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Degradation of Amoxicillin in Water by Fenton, Photo-fenton and Photocatalysis Using Copper Oxide

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

In recent years, the presence of drug residues in water has become a major environmental issue. Among these pollutants is amoxicillin. Our aim is to propose effective methods for decontaminating wastewater containing amoxicillin. This study was carried out using the chemical oxygen demand method. This work has shown that hydroxyl radicals can effectively degrade amoxicillin. The rate of

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hydroxyl radical production from hydrogen peroxide and iron (II) ions increases in the presence of sunlight. Amoxicillin oxidation is optimal at a pH of 3 and a $[H_2O_2]/[Fe^{2+}]$ ratio of 13.33. Amoxicillin degradation is faster at low concentrations than at high concentrations. The oxidation of amoxicillin by photo-Fenton results in degradation rates of up to 99%. A study of the adsorption of amoxicillin on copper oxides showed that amoxicillin adsorbs weakly to the amoxicillin surface, with an adsorption rate of 17%. However, in the presence of amoxicillin, hydrogen peroxide and sunlight, degradation rates of up to 99% were obtained. This work has shown that the degradation of amoxicillin is better with solar photo Fenton and solar photocatalysis in the presence of copper oxide than with the Fenton process.

Keywords: Fenton; photo-Fenton; amoxicillin; photocatalysis; degradation; sunlight.

1. INTRODUCTION

In an age of increasing industrialization and perpetual technical evolution, new products enter the market every day (George & Pandey 2024). The pharmaceutical industry is a case in point, constantly developing new molecules to meet the growing demands of patients and consumers (Beatriz & Fernando 2023, Diniz et al. 2023). There is a huge diversity of drugs, consumed by the population at different frequencies (Wu & Li 2023, Larabi et al. 2023). Consequently, in view of this extensive use of pharmaceutical products by the population, it may be suspected that these compounds could be released into the environment where anthropogenic activity is present (Krychkovska et al. 2024, Helwig et al. 2024). In fact, pharmaceutical compounds can be released into the environment via three different routes: wastewater discharge, sanitary landfill sites and agricultural use via excretion of drugs by animals (Castellano-Hinojosa et al. 2023, Sadia et al. 2016, Sadia et al. 2023). However, wastewater discharge is the main route by which pharmaceuticals enter the environment (Sadia et al. 2016, Kouadio et al. 2021, Kimou et al. 2021). Indeed, wastewater can be contaminated by pharmaceutical compounds due to excretion by the body of the compound at a certain percentage, via elimination in the toilet (Zhang et al. 2023). These contaminated wastewaters are conveyed by the sewage system to treatment plants, where they are treated before being discharged into the receiving environment. However, the volume and diversity of compounds found on the market complicate treatment efficiency. Indeed, some of these molecules are likely, because of their physico-chemical characteristics, to pass through the various stages of the treatment process. These compounds will then be released into the environment in trace quantities via the effluent (Peng & Li 2024, Peterse et al. 2024, Tang et al. 2024). One of these persistent pollutants is amoxicillin (AMX). It is commonly found in wastewater treatment plant effluent, surface water and groundwater (Sadia et al. 2020). It is therefore necessary to propose effective methods for wastewater treatment.

For water treatment, there are several methods available, such as adsorption, extraction, incineration, biological methods and advanced oxidation processes (Kouadio et al. 2021, Kouakou et al. 2023, Tchonrontcha et al. 2024, Kambiré et al. 2022). The use of these methods depends on their cost and degradability. The adsorption method is widely used in wastewater treatment. However, its disadvantage is that it transfers pollutants from one aqueous phase to a new phase, and leads for the most part to the formation of concentrated sludge, creating a secondary waste problem, or to material regeneration which is often very costly (Kouakou YU et al. 2021, Kambiré et al. 2021). Biological methods rely on the use of microorganisms under aerobic or anaerobic conditions (Sadia et al. 2021, Sadia et al. 2020). However, when faced with toxic compounds that are difficult to biodegrade, these microorganisms prove ineffective (Sadia et al. 2021, Sadia et al. 2020).

In this context, advanced oxidation processes can play an important role. Advanced oxidation processes (H_2O_2/Fe^{2+}, H_2O_2/O_3, O_3/UV, H_2O_2/UV, Fe^{2+}/H_2O_2/UV, TiO_2/UV) represent an interesting alternative. (Kambiré et al. 2020, Zhaobo et al. 2023, Fuhang et al. 2023, Lanjwani et al. 2023). In fact, they enable this drug to be mineralized through the in-situ creation of radicals, notably hydroxyl radicals ($OH^{\cdot}$). The latter are highly reactive species, capable of mineralizing most organic compounds. (Kouakou et al. 2023, Sadia et al. 2021, Kouakou KE et al. 2021). Fenton process is a method that produces hydroxyl radicals from the mixture of hydrogen peroxide and Fe^{2+}, then regenerates the Fe^{2+} (Eqs. 1 and 2) (Kambiré et al. 2020).

$$Fe^{2+}+H_2O_2+H^+ \rightarrow Fe^{3+}+ H_2O+HO^{\bullet} \quad (1)$$

$$2\ Fe^{3+}+H_2O_2 \rightarrow 2\ Fe^{2+}+O_2+2H^+ \quad (2)$$

According to the literature, the Fenton process can completely mineralize organic compounds such as amoxicilin (Eq. 3) [20].

