP on its degradation by the Fe^{III}-GA/H_2O_2 system (0.1 and 5 mM), pH = 7.0 ± 0.1, T = 25°C.

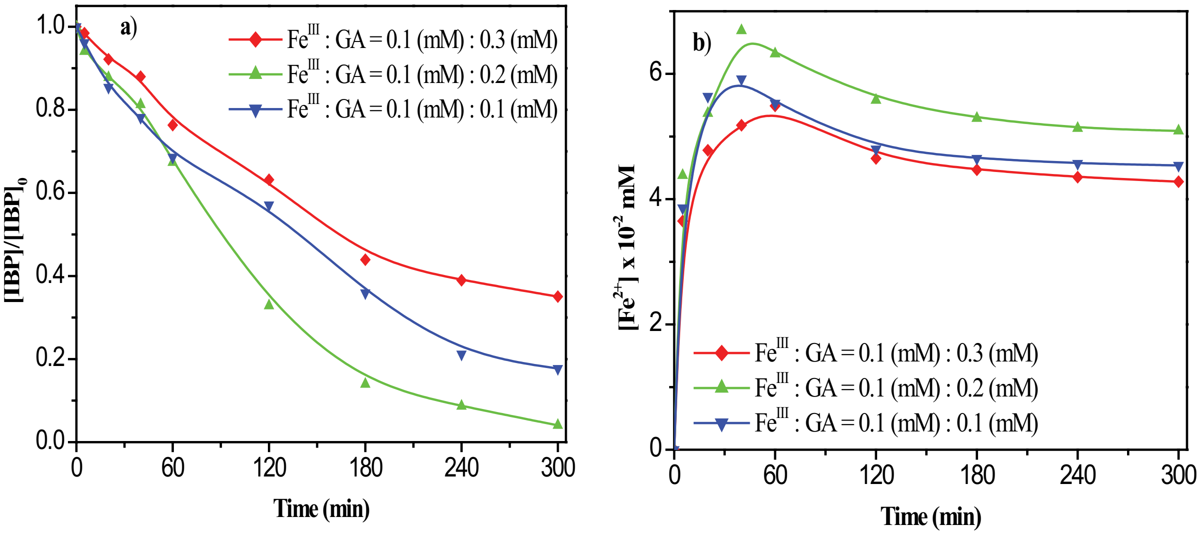

Fig. 9. (a) Effect of Fe^{III}:GA molar ratio on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system, [H_2O_2] = 5 mM, pH = 7.0 ± 0.1, T = 25°C and (b) Fe^{II} formation.

The competition between substrate molecules and •OH radicals was more powerful for high levels of IBP. These results show how the insufficient amount of •OH radicals generated in the IBP removal process is due to the fixed H_2O_2 concentration in all experiments. On the contrary, when substrate molecules were small in number, the competition between them and •OH radicals was lower due to the higher availability of the generated reactive species.

3.7. Effect of pH on IBP degradation

In Fenton-type processes, pH is an important parameter in wastewater treatment. To confirm the effect of pH on the rate of H_2O_2 decomposition by Fe^{III}-GA, aerated solutions were conducted with initial pH ranging from 3 to 9 and concentrations of 5 mM H_2O_2 and 0.1 mM Fe^{III}-GA. According to Fig. 11a, it appears that the rate of oxidation of IBP is inversely proportional to the increase in the initial pH values. Indeed, the degradation process was positively influenced in the acidic medium, and the reaction was optimum at pH 3. Additionally, the degradation of IBP was significant with disappearance of 95.96%, which was obtained after 5 h of reaction at pH 7. However, the rate of IBP destruction is slowed down at basic pH values.

The formation of Fe^{II} was followed under the same operating conditions. As shown in Fig. 11b, it appears that the formation kinetics of Fe^{II} act in a similar way to the destruction reaction, and the plateau concentrations decrease slightly with increasing pH. Indeed, the Fe^{II} content reaches a maximum of 6.72×10^{-2} mM after 40 min of reaction at the acid pH value (pH = 3). On the one hand, these results can be explained by the reoxidation of Fe^{II} with dissolved oxygen, and by the presence of the most active species that are generated at pH 3. GA is known to be present as a gallate anion at pH ≥ 7 [45]. Furthermore, it is easily oxidizable in the presence of dissolved oxygen [37], thus, preventing the pathway for Fe^{II} recovery, and this corresponds to the kinetics of ferric ion formation. For this reason, the amount of Fe^{II} in the plateau reduces gradually when the pH takes values above 7.

