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DEGRADATION OF PHARMACEUTICALS FROM SIMULATED AND REAL HOSPITAL WASTEWATER APPLYING THE CONVENTIONAL FENTON PROCESS: OPTIMIZATION CONDITIONS AND APPLICATION

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This study investigated the treatment of simulated and real hospital wastewater spiked with amoxicillin (AMX), ceftriaxone (CTX), and/or Telebrix (TLX) using the Fenton process. First, the optimal treatment conditions were determined on simulated wastewater by varying the initial concentration of AMX, the H_2O_2/Fe^{2+} ratio (k), and the initial pH. Subsequently, the effects of inorganic ions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}), considered both individually and in combination, as well as temperature and the different pharmaceutical compounds, were evaluated under the established optimal conditions. Finally, experiments were performed on real hospital wastewater. Chemical oxygen demand (COD) and spectrophotometric analysis (used to monitor AMX concentration) were employed to assess treatment performance. The results showed that the optimal conditions for the Fenton process were: 0.5 mM AMX, k = 2, and pH 3. The process does not degrade all pharmaceutical compounds with the same efficiency, and its performance decreases at high temperatures and in the presence of inorganic ions. Moreover, the Fenton process exhibited limited efficiency (37.05% COD removal) when applied to real hospital wastewater due to its high inorganic ion content. However, the successive addition of Fenton's reagent significantly improved COD removal, reaching 88.96% in real wastewater.

Keywords: Fenton process, pharmaceuticals, hospital wastewater, iron, advanced oxidation process

1. Introduction

The issue of discharging untreated hospital wastewater into nature is a real concern in Côte d'Ivoire. Indeed, most hospitals do not have a functional wastewater treatment plant. This is the case at the Treichville University Teaching Hospital (THT) in Abidjan, whose wastewater treatment plant, which was supposed to treat its wastewater, has not been operational since 1975. Since then, its effluent has been directly and continuously discharged into Ebrié Lagoon. It should be noted that fishing, bathing and transportation activities take place there, not to mention the presence of residential areas nearby, thereby endangering both aquatic and human life. According to investigations conducted by Sadia et al., wastewater produced at THT contains some inorganic ions such as chlorides, nitrates and phosphates [1]. This survey also revealed that amoxicillin (AMX), ceftriaxone (CTX) and Telebrix (TLX) were commonly prescribed for inpatients or imaging purposes in this hospital. AMX and CTX are antibiotics in the penicillin and cephalosporin families, respectively. TLX is an iodinated contrast medium used for radiological examinations. Not all three drugs are biodegradable organic compounds. The majority of antibiotics administered orally to patients are only partially metabolized, while the remaining 25-75% are released from the body into the environment [2],[3]. The continuous and direct discharge of hospital wastewater, which may contain pharmaceuticals, could pose a real risk to aquatic ecosystems and human health.

Numerous studies have shown the presence of pharmaceuticals such as antibiotics in soil, urban wastewater, groundwater and surface water at very low concentrations [4]-[7]. The persistence of antibiotics such as AMX and their residues in ecosystems can lead to drug allergies and toxicological problems [8] as well as the development of antibiotic-resistant bacteria [9],[10]. Due to the potential adverse effects of pharmaceuticals on the human body and natural life, it is important to develop effective methods to remove them from contaminated water.

Conventional wastewater treatment processes, such as biological processes or adsorption, have proven to be ineffective regarding the removal of most pharmaceutical compounds that are not readily biodegradable. In this context, advanced oxidation processes offer an alternative. These processes are based on the in-situ generation of powerful reactive species, in this case,

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hydroxyl radicals, which are essential for degrading and mineralizing organic compounds. Several advanced oxidation processes (AOPs) exist, including the processes anodic oxidation [11], Sono-Fenton [12], Fenton-like [13], electro-Fenton [14],[15], ozonation [16], photo-Fenton [17] and Fenton [18]-[20].

The classical Fenton process involves reactions between Fe^{2+} and H_2O_2 to produce hydroxyl radicals. The efficiency of the Fenton process is strongly dependent on several parameters, including the concentration of H_2O_2 and Fe^{2+}, the molar ratio of H_2O_2 to Fe^{2+}, the properties of the organic matter and the pH of the solution [2, 21-22]. The application of the Fenton process for the degradation of organic compounds has been widely researched. For example, Li et al. studied the treatment of simulated pharmaceutical wastewater containing n-butanol, ethyl p-nitrobenzoate, 4,7-dichloroquinoline and ethyl acetoacetate by the Fenton process [23]. The operational parameters investigated were the initial pH, the molar ratio of H_2O_2 to Fe^{2+} and H_2O_2 dosage. Their work revealed that, under optimal degradation conditions (initial pH = 2.5, $[H_2O_2]/[Fe^{2+}] = 20$, $H_2O_2 = 0.6Q$, where Q is the theoretical dosage of the Fenton's reagent, and reaction time = 30 mins), the Fenton process was able to remove all the pollutants studied at different rates of efficiency. The highest degradation rate (100%) was obtained with 4,7-dichloroquinoline and the lowest (56%) with n-butanol. Similarly, Sönmez et al. showed that the optimal concentrations of Fenton's reagent (H_2O_2 and Fe^{2+}) for degradation depend on the organic compounds present [24]. Thus, 0.6 mg/L H_2O_2 and 6-8 mg/L Fe^{2+} are required to completely degrade carbamazepine. For caffeine and paracetamol, higher concentrations are needed to achieve a 100% degradation rate (7.5 mg/L H_2O_2 and 6 mg/L Fe^{2+} for caffeine compared to 5 mg/L H_2O_2 and 10 mg/L Fe^{2+} for paracetamol). Furthermore, Li et al. reported that pharmaceutical species such as acetaminophen, atenolol, carbamazepine, metoprolol, dilantin, diclofenac, pentoxifylline, oxybenzone, caffeine, fluoxetine, gemfibrozil, ibuprofen, naproxen, propranolol, sulfamethoxazole, bisphenol A and trimethoprim were completely degraded by the Fenton process at a concentration of 20 mg/L Fe^{2+} and a H_2O_2 to Fe^{2+} molar ratio of 2.5 [25]. The optimal experimental conditions for the treatment of cosmetic wastewater from car care products determined by Cüce and Temel are pH 3, concentrations of 300 mg/L Fe^{2+} and 1050 mg/L H_2O_2 as well as a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 600/300 [26].