$$C_{16}H_{19}N_3O_5S + 47H_2O_2 + Fe^{2+} \rightarrow 16CO_2 + 54H_2O + 3HNO_3 + H_2SO_4 + Fe^{2+} \quad (3)$$

The photo-Fenton process increases hydroxyl radical production through photoreduction of Fe^{3+} to Fe^{2+} and photolysis of peroxide, as shown in Eqs 4 and 5 (Verma et al. 2019). This helps improve the degradation rate of organic compounds.

$$Fe(OH)_2 + h\upsilon \rightarrow Fe^{2+} + HO^{\bullet} \quad (4)$$

$$H_2O_2 + h\upsilon \rightarrow 2\ HO^{\bullet} \quad (5)$$

Photocatalysis is an advanced oxidation process that combines light radiation with a photocatalyst. The principle of photocatalytic oxidation is based on the absorption of photons by the photocatalyst and the resulting separation of charges (Pohan et al. 2019, Younes & Ki-Hyun 2024, Jia-Hang et al. 2024). In the presence of copper oxides and sunlight we produce hydroxyl radicals according to Eqs 6 and 7 in addition to the production of hydroxyl radicals by the reaction of Eq. 5 (Kambiré et al. 2023).

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + OH^- \quad (6)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu(OH)^{2+} + HO^{\bullet} \quad (7)$$

The aim of this project is to treat water polluted by amoxicillin using homogeneous and heterogeneous photocatalysis under solar irradiation. For homogeneous photocatalysis, we will study the impact of solar radiation on the Fenton reaction. Then, at the level of solar photocatalysis, we will study the photocatalytic degradation of amoxicillin in the presence of copper oxide under solar irradiation.

2. MATERIALS AND METHODS

2.1 Amoxicilin Analysis

The concentration of amoxicillin was determined by measuring the Chemical Oxygen Demand (COD). To measure COD, a 20 mL volume of each solution was taken and filtered successively through an ordinary FILTER-LAB filter to retain the sludge, then a second time and a third time through FILTER-LAB filters with a porosity of 0.45 µm and a diameter of 47mm. 2 mL of each solution are introduced into the HACH COD tubes and then heated in the digester at 150°C for 120 minutes (Sadia et al. 2020, Sadia et al. 2021). Before each sampling, evaporation losses are compensated for. The degradation rate at time t is determined using eq. 8.

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \quad (8)$$

Where

D_t = percentage of degradation at time t;

C_A = COD measured in the test suspension, measured after 3 h of incubation (mg/L);

C_t = COD measured in the test suspension at time t (mg/L);

C_B = COD measured in the control at time t (mg/L);

C_{BA} = COD measured in the control after 3 h of incubation (mg/L).

The same calculation is made with the reference solution.

During the study of the Fenton process, samples were taken and analyzed using a HACH DR-6000 UV-visible spectrophotometer.

2.2 Copper Oxides

The copper oxides used in this work are a commercial product from Prolabo. Its purity is 99%. These oxides were crushed with a mortar to obtain sizes ranging from 100 to 400 nm.

2.3 Reagents

Amoxicillin was purchased from a pharmacy in Abidjan (Ivory Coast). The semi-developed formula of amoxicillin is given in Fig. 1. Hydrogen peroxide (H_2O_2) and copper oxide were supplied by Expertise Chimique and SCHARLAU respectively. Ferrous sulfate ($FeSO_4$), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were supplied by Fluka. Copper oxide used in this work comes from Prolabo with a purity of 99%.