Table 2
Plots of the first-order-rate constant (k) as a function of the IBP concentration

[IBP] (mM)	0.01	0.05	0.10
K (min^{-1})	2.74×10^{-2}	6.03×10^{-3}	4.03×10^{-3}
R^2	0.925	0.984	0.915

3.8. Influence of temperature on IBP degradation

Temperature is an important parameter in Fenton's chemistry. To show its influence in the modified Fenton-like process, aerated solutions containing 0.05 mM IBP were treated by varying the temperature of the medium from 25°C to 55°C using 0.1 mM Fe^{III}-GA complex and 5 mM H_2O_2 at neutral pH. According to the results of Fig. 12a, the oxidation rate of IBP increases quickly with increasing temperature in the studied range. Indeed, the removal of IBP increases from 67.16% to 99.14% in the temperature range of 25°C to 55°C after 2 h of reaction. Thus, the temperature has a positive effect on the degradation efficiency of IBP by increasing the number of collisions between molecules, which is probably due to the increase in oxidation rate. On the other hand, Fe^{II} forms rapidly at the beginning of the reaction and reaches a maximum from 6.69×10^{-2} to 7.36×10^{-2} mM for the same temperature range of 25°C–55°C after 40 min of reaction as shown in Fig. 12b.

These results are similar to those reported in the literature. Temperature is an important factor in the classical or modified Fenton-like system and its increase can lead to an increase in the rate of pollutant removal [46–51]. Moreover, the reaction rate between hydrogen peroxide and any form of ferrous and/or ferric chelated or free iron increases with increasing temperature [47]. As shown in Fig. 12b, the

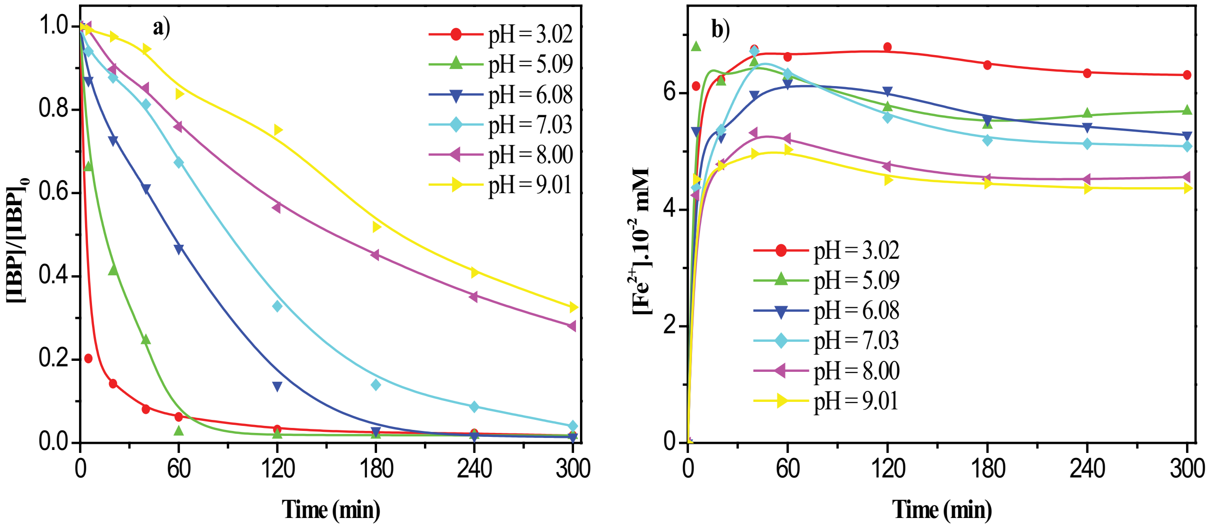

Fig. 11. (a) Effect of pH on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system (0.1 and 5 mM), pH = 7.0 ± 0.1, T = 25°C and (b) Fe^{II} formation.

formation of ferrous iron is proportional to the rate of degradation of the pollutant, and therefore, to the rate of production of hydroxyl radicals.