The objective of this work was to investigate the efficiency of the Fenton process regarding the degradation of pharmaceutical compounds (AMX, CTX, and TLX) contained in simulated and real hospital wastewater. The first step involved investigating amoxicillin-doped simulated wastewater to determine the optimal conditions for degradation by optimizing operational parameters such as the concentration of the compound, the $[H_2O_2]/[Fe^{2+}]$ molar ratio and the initial pH of the solution. These optimal conditions were subsequently applied for the degradation of CTX and TLX as well as for the study of the effects of inorganic ions (KCl, KNO_3, K_2SO_4 and K_2HPO_4) and the temperature. In the last step, the physicochemical parameters of real hospital wastewater collected at THT were evaluated before being treated under the optimal operational conditions determined for the simulated wastewater. To the best of our knowledge, such a research study has yet to be conducted. This work intends to provide a green and efficient method for the treatment of hospital wastewater.

2. Experimental

2.1. Reagents

AMX, CTX and TLX were manufactured by Bailly-Creat, LDP TORLAN and Guerbet, respectively, as well as purchased from pharmacies in the city of Abidjan. Potassium hydrogen phosphate (K_2HPO_4), iron(II) sulfate heptahydrate ($FeSO_4*7H_2O$), potassium sulfate (K_2SO_4) and potassium nitrate (KNO_3) were obtained from Merck. Sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) were obtained from Panreac and Scharlau, respectively, while sulfuric acid (H_2SO_4) and potassium chloride (KCl) were obtained from Sigma-Aldrich. Potassium permanganate ($KMnO_4$) was purchased from Fluka. All the chemicals, except for the pharmaceutical compounds, were of analytical grade. The different solutions were prepared in ultrapure distilled water.

2.2. Experimental procedure

A 500 mL solution containing the drug was prepared before each experiment in distilled water. In addition, the initial pH of the solution was adjusted to the desired value using 1 M NaOH and H_2SO_4. The wastewater treatment experiments were conducted in a 600 mL beaker used as a reactor at room temperature for a duration of 60 mins. The appropriate amounts of $FeSO_4*7H_2O$ were added to the reaction medium. The resulting mixture was magnetically stirred to ensure the dissolution of the iron sulfate and homogenization of the solution. Finally, hydrogen peroxide was introduced to the reaction mixture to initiate the degradation process. To complex the residual iron and stop the reaction, the collected samples (10 mL) at defined time intervals were added to a beaker containing 1 mL of 1 M NaOH. The samples were filtered 3 times with an ordinary filter 250 mm in diameter (Lab filter) and placed in a water bath heated to 45°C for 10 minutes to remove the residual amount. The experimental setup is shown in *Figure 1*.

2.3. Determination of the Cl^-, NO_3^- and PO_4^{3-} concentrations as well as total suspended solids

Nitrate and phosphate ion concentrations were determined using NitraVer 5 and PhosVer 3 powders, respectively, as well as measured with a DR6000 UV-Vis spectrophotometer at wavelengths of 500 and 800 nm, respectively, as described by Sadia et al. [1]. Total suspended solids (TSS) were determined by weighing a filter containing total suspended solids having been heated for one hour at 105°C. The chloride content was determined volumetrically by Mohr's method in the presence of silver nitrate. The real wastewater was taken from Treichville University Teaching Hospital.

2.4. Analytical methods

The chemical oxygen demand (COD), a global parameter which corresponds to the amount of oxygen consumed for the complete oxidation of the organic matter and some oxidizable inorganic compounds contained in the sample analyzed, was then determined. During the experiments, 2 mL of the samples were taken at well-defined time intervals and placed in pre-dosed HACH tubes which were then heated in a digester at 150 °C for 120 minutes. After cooling, the COD value was read directly using a DR6000 UV-Vis spectrophotometer. The COD reduction rate was determined using this formula:

$$\Delta(COD) = \frac{COD_0 - COD_t}{COD_0} x100 \quad (1),$$

where COD_0 and COD_t denote the initial and final COD (mg O_2/L), respectively.

The normalized COD (COD^*) was calculated as follows:

$$COD^* = \frac{COD_t}{COD_0} \quad (2).$$

The change in the hydrogen peroxide concentration was monitored during the experiments by dosing a beaker containing 5 mL of both the sample and H_2SO_4 (1 M) with 0.01 M $KMnO_4$ according to the following equation:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + \\ + 5O_2 + 8H_2O \quad (3).$$

Equilibrium was reached when the solution turned a persistent pale pink color [27].

3. Results and discussion

In this section, the initial concentration of amoxicillin, $[H_2O_2]/[Fe^{2+}]$ ratio and pH will be investigated in order to identify the optimum treatment conditions which will then be applied.

3.1. Determination of the optimal conditions

3.1.1. *Effect of the initial concentration of AMX*

The effect of the AMX concentration on the performance of the Fenton process was evaluated at concentrations ranging from 0.395 to 2.37 mM at pH 3 and with a H_2O_2 to Fe^{2+} molar ratio of 2 ($[H_2O_2]$ = 60 mM and $[Fe^{2+}]$ = 30 mM) over a reaction time of 60 minutes.