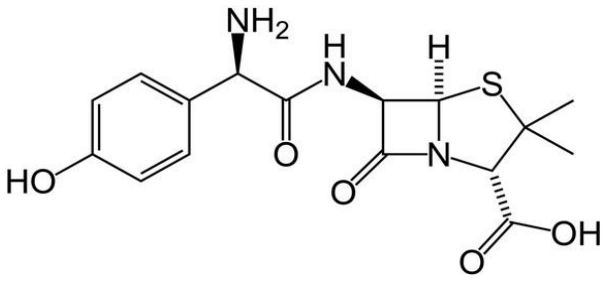

Fig. 1. Semi-developed formula of amoxicillin

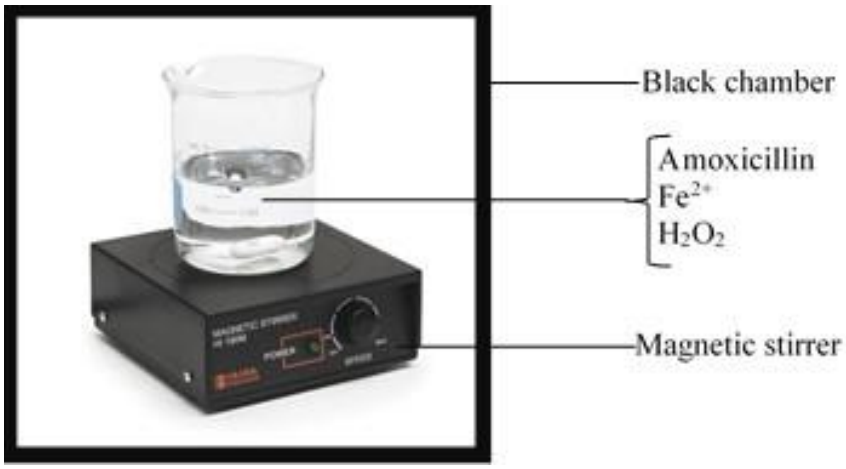

Fig. 2. Schematic representation of Fenton process

2.4 Amoxicillin Degradation Tests

2.4.1 Degradation of amoxicillin by the Fenton process

The oxidation of amoxicillin was studied in a homogeneous medium using Fenton process. In this study, amoxicillin was degraded using a mixture of hydrogen peroxide and ferrous ions in an acid medium. The concentration of amoxicillin was varied from 5 mg/L to 20 mg/L. Hydrogen peroxide concentrations ranged from 50 mg/L to 250 mg/L, and ferrous ions from 5 mg/L to 15 mg/L. Samples of the reaction medium were taken and analyzed. This study was carried out in the dark, using aluminum foil to protect the reaction medium from light. The schematic diagram of the apparatus used for Fenton reaction is shown in Fig. 2.

2.4.2 Amoxicillin degradation by the Photo-Fenton process

We used the optimum conditions obtained with the Fenton process, and the experiments were carried out in the presence of sunlight. We set the hydrogen peroxide concentration at 200 mg/L, the ferrous ion concentration at 15 mg/L and the pH at 3, varying the amoxicillin concentration (5 mg/L; 10 mg/L; 15 mg/L and 20 mg/L).

2.4.3 Amoxicillin photodegradation in the presence of copper oxide

In this section, the adsorption of amoxicillin on copper oxides was studied by contacting 1 g/L copper oxide with 5 mg/L amoxicillin at pH=3. Next, the photocatalytic degradation of amoxicillin was studied by setting the hydrogen peroxide concentration at 200 mg/L, the copper oxide concentration at 1 g/L and the pH at 3, varying the amoxicillin concentration (5 mg/L; 10 mg/L; 15 mg/L and 20 mg/L).

3. RESULTS AND DISCUSSION

3.1 Study of Amoxicillin Oxidation by the Fenton Process

3.1.1 Study of the pH influence

Amoxicillin degradation was carried out in solutions at different pH values. Fe^{2+}, amoxicillin

and H_2O_2 concentrations were kept constant. The results obtained are shown in Fig. 3. In general, a rapid increase in the degradation rate is observed in the first 20 min of the experiment, followed by a slow increase until 30 min, when a maximum is reached. We also note that the degradation rate increases as the pH rises from 2 (58%) to 3 (79.5%), only to fall again as the pH rises above 3.

This work shows that the best pH for amoxicillin degradation is pH = 3. At very acidic pH, H_2O_2 becomes highly unstable following the formation of oxonium ion ($H_3O_2^+$) by solvating a proton (Eq. 9). This acidic form of electrophilic hydrogen peroxide severely restricts its reactivity with ferrous iron. This greatly reduces the number of hydroxyl radicals generated by the decomposition of H_2O_2 by Fe^{2+}. Moreover, low pH levels favor the consumption of hydroxyl radicals by hydrogen peroxide. At pH < 2.5, ferrous iron is essentially in the form of an aqueous complex $[Fe(H_2O)_6]^{2+}$ in equilibrium with its conjugated form Kambiré et al. (2022) and Hu et al. (2008).

$$H_2O_2+H^+ \rightarrow H_3O_2^+ \quad (9)$$

$$[Fe\ (H_2O)_6]^{2+} \leftrightarrow [Fe\ (OH)\ (H_2O)_5]^+ + H^+ \quad (10)$$

Kinetically, the $[Fe(OH)\ (H_2O)_5]^+$ is much more reactive with hydrogen peroxide than the $[Fe(H_2O)_6]^{2+}$. Thus, the speed of the initial step in the mechanism of H_2O_2 decomposition by Fe^{2+} increases with pH in the range 1 < pH < 3. Consequently, for pH < 2.5, the Fenton reaction generates fewer $HO^{\bullet}$ radicals, which experimentally translates into a decrease in the degradation rate of organic compounds.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\ (s) + 3\ H^+ \quad (11)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (12)$$

These particles aggregate to form a precipitate from $Fe(OH)_3$ (Hug et al. 2023, Kambiré et al. 2020) and their concentration increases with pH. Following precipitation, species concentrations restrict the ability to produce hydroxyl radicals from the Fenton reaction (Eq. 12). Regeneration of Fe^{2+} from precipitated Fe^{3+} is very slow and represents the limiting kinetic step. Moreover, at pH > 4, hydrogen peroxide is unstable, decomposing into O_2 and H_2O and losing its oxidation capacity (Kambiré et al. 2022). Based on the above, the pH favorable to amoxicillin oxidation is 3. This pH was chosen for further work.

The gradual decrease in the abatement rate with initial concentration could be explained by competitive reactions between amoxicillin molecules and those of intermediates formed during the Fenton oxidation process (Hu et al. 2008). The amoxicillin molecules and intermediates formed will compete to react with $HO^{\bullet}$ radicals. This increases the competitive effect with the initial concentration of amoxicillin (Hu et al. 2008, Hug et al. 2003).