3.9. Contribution of hydroxyl radicals in the modified Fenton-like process

The effect of tert-butanol (t-BuOH), known as an effective scavenger for •OH radicals ($6 \times 10^8\ M^{-1}\ s^{-1}$ [52]), on the modified Fenton-like process was evaluated. Aerated solutions containing the mixture IBP/Fe^{III}-GA/H_2O_2 (0.05, 0.1 and 5 mM) were examined in the absence and presence of 1% t-BuOH at an ambient temperature of 25°C and in a neutral medium. According to the results obtained by Fig. 13a, the addition of t-BuOH completely inhibited the removal of IBP indicating the involvement of hydroxyl radical species in the degradation process. Furthermore, the kinetics of Fe^{II} formation during the reaction has a similar pattern for the same experimental conditions as shown in Fig. 13b. Moreover, in the presence of 1% t-BuOH, the Fe^{II} formation was accentuated in the first phase where a concentration of 5.82×10^{-2} mM was obtained after 5 min of reaction, whereas in its absence, it was 6.69×10^{-2} mM for 40 min of reaction. These results can be explained by the fact that tertiary butanol rapidly traps the first •OH radical formed and thus prevents the re-oxidation of Fe^{II} to Fe^{III}.

3.10. Mineralization

Mineralization is an important parameter in the chemical oxidation of organic pollutants present in water. Since IBP and Fe^{III}-GA complex contribute to the TOC values in the oxidation process, the study of the TOC variation is necessary.

The TOC evolution of the complex alone and the pollutant-complex mixture IBP/Fe^{III}-GA/H_2O_2 (0.05, 0.1 and

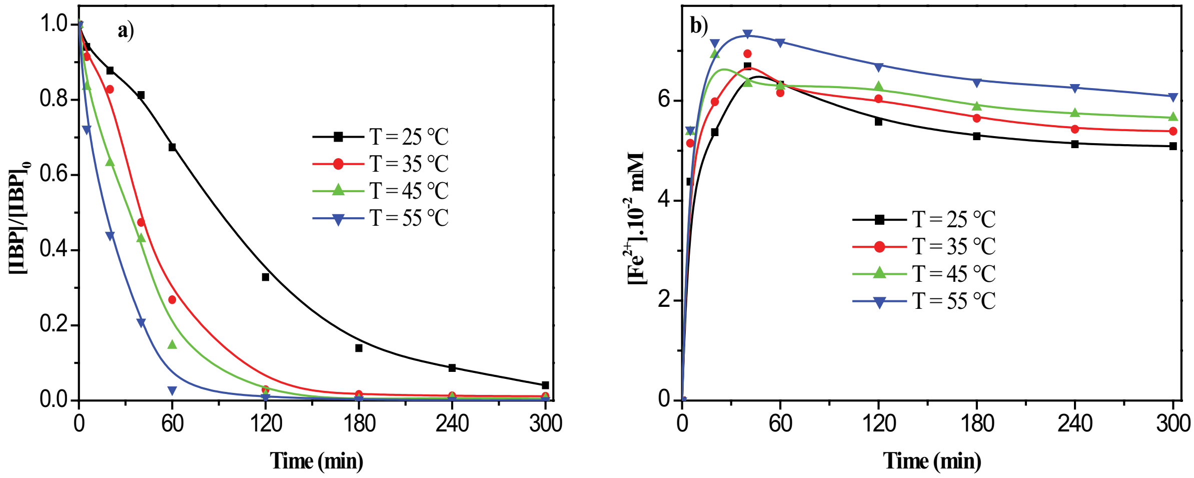

Fig. 12. (a) Effect of temperature on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system (0.1 and 5 mM), pH = 7.0 ± 0.1 and (b) Fe^{II} formation.