In *Figure 2A*, all the curves display two distinct parts, namely a very rapid decrease in COD during the first 10 minutes followed by a very slow phase during which the degradation rate of the organic compound remains almost constant over the last 50 minutes of the experiment. In fact, according to Lu et al. [28], the first stage is called the Fe^{2+}/H_2O_2 stage when ferrous ions react rapidly with hydrogen peroxide to form hydroxyl radicals which in turn rapidly oxidize the pharmaceutical substance as described by the following equation:

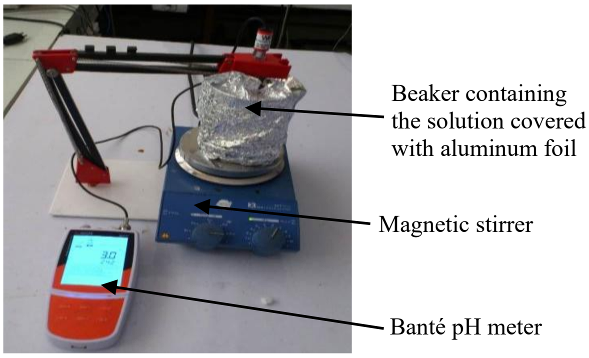

Figure 1: Experimental setup of the Fenton process

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\cdot}OH + HO^- \quad (4).$$

Equation 4 yields a rate constant between 63 and 76 $M^{-1}S^{-1}$.

In the slow stage, the ferric ions produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals ($HO_2^{\cdot}$) and regenerate ferrous ions:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{\cdot} + H^+ \quad (5).$$

The reaction in *Equation 5* occurs with a kinetic constant of 0.01-0.02 $M^{-1}S^{-1}$ which is much lower than that of *Equation 4*.

Since the formed hydroperoxyl radicals have a very low oxidation capacity compared to that of hydroxyl radicals, degradation in the second step, referred to as Fe^{3+}/H_2O_2, is very slow [28].

Moreover, the degradation rate decreases as the concentration of AMX increases possibly due to the formation of reactive intermediates that may compete with the parent compound [29]. In addition, the formation of complexes in the reaction medium as the concentration of the organic compound increases and/or the formation of hydroxyl radicals is limited can also explain the decrease in the COD removal rate as the AMX concentration increases.

Figure 2B shows the time-dependent change in hydrogen peroxide concentration during AMX degradation, with initial AMX concentrations of 0.395 and 2 mM and 60 mM initial H_2O_2 concentration. As shown in the figure, the H_2O_2 concentration decreased very rapidly during the first 10 minutes and then remained nearly constant for the rest of the reaction time. This finding is consistent with the observations presented in *Figure 2A*. Furthermore, at the same initial H_2O_2 concentration, more than 97.5% of the H_2O_2 was consumed in the 0.395 mM AMX system, whereas only 90% was consumed in the 2 mM system after 10 minutes

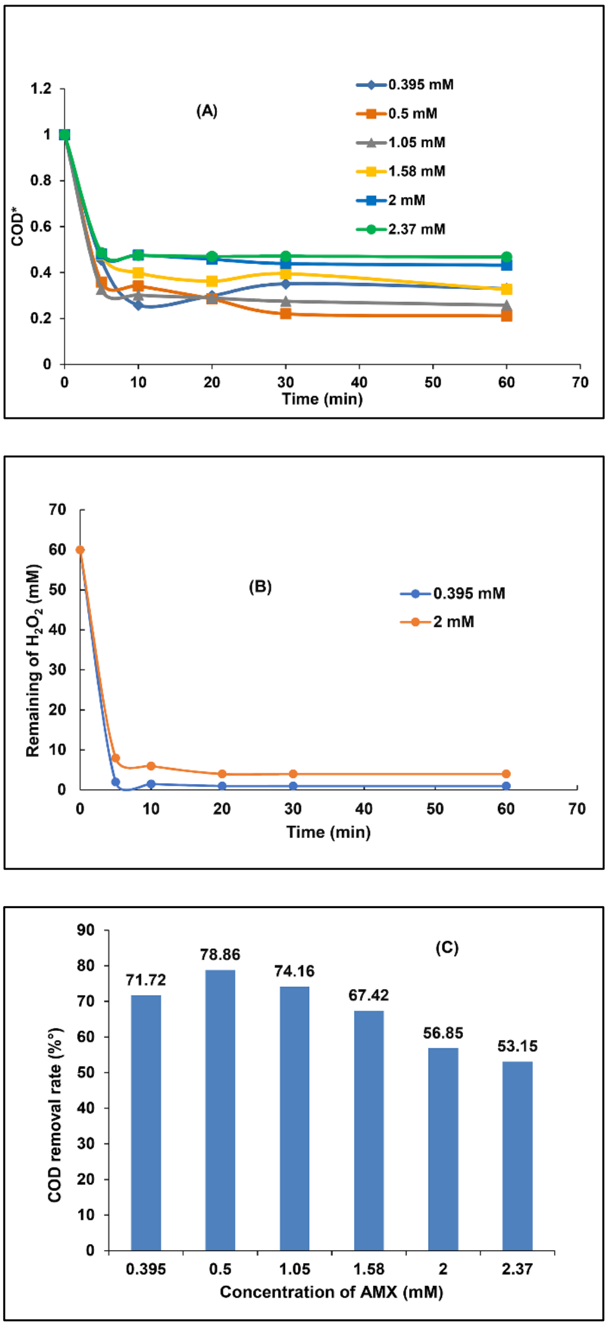

Figure 2: A) The effect of the AMX concentration on the degradation process by the Fenton process at pH 3 in a stirred solution of $[Fe^{2+}]$=30 mM and $[H_2O_2]$=60 mM at T=25 °C; B) The evolution of the remaining H_2O_2 concentration during the AMX degradation process by the Fenton process; C) COD abatement rate at different concentrations of AMX after a reaction time of 60 mins

of reaction, indicating that an increase in the initial concentration of AMX results in an increase in the degradation time.

According to *Figure 2C*, the COD removal rates determined after 60 mins were 71.72, 78.86, 74.16, 67.42, 56.85 and 53.15% for AMX concentrations of 0.395, 0.500, 1.05, 1.58, 2.00 and 2.37 mM, respectively. The highest degradation efficiency was achieved at 0.500 mM AMX.