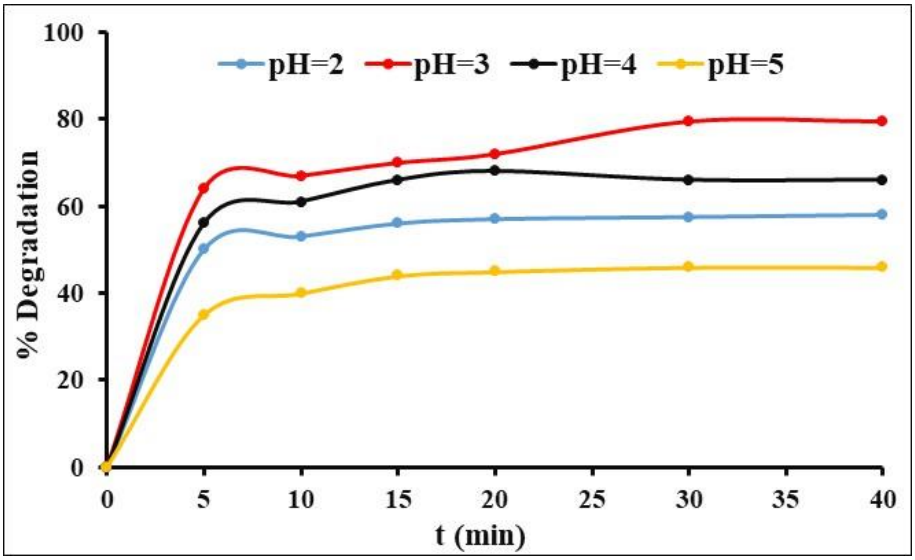

Fig. 3. Effect of pH on amoxicillin degradation as a function of time, [amoxicillin] = 5 mg/L, $[Fe^{2+}]$ = 15 mg/L, $[H_2O_2]$ = 100 mg/L, T=25°C

3.1.2 Study of the influence of the initial amoxicillin concentration

The quantity of material to be degraded is one of the factors determining the efficiency of the treatment process. Thus, various initial concentrations of amoxicillin were studied by fixing the values in concentration of H_2O_2, Fe^{2+} and pH. The results obtained are presented in Fig. 4, which shows that degradation efficiency decreases with increasing initial amoxicillin concentration. Degradation rates of 79.5%, 72%, 63% and 56% are observed for 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L respectively. This is in line with the results reported in the literature (Vajnhandl & Le Marechal 2007, Behnajady et al. 2008, Wang et al. 2008). Thus, a high rate of degradation is observed for low concentrations of amoxicillin.

The gradual decrease in the abatement rate with initial concentration could be explained by competitive reactions between amoxicillin molecules and those of intermediates formed during the Fenton oxidation process (Hu et al. 2008). The amoxicillin molecules and intermediates formed will compete to react with $HO^{\bullet}$. This increases the competitive effect with the initial concentration of amoxicillin (Hu et al. 2008).

During the degradation of amoxicillin by the Fenton process, the absorbance of the sampled solutions was monitored over time. The results are shown in Fig. 5. This figure shows that after 5 min of degradation, there is an increase in absorbance. This indicates the production of intermediates which absorb at the same wavelength as amoxicillin. The absorbance then decreases with time. These results confirm that amoxicillin undergoes oxidation by passing through intermediate compounds which are then oxidized until the molecule is completely degraded.

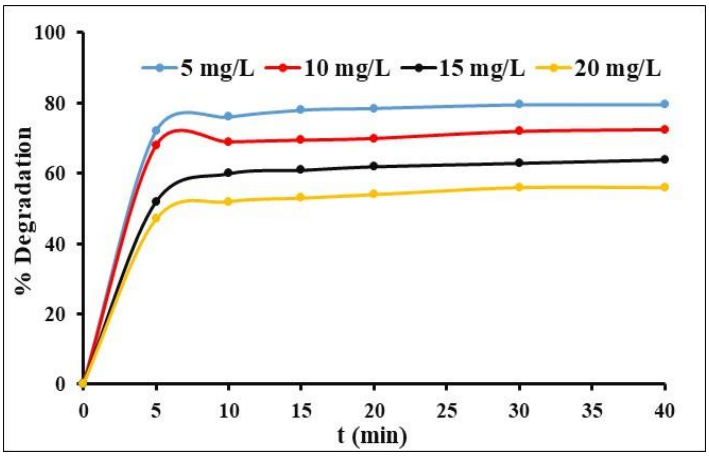

Fig. 4. Effect of amoxicillin concentration on its degradation as a function of time [Fe^{2+}] = 15 mg/L, [H_2O_2] = 100 mg/L, pH=3, T=25°C