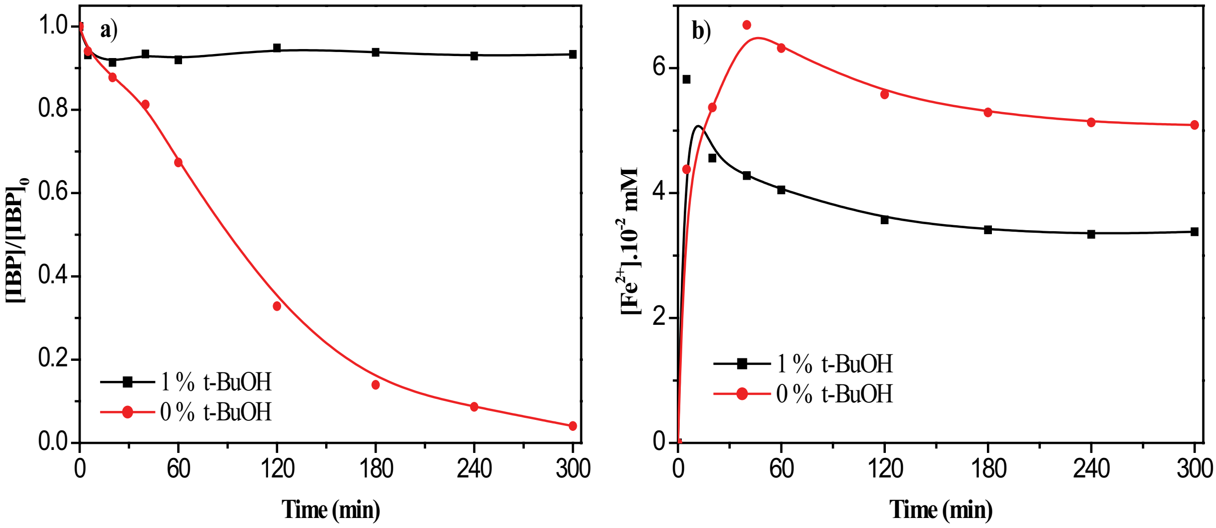

Fig. 13. (a) Effect of t-BuOH on the degradation of IBP (0.05 mM) by the Fe^{III}-GA/H_2O_2 system (0.1 and 5 mM), pH = 7.0 ± 0.1, T = 25°C and (b) Fe^{II} formation.

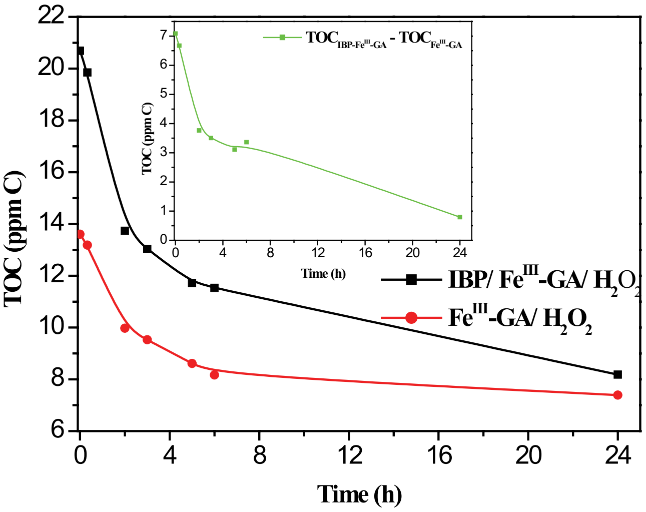

Fig. 14. Evolutions of TOC of IBP (0.05 mM) in Fe^{III}-GA/H_2O_2 system (0.1 mM, 5 mM), pH = 7.0 ± 0.1, T = 25°C.

5 mM) was monitored at neutral pH and 25°C. Fig. 14 shows a reduction of 45.69% and 60.46% for $TOC_{Fe(III)-GA}$ and $TOC_{IBP/Fe(III)-GA}$, respectively, after 24 h of reaction. This can be explained by the fact that GA can be degraded due to radical attack by $^{\bullet}OH$ [40] and thus lead to open-cycle products by further oxidation [53]. On the other hand, the TOC of IBP was obtained by subtraction of $TOC_{IBP/Fe(III)-GA} - TOC_{Fe(III)-GA}$ and the result showed mineralization of 88.81%. This result demonstrates the efficiency of the iron(III)-gallic acid complex. Incomplete mineralization can be attributed to intermediate oxidation products, which may be resistant to this mode of destruction or require more prolonged treatment.

4. Conclusion

The results obtained in this work indicate that iron complex synthesized (Fe^{III}-GA) by means of a greener approach using natural compounds can remove IBP from an aqueous medium through chemical oxidation. GA was used as a complexing agent to solubilize Fe^{III} in a neutral aqueous solution. The molar ratio Fe^{III}:GA 1:2 reveals a complexation of 90.9% with high stability constant of logβ = 11.66. The experiments were conducted at neutral pH which is a key parameter influencing the removal efficiency of IBP. The experimental degradation conditions were chosen with 5 mM of H_2O_2, 0.1 mM of Fe^{III}-GA complex with a stoichiometry (Fe^{III}:GA) of 1:2 at pH 7. The removal of IBP by Fe^{III}:GA promotes the formation of $^{\bullet}OH$ radicals by accelerating the reduction of Fe^{III}, and therefore, improving degradation efficiency. Also, the increase in the temperature of the medium has a positive effect on the oxidation rate of IBP. The addition of 1% tertiary butanol, used as a hydroxyl radical scavenger, completely inhibits the destruction of IBP. This inhibition indicates the involvement of the $^{\bullet}OH$ radical species taking part in the process. TOC experiments showed mineralization of 88.81% of organic carbon after 24 h of IBP treatment in the presence of Fe^{III}-GA complex in a neutral medium. Our results enrich academic knowledge on the feasibility of using AOPs based on the organic iron complex as a possible green technology.

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