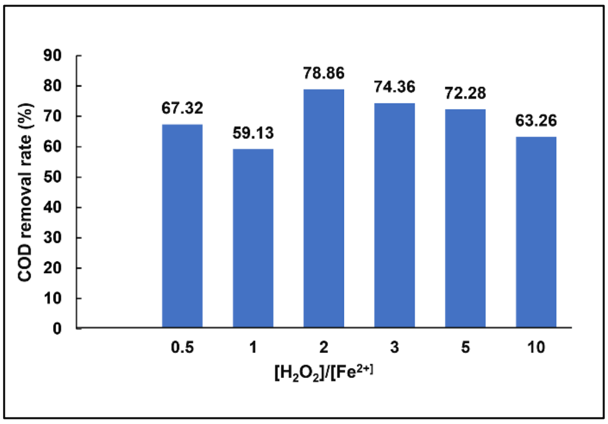

Figure 3: COD removal rates for different molar ratios of reagents after a reaction time of 60 minutes with 0.500 mM amoxicillin at pH 3

3.1.2. Effect of the H_2O_2 to Fe^{2+} molar ratio

The molar ratio of Fenton's reagent ($k = [H_2O_2]/[Fe^{2+}]$) is one of the parameters that significantly influences how efficient the Fenton process is. To determine the optimal ratio, the Fe^{2+} concentration was maintained at 30 mM, while the H_2O_2 concentration was adjusted between 30 to 300 mM, yielding ratios ranging from 1 and 10. The experimental conditions were set as follows: AMX concentration of 0.500 mM; pH 3 and treatment duration of 60 minutes. The degradation efficiency of amoxicillin by the Fenton process depends on the $[H_2O_2]/[Fe^{2+}]$ molar ratio as indicated in *Figure 3*. The COD removal rate increased from 59.13 to 78.86% when the $[H_2O_2]/[Fe^{2+}]$ molar ratio increased from 1 to 2, respectively. Increasing the molar ratio, that is, the increase in the H_2O_2 concentration, led to an improvement in the degradation efficiency of AMX. On the other hand, a very high concentration of H_2O_2 ($k>2$) inhibited the Fenton process with regard to the degradation of the model organic compound. When the molar ratio of Fenton's reagent was less than 2, the amount of hydroxyl radicals generated was insufficient to effectively degrade the pharmaceutical compound due to the low amount of H_2O_2. In contrast, when the molar ratio was greater than 2, an excess of H_2O_2 could occur, resulting in a generation of a large amount of hydroxyl radicals, thereby triggering competing side reactions that diminish the efficiency of AMX degradation.

According to our results, the best COD removal rate was obtained when $[H_2O_2]/[Fe^{2+}]$ was 2, which is practically the same as the value in the literature. This is the case for Dehghani et al. [30], who found a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 1.5 for the degradation of sulfonamide by the Fenton process. Similarly, Li et al. reported an optimum value of 1.5 for the degradation of pharmaceutical species [25]. Cüce and Temel reported a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 2, namely 600/300 [26].

In accordance with the literature, the concentrations of iron and hydrogen peroxide are important parameters in the Fenton process [30]. An excessive or insufficient amount of either reagent can significantly reduce the efficiency of the process. Studies have shown that for

$[H_2O_2]/[Fe^{2+}]$ ratios greater than 10, an excess of hydrogen peroxide in the solution can lead to the scavenging of hydroxyl radicals according to the following equation [31]:

$$H_2O_2+{\cdot}OH \rightarrow H_2O+{\cdot}HO_2 \qquad (6),$$

and recombination of such radicals to form H_2O_2 according to the equation below [32]:

$${\cdot}OH+{\cdot}OH \rightarrow H_2O_2 \qquad (7).$$

These generated species are less reactive than hydroxyl radicals.

3.1.3. Effect of the initial pH of the solution

The Fenton process is strongly dependent on pH, which plays an important role in the mechanism of hydroxyl radical production. In order to determine the optimum pH, five acidic pH values (1.7, 2.0, 3.0, 3.5 and 4.0) were investigated using 0.500 mM amoxicillin, a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 2 and an experimentation duration of 60 mins. Numerous studies have indicated that the optimum initial pH is between 2.5 and 4.0 to achieve the best degradation rates of organic compounds [26]. As shown in *Figure 4A*, the degradation rate of AMX remained consistent at all initial pH values during the first 10 mins of the experiment. The COD removal rates determined after 60 mins of treatment (*Figure 4B*) increased from 64.72 to 78.86% as the pH increased from 1.7 to 3.0. Beyond pH 3, a decrease in the efficiency of the Fenton process for the AMX treatment was observed, since the rates obtained were lower than those obtained at pH 3 (64.98 and 55.23% at pH 3.5 and 4.0, respectively). The best degradation rate was therefore obtained at an initial pH of 3.0. Other authors have also reported the same optimum pH for the degradation of organic compounds [23],[24]. In fact, the pH of the solution is a very sensitive parameter in the Fenton process as it governs the formation of hydroxyl radicals, the main oxidative species of organic compounds, in the reaction medium. Thus, at high pHs (pH>4), hydroxyl radicals are generated very slowly due to the formation of hydroxoferric complexes and the precipitation of ferric oxyhydroxide ($Fe(OH)_3$) [33],[34]. Furthermore, H_2O_2 easily decomposes into O_2 and H_2O [35]:

$$2H_2O_2 \rightarrow O_2+2H_2O \qquad (8).$$

When the pH is very acidic (pH<2), the degradation rate of organic compounds decreases due to the formation of $[Fe(H_2O)_6]^{2+}$ complex [33],[34], which react more slowly with peroxide than the $[Fe(OH)(H_2O)_5]^{2+}$ complex, that are formed at pH values between 2 and 3 [33],[34]. In addition, peroxide reacts with H^+ protons to form an hydroxyoxidanium ion ($H_3O_2^+$), which is very stable and therefore not highly reactive with Fe^{2+} [36]:

$$H_2O_2+H^+ \rightarrow H_3O_2^+ \qquad (9).$$

Furthermore, excess H^+ can react with hydroxyl radicals to form H_2O [23]:

$$H^++{\cdot}OH+e\text{-} \rightarrow H_2O \qquad (10).$$

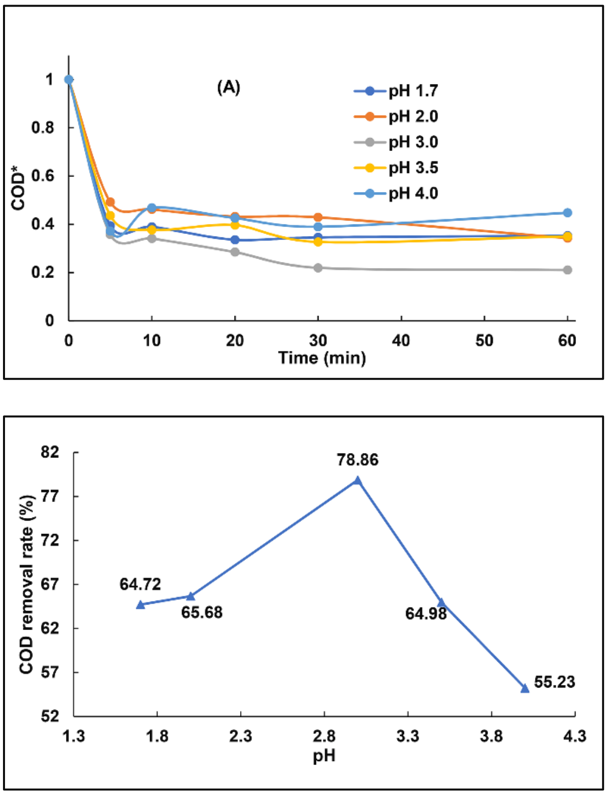

Figure 4: A) The effect of pH on the change in the AMX degradation rate as a function of time with a molar ratio of k=2, [AMX]=0.500 mM; t=60 mins; B) COD abatement rate at different pHs after 60 mins of amoxicillin treatment and a molar ratio of k=2

Under the present experimental conditions, the optimal operating parameters for maximum degradation of amoxicillin were determined to be an AMX concentration of 0.500 mM, a pH value of 3, and a molar ratio of $[H_2O_2]/[Fe^{2+}] = 2$. The influence of inorganic ions, temperature and pharmaceuticals on the efficacy of this technology under the previously determined optimum conditions will be further investigated. Next, these optimum conditions will be applied to the treatment of real hospital wastewater.

3.2. Investigations under optimal conditions

3.2.1. Influence of inorganic ions

The influence of chloride, sulfate, nitrate and phosphate ions was investigated during the degradation of amoxicillin (0.500 mM) by the Fenton process. The evolution of the COD removal rate as a function of the inorganic ion concentration (200 mM) is displayed in *Figure 5*. The presence of inorganic ions in the reaction medium appeared to have a detrimental effect on the performance of the conventional Fenton process. The observation was the same whether a single type of ion or all ions are present simultaneously in the reaction medium. Indeed, the degradation rate of AMX in the absence of inorganic ions was much higher than that in the presence of inorganic ions. The COD removal rates obtained in the presence of 200 mM Cl^-, NO_3^-, SO_4^{2-} and

Table 1: The effect of inorganic ions on the COD removal rate

Inorganic ions	Concentration (mg/L)	COD removal ratio (%)
NO_3^-	10	64.63
	74	54.92
Cl^-	13	60.00
	35	62.54
	70	52.99
SO_4^{2-}	10	56.83
	35	54.55
	71	47.01
PO_4^{3-}	10	44.53
	35	48.66

PO_4^{3-} were 67.72, 51.31, 50.18 and 46.85%, respectively. The performance of the Fenton process decreased further when all the inorganic ions were present in the reaction medium simultaneously. The abatement rate obtained after a reaction time of 60 minutes under these conditions was 44.59%. Regarding the results obtained, inorganic ions strongly slow down the degradation rate of AMX in the following order of an increasingly negative effect: $Cl^- < NO_3^- < SO_4^{2-} < PO_4^{3-}$. De Oliveira et al. also showed that sulfate ions inhibited the oxidation of caffeine by the Fenton process more than chloride ions [37].

Several studies were carried out with different concentrations of inorganic ions (*Table 1*). The results confirmed inhibition of the Fenton process by inorganic ions at all concentrations studied. Research has shown that the Fenton process is very sensitive to inorganic ions present in solution [38]. These ions can form complexes with Fe(II):

$$Fe^{2+} + Cl^- \rightarrow FeCl^+ \quad (11),$$

$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \quad (12),$$

$$Fe^{2+} + H_2PO_4^- \rightarrow FeH_2PO_4^+ \quad (13),$$

$$Fe^{2+} + NO_3^- \rightarrow FeNO_3^+ \quad (14),$$

thereby affecting the distribution and reactivity of free Fe^{2+} ions. The formation of inorganic complexes leads to a reduction in the production of hydroxyl radicals as Fe^{2+} ions are no longer available to react with H_2O_2.