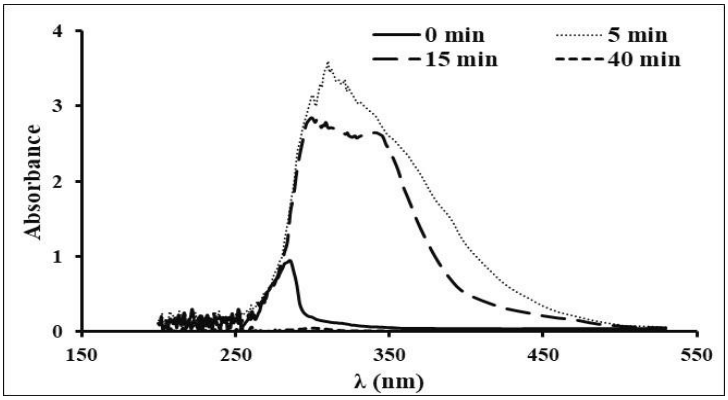

Fig. 5. Amoxicillin spectrum, [amoxicillin] = 5 mg/L, [Fe^{2+}] = 15 mg/L, [H_2O_2] = 100 mg/L, pH=3, T=25°C

3.1.3 Study of the influence of initial Fe^{2+} concentration

Fig. 6 shows that the rate of amoxicillin degradation varies with Fe^{2+} concentration. The rate of degradation increases from 5 mg/L to 15 mg/L Fe^{2+}. Then, above 15 mg/L, it decreases. Above 15 mg/L, Fe^{2+} are engaged in a secondary reaction, consuming hydroxyl radicals, and the degradation of amoxicillin decreases. The final result is that amoxicillin degradation is greatest at 15 mg/L Fe^{2+}, with a degradation rate of 79.5%. Above 15 mg/L, amoxicillin degradation decreases with increasing iron II concentration. When the Fe^{2+} concentration is very high, parasitic reactions such as Eq. 13 occur. These reactions compete with the degradation reaction of organic compounds (Eq. 14). This reduces the oxidation of organic compounds (Kambiré et al. 2022).

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

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \rightarrow produit \quad (14)$$

According to Eq. 15, Fe^{2+} react with hydrogen peroxide to give Fe^{3+}. So if the concentration of Fe^{2+} is high, the quantity of Fe^{3+} produced will be high. However, Fe^{3+} decomposes hydrogen peroxide according to Eq. 16. The decrease in the rate of degradation with an excess of Fe^{2+} is also linked to the decomposition of H_2O_2 by the Fe^{3+} produced (Kambiré et al. 2022).

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + H_2O + HO^{\bullet} \quad (15)$$

$$2Fe^{3+} + H_2O_2 \rightarrow 2\,Fe^{2+} + O_2 + 2H^{+} \quad (16)$$

3.1.4 Study of the influence of initial H_2O_2 concentration

The initial H_2O_2 concentration was studied. The results obtained are shown in Fig. 7, where it can be seen that the degradation rate increases for initial H_2O_2 concentrations ranging from 50 mg/L to 200 mg/L. Amoxicillin's degradation rate rises from 73 to 85.5%. Above 200 mg/L, the amoxicillin degradation rate decreases. At 250 mg/L, it drops to 82%. This shows that 200 mg/L is the optimum H_2O_2 concentration for amoxicillin degradation under the conditions studied. Increasing the H_2O_2 concentration causes an increase in the amount of $OH^{\cdot}$ and consequently it increases the rate of amoxicillin degradation. However, too high a concentration of peroxide causes hydroxyl radical scavenging due to excess hydrogen peroxide forming hydroperoxyl radicals ($HO_2^{\bullet}$) and causes a decrease in the degradation rate of the organic compound (Nidheesh et al. 2013, Muranov 2024, Behnajady et al. 2008).

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (17)$$

$[H_2O_2]/[Fe^{2+}]$ ratio is a very important parameter in the Fenton process. This ratio was calculated from the results shown in Fig. 7. The results obtained are presented in Table 1. According to the results in Table 1, degradation of the organic compound is optimal when the ratio $[H_2O_2]$ / $[Fe^{2+}]$ is equal to 13.33. With this ration, a degradation rate of 85.5% was achieved.

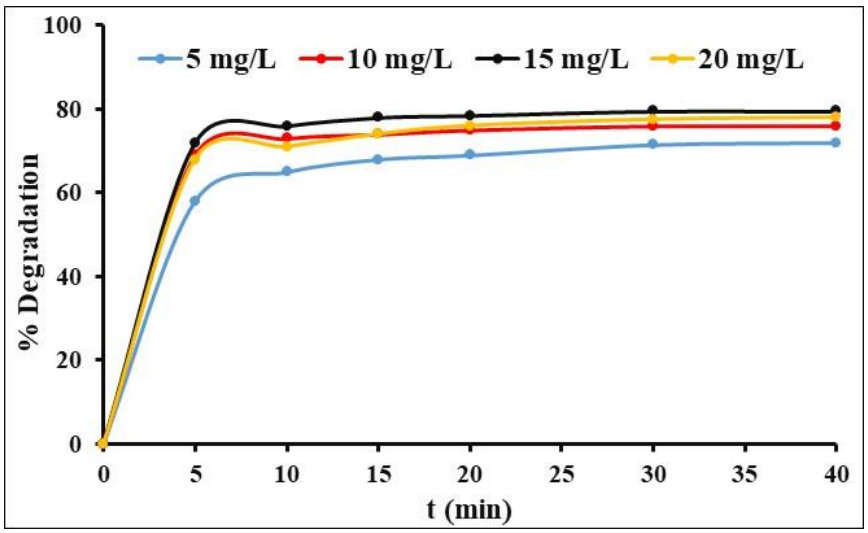

Fig. 6. Effect of Fe^{2+} concentration on amoxicillin degradation as a function of time, [amoxicillin] = 5 mg/L, $[H_2O_2]$ = 100 mg/L, pH=3, T=25°C