The presence of Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} promotes competition between organic matter and hydroxyl radicals, delaying the oxidation of amoxicillin. Inorganic ions react with hydroxyl radicals, leading to the generation of inorganic radicals with less potent oxidizing powers than hydroxyl radicals:

$$Cl^- + {}^{\cdot}OH \rightarrow ClOH^{\cdot -} \quad k = 4.30\text{x}10^9\ Lmol^{-1}s^{-1} \quad (15),$$

$$HSO_4^- + {}^{\cdot}OH \rightarrow SO_4^{-\cdot} \quad k = 1.40\text{x}10^7\ Lmol^{-1}s^{-1} \quad (16).$$

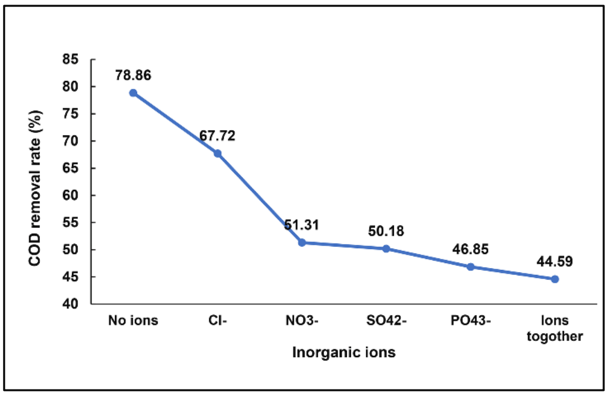

Figure 5: The effect of inorganic ions on the AMX degradation rate as a function of time when pH=3, k=2, [AMX]=0.500 mM, $[NO_3^-]=[Cl^-]=[SO_4^{2-}]=[PO_4^{3-}]$=200 mg/L and t=60 mins

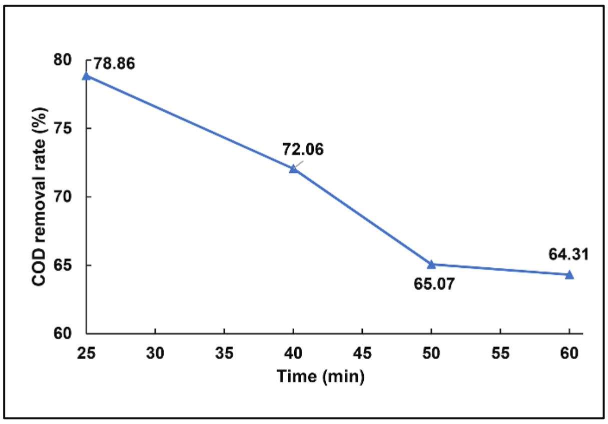

Figure 6: The effect of temperature on the degradation of amoxicillin at pH 3, [AMX]=0.500 mM and k=2

3.2.2. The effect of temperature on the degradation of AMX

Temperature is an important parameter in determining the kinetics of the Fenton reaction. Indeed, according to many studies, increasing the temperature accelerates the rate of consumption of H_2O_2, indicating better decomposition of H_2O_2 into iron-catalyzed radicals as the temperature increases. This process improves the percentage of degradation of organic compounds [39]. However, when the temperature surpasses its optimum, the performance of the Fenton reaction diminishes because an elevated temperature favors the decomposition of H_2O_2 into O_2 and H_2O. The literature presents varying views on the optimal temperature. Lin et al. reported that the optimum temperature for the degradation of phenol was 30 °C [40], while Guo et al. established in their study that 40 °C yielded the best results for the degradation of amoxicillin [41]. Above this temperature, a decrease in the rate of organic degradation was observed. Conversely, Homem et al. reported that the degradation rate of amoxicillin increased as the temperature increased progressively within the 22-57°C range [20].

Table 2: Physico-chemical characteristics of real hospital wastewater at THT

Parameters (units)	Values
Temperature (°C)	24.8
pH	6.71
Nitrates (NO_3^-) (mg/L)	1.11
Phosphates (PO_4^{3-}) (mg/L)	1.26
Chlorides (Cl^-) (mg/L)	29.33
Conductivity (µS/cm)	103
Suspended matter (mg/L)	11.5

In this work, the effect of temperature on the degradation of AMX was investigated under the optimum conditions defined above. The COD removal rates calculated at four different temperatures (25, 40, 50 and 60 °C) are presented in *Figure 6*, which demonstrates that the COD removal rate declines with increasing temperature. The rates obtained are 78.86, 72.06, 65.07 and 64.31% at 25, 40, 50 and 60 °C, respectively. Under our experimental conditions, an increase in temperature has a detrimental effect on the degradation of the pharmaceutical compound.

3.2.3. Degradation of pharmaceutical compounds

The pharmaceutical compounds AMX, CTX and TLX were oxidized by the Fenton process under the optimum conditions obtained in the simulated wastewater. The degradation rates of the pharmaceuticals as a function of the reaction time are shown in *Figure 7A*.

The results indicate that the Fenton process does not degrade pharmaceutical compounds at the same rate. For instance, at an identical concentration, namely [AMX] = [CTX] = [TLX] = 0.500 mM, the Fenton process achieves fast degradation of amoxicillin (blue line) compared to ceftriaxone (orange line) or telebrix (grey line). The difference in the degradation efficiency is probably related to the molecular structures of the target compound and steric hindrance effects, which may impede the accessibility of certain functional groups to hydroxyl radical attack. In addition, the Fenton reaction is further slowed down when the compounds are simultaneously present (yellow line) in the reaction medium. Furthermore, the degradation of pharmaceutical antibiotic compounds (AMX and CTX) is more favorable than that of the iodinated contrast product (TLX). For example, Li et al. reported differences in the reactivity of Fenton's reagent with regard to the degradation of the compounds n-butanol, ethyl p-nitrobenzoate, 4,7-dichloroquinoline and ethyl acetoacetate [23].

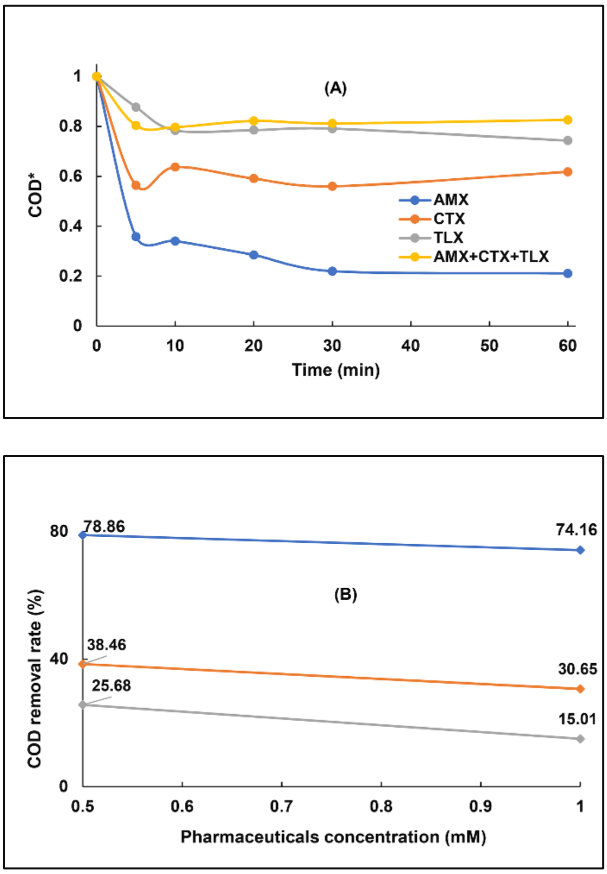

Figure 7: A) Change in the normalized COD removal rate when [AMX]=[CTX]=[TLX]=0.500 mM and when AMX, CTX and TLX are simultaneously present, pH=3, k=2, t=60 mins; B) COD abatement rate of different pharmaceutical compounds at different concentrations: [AMX]=0.500 and 1.00 mM, [CTX]=0.500 and 1.00 mM, and [TLX]=0.500 and 1.00 mM

The COD removal efficiencies of each pharmaceutical compound as a function of the initial concentration (0.500 and 1.00 mM) is displayed in *Figure 7B*. The results reveal that organic compound degradation rates decline with increasing initial concentration. For amoxicillin, the degradation rate ranged from 78.86 to 74.16% when its concentration varied between 0.500 and 1.00 mM, respectively (blue line). For ceftriaxone, the degradation rate ranged from 38.46 to 30.65% when its concentration varied between 0.500 and 1.00 mM, respectively (orange line). For Telebrix, the COD removal rate ranged from 25.68 to 15.01% when its concentration varied between 0.500 and 1.00 mM, respectively (grey line).

3.3. Application to the treatment of real hospital wastewater

Physico-chemical parameters of real wastewater from THT were determined and recorded in *Table 2*. The analysis of this wastewater revealed the presence of inorganic ions such as NO_3^- (1.11 mg/L), PO_4^{3-} (1.26 mg/L) and Cl^- (29.33 mg/L). The chloride ion concentration was 23.28-fold higher than that of phosphate ions and 26.42-fold higher than that of nitrate ions.

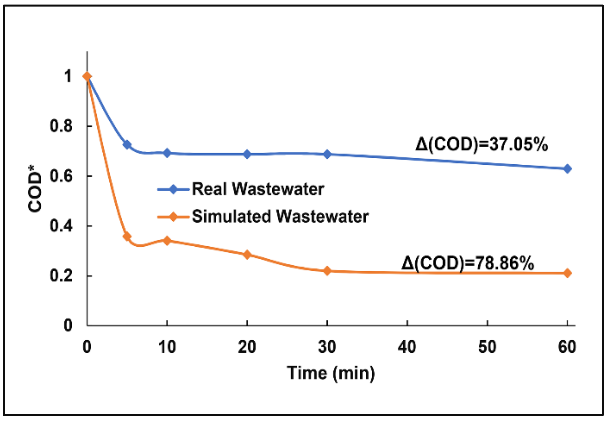

Figure 8: COD* evolution curves of simulated and real wastewater containing amoxicillin. Operating conditions: [AMX]=0.500 mM, pH=3, T=25 °C and k=2

A comparison of the change in the chemical oxygen demand of the simulated effluent (orange curve) and real effluent from THT (blue curve) is illustrated in *Figure 8*. Both types of wastewater were spiked with 0.500 mM amoxicillin. Compared to the simulated wastewater, the degradation rate of AMX in the real wastewater proceeded considerably more slowly. After a reaction time of 60 mins, the COD removal rate reached 37.05%, approximately 2.13-fold lower than that achieved with the simulated wastewater (78.86%) but close to that calculated in the presence of Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} ions simultaneously present in the simulated wastewater (44.59%). The effectiveness of the Fenton process with regard to breaking down AMX in the real wastewater was significantly reduced which is not unexpected, as the presence of inorganic ions in simulated wastewater has been demonstrated to hinder Fenton process performance. However, inorganic ions (Cl^-, NO_3^- and PO_4^{3-}) were present in the real effluent from THT investigated in this study. In the case of hospital wastewater spiked with AMX, this could partly explain the low COD removal rate obtained.