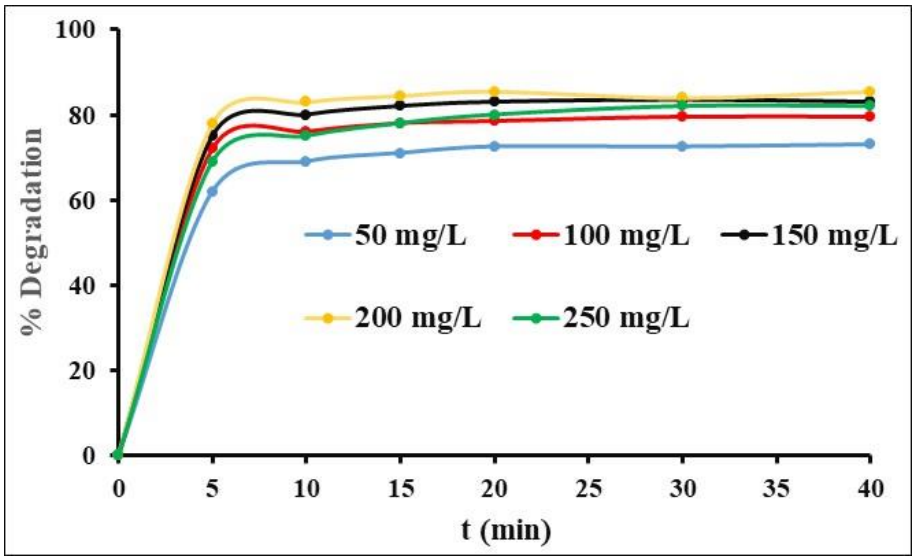

Fig. 7. Effect of H_2O_2 concentration on amoxicillin degradation as a function of time, [amoxicillin] = 5 mg/L, [Fe^{2+}] = 15 mg/L, pH=3, T=25°C

Table 1. Effect of [H_2O_2] / [Fe^{2+}] ratio on amoxicillin degradation, [amoxicillin] = 5 mg/L, pH=3, T=25°

[H_2O_2] / [Fe^{2+}] ratio	% degradation
3.33	73
6.67	79.5
10	83
13.33	85.5
16.67	82

3.2 Study of Amoxicillin Oxidation using the Solar Photo-Fenton Process

The influence of sunlight on the Fenton reaction was studied. The results obtained are shown in Fig. 8. This process is based on the Fenton reaction coupled with UV-visible irradiation. Fig. 8 shows degradation rates ranging from 85.5% to 99%. These results are significantly better than those obtained in the absence of sunlight. These results clearly show that photo-Fenton degrades amoxicillin better than the Fenton process. This is due to the multipathway production of hydroxyl radicals with the photo-Fenton process. These pathways are:

- direct reactions of H_2O_2 with Fe^{2+} introduced into the solution at the start of the reaction (Eq. 18) or formed by photoreduction of Fe^{3+} during the reaction (Eq. 19).

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + HO^{\cdot} \quad (18)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\cdot} + H^+ \quad (19)$$

- H_2O_2 photolysis

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \quad (20)$$

The effectiveness of photo-Fenton treatment depends essentially on the concentrations of Fe^{2+} and H_2O_2, and of course on light intensity (Sharifi & Mohades 2024). The production of hydroxyl radicals by these different pathways explains the improved rate of amoxicillin degradation.

3.3 Photocatalytic Oxidation of Amoxicillin in the Presence of Copper Oxide

3.3.1 X-ray diffraction of copper oxide

Fig. 9 shows the histograms obtained after XRD characterization of the powder obtained after grinding the copper oxide pellets. The diffraction spectrum shows peaks at 29.8° (110), 36.8° (111), 42.5° (200), 61.8° (211), 73.8° (220) and 78.2° (311) (Daoud et al. 2013). These lattice planes are matched to the cubic crystal system of Cu_2O by referring to the files of JCPDS No.

05-0667 (Joint Committee on Powder Diffraction Standards (JCPDS) No. 05-0667) attesting to the presence of Cu_2O in the prepared powder. In addition, localized diffraction peaks at 36° (-111), 38.9° (111), 49° (-202), 53° (202), 58° (202), 66° (022) and 68.8° (220), are consistent with the monoclinic mode of CuO (Gravereau 2011). These results indicate that the resulting powder contains both CuO and Cu_2O particles.

3.3.2 Study of amoxicillin adsorption on copper oxide

Before studying the photocatalytic oxidation of amoxicillin in the presence of copper oxide, it is necessary to study the adsorption of amoxicillin on the surface of copper oxides. Adsorption is a highly effective separation technique, widely used in wastewater treatment due to its low cost, simple design and ease of use (Zaviska et al. 2009). The extent of this technique depends on the nature of the adsorbate (molecular weight, molecular structure, polarity, solution concentration, etc.) and the adsorbent (particle size, specific surface area, surface charge, etc.).

Thus, the adsorption of amoxicillin on copper oxides was studied. In Fig. 10, the rate of amoxicillin elimination was recorded for 1 g/L CuOx, 5 mg/L amoxicillin and pH = 3. This figure shows low adsorption (17%) of amoxicillin on the copper oxide surface after a contact time of 45 min. Thereafter, the adsorption rate remains constant. This shows that equilibrium is reached after 45 min (Kambiré et al. 2021, Kouakou YU et al. 2021).

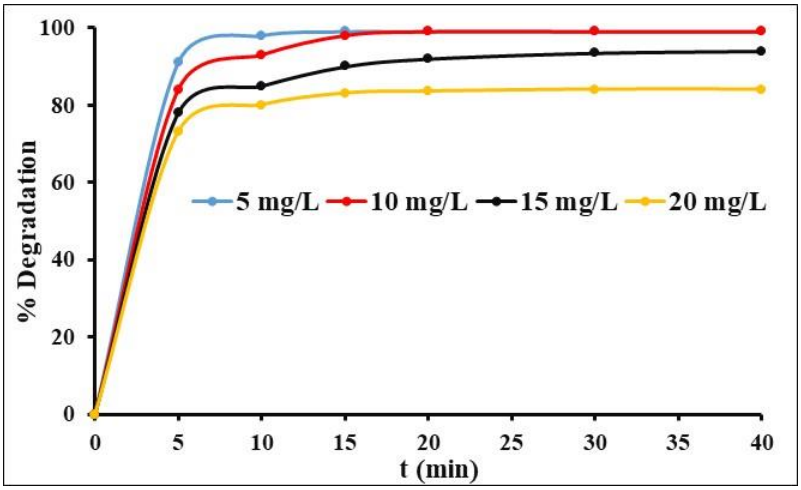

Fig. 8. Sunlight degradation of different amoxicillin concentrations as a function of time, [amoxicillin] = 5 mg/L, [Fe^{2+}] = 15 mg/L, [H_2O_2] = 200 mg/L, pH=3, T = 39 ± 2°C

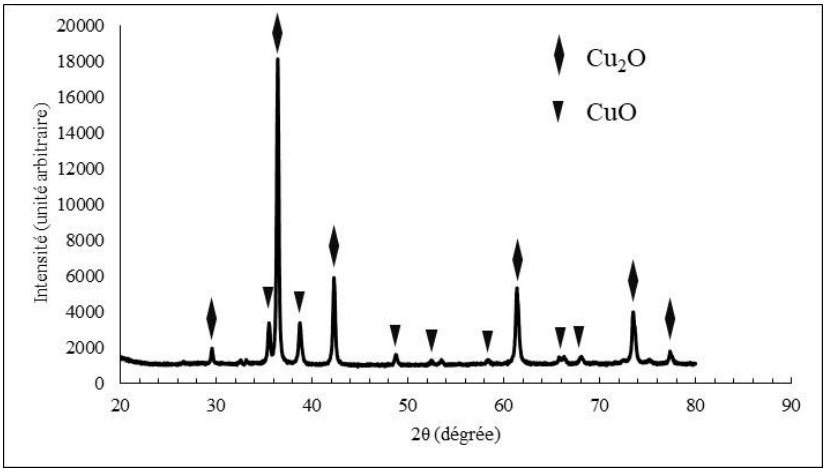

Fig. 9. X-ray diffraction of copper oxide

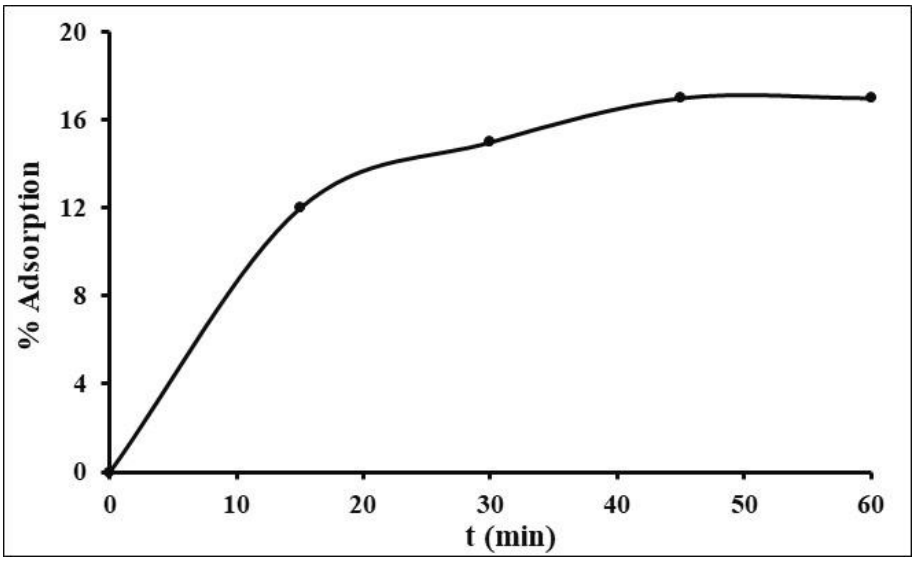

Fig. 10. Adsorption rate of amoxicillin on copper oxides as a function of time, [CuO_X] = 1 g/L, [amoxicillin] = 5 mg/L, pH=3, T = 25°C

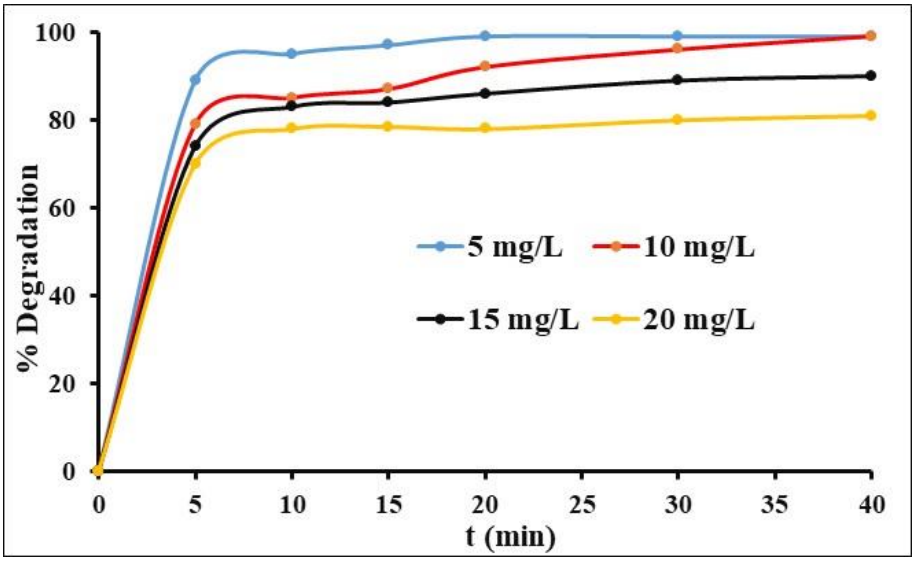

Fig. 11. Solar photocatalytic degradation of different concentrations of amoxicillin in the presence of copper oxide as a function of time, [CuO_X] = 1 g/L, [amoxicillin] = 5 mg/L, [H_2O_2] = 200 mg/L, pH=3, T = 40 ± 1°C

3.3.3 Amoxicillin oxidation in a copper oxide suspension in the presence of sunlight

The solar photocatalytic oxidation of amoxicillin was studied in the presence of copper oxide. Prior to photocatalytic oxidation, amoxicillin adsorption was carried out by contacting amoxicillin and copper oxides in the dark for 45 min (equilibrium time). The results obtained are shown in Fig. 11. According to this figure, the efficiency of degradation decreases as the initial concentration of amoxicillin increases. Almost complete degradation (99%) is observed after 20 min for 5 mg/L amoxicillin. A degradation rate of 99% is also reached after 40 min of solar irradiation for an amoxicillin concentration of 10 mg/L. At higher concentrations (15 mg/L and 20 mg/L), degradation is relatively slow, with rates of 90% and 81% after 40 min for 15 mg/L and 20 mg/L respectively. Indeed, the higher the concentration of the solution, the opaquer it becomes and the lower the penetration of solar rays. The decrease in the degradation rate as the concentration increases would appear to be due

to the increasing formation of a screen by the pollutant, making it virtually impossible for light to penetrate the solution (Kambiré et al. 2023). These results show that amoxicillin degradation is better with solar photo-Fenton and solar photocatalysis in the presence of copper oxide than with the Fenton process. Indeed, amoxicillin degradation rates of 99% were obtained with solar photo-Fenton and solar photocatalysis in the presence of copper oxide, and a degradation rate of 85.5% was obtained with the Fenton process.

This high level of amoxicillin degradation is due to the increased production of $HO^{\bullet}$. Hydrogen peroxide reacts with copper oxides to produce hydroxyl radicals according to Eqs 21 and 22 (Kambiré et al. 2023).

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + OH^{-} \quad (21)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu(OH)^{2+} + HO^{\bullet} \quad (22)$$

In the presence of sunlight, photolysis of hydrogen peroxide (Eq. 23) contributes to the degradation of organic molecules in aqueous solution. It is considered an important source of $HO^{\bullet}$. This explains the high degradation rates obtained in the presence of sunlight (Kambiré et al. 2023).

$$H_2O_2 \xrightarrow{h\upsilon} 2\,HO^{\bullet} \quad (23)$$

4. CONCLUSION

This study showed that the mixture of hydrogen peroxide and iron (II) ions produces hydroxide radicals responsible for the degradation of amoxicillin. According to the results obtained, for maximum oxidation of amoxicillin, a pH equal to 3 and a $[H_2O_2]/[Fe^{2+}]$ ratio equal to 13.33 are required. The oxidation reaction of amoxicillin by the Fenton reaction is a rapid one, occurring in 30 min with a degradation rate of up to 85.5%. During the Fenton reaction, Fe^{2+} are transformed into Fe^{3+}, which decompose hydrogen peroxide. However, in the presence of sunlight, Fe^{2+} are regenerated from Fe^{3+} and hydrogen peroxide is photolyzed, increasing the rate of amoxicillin degradation. Solar photo-Fenton thus improves the Fenton yield, with a degradation rate of 99%. A study of the adsorption of amoxicillin on these copper oxides showed that amoxicillin adsorbs weakly to the oxide surface, with an adsorption rate of 17%. However, in the presence of hydrogen peroxide and sunlight, degradation rates of up to 99% were obtained.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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