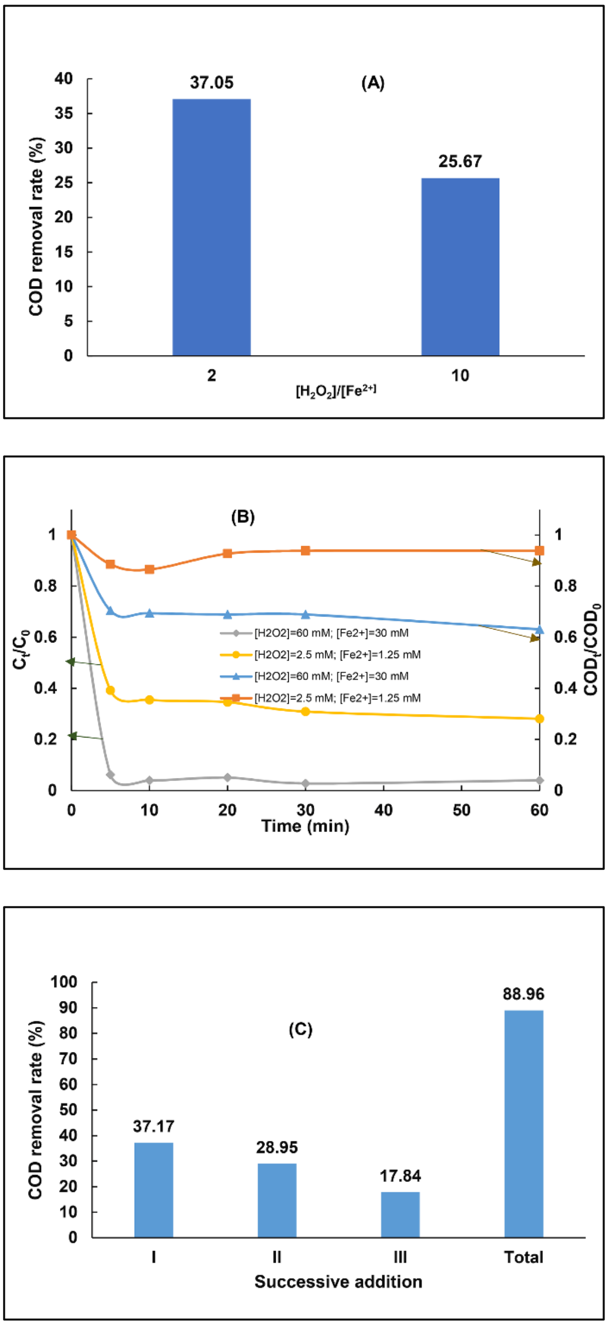

Figure 9: A) The effect of the molar ratio of H_2O_2 to Fe^{2+} on the treatment of real wastewater from Treichville University Teaching Hospital; B) Comparison of the change in the AMX concentration and COD using different concentrations of Fenton's reagent and a molar ratio of 2; C) The effect of successive additions of Fenton's reagent. Operating conditions: [AMX]=0.500 mM, pH=3, T=25 °C and k=2

However, the complex composition of the matrix may also explain the poor performance of the Fenton process. To improve the efficiency of the Fenton process for real wastewater treatment, further investigations were carried out. One of the alternatives was to increase the $[H_2O_2]/[Fe^{2+}]$ molar ratio from 2 to 10 (*Figure 9A*). According to this figure, increasing the molar ratio leads to a decrease in the efficiency of treating the real wastewater with COD removal efficiencies of 37.05 and 25.67% for k=2 and k=10, respectively. The change in the concentration of amoxicillin and COD during the Fenton reaction is displayed in *Figure 9B*. In this experiment, the molar ratio was kept constant (k = 2) but the concentrations of the reactants changed. Overall, the results demonstrate that high levels of reagents (60 mM $[H_2O_2]$ and 30 mM $[Fe^{2+}]$) are more effective than low levels (2.50 mM $[H_2O_2]$ and 1.25 mM $[Fe^{2+}]$) in terms of treating wastewater under our optimum conditions. In the latter case, no sludge was formed in the reaction medium and the coloration at the end of the reaction was green. The amount of reagents used seems to play an important role in the Fenton process. In our study, maintaining the molar ratio of Fenton' reagent unchanged while reducing the reagent concentration resulted in a substantial decrease in both the degradation rate and the chemical oxygen demand. Furthermore, the AMX concentration (represented by yellow and grey curves) decreased faster than the COD (represented by blue and orange curves) in both cases. The formation of intermediate species during the reaction may explain the observed differences. The concentration of an organic compound is a compound-specific parameter, whereas COD is a global parameter that takes into account all the organic compounds in the reaction medium. Additionally, AMX degradation rates of 96.0 and 71.9% were obtained at the end of the reaction, whereas COD removal rates of 37.05 and 6.25% were obtained for high ($[H_2O_2] = 60$ mM and $[Fe^{2+}] = 30$ mM) and low ($[H_2O_2] = 2.50$ mM and $[Fe^{2+}] = 1.25$ mM) concentrations of the reagents, respectively. These values indicate that the degradation rate of AMX results in the formation of intermediates in the reaction medium.

To improve the performance of the Fenton process for the treatment of real hospital effluent containing pharmaceuticals, another alternative was tested. The successive addition of Fenton's reagent to the reaction medium at 20 min intervals after filtration was the method adopted. The process was repeated three times. The COD removal rates of 37.17, 28.95 and 17.84% for stages I, II and III, respectively, are shown in *Figure 9C*. After each addition of Fenton's reagent, the efficiency of our technology decreased, possibly because the degradation of amoxicillin using the Fenton process produces by-products that can be recalcitrant to degradation such as carboxylic acids [42]. Furthermore, the combined action of adding this reagent sequentially led to a clear improvement in the total abatement rate of 88.96%.

4. Conclusions

The optimal experimental conditions established in the simulated wastewater were a concentration of 0.500 mM amoxicillin, a pH of 3 and $k = 2$. Under these conditions, the COD removal rates were 78.86, 38.46 and 25.68% for amoxicillin, ceftriaxone and Telebrix, respectively. A low COD removal rate was observed when all three pharmaceuticals were present in the reaction medium (17.36%). The presence of inorganic ions strongly inhibits the efficiency of the Fenton process due to the formation of complexes between iron and these inorganic ions on the one hand and to the trapping of hydroxyl radicals by these ions on the other. Ion inhibition occurred in the following descending sequence: Cl^- (67.72%) < NO_3^- (51.31%) < SO_4^{2-} (50.18%) < PO_4^{3-} (46.85%). The inhibitory effect of ions was most pronounced when they were present simultaneously in the reaction medium (44.59%). The efficiency of the Fenton process also decreased at higher temperatures. The physicochemical characterization of the tested real wastewater showed that it contains concentrations of Cl^-, NO_3^- and PO_4^{3-} of 29.33, 1.11 and 1.26 mg/L, respectively. The pH was 6.71, temperature 24.8 °C, conductivity 103 µS/cm and suspended solids concentration 11.5 mg/L. This work showed that treating real hospital wastewater under optimal Fenton treatment conditions is difficult because the COD removal rate (37.05%) is approximately 2.13 times lower than that determined under optimal conditions with simulated wastewater. Reducing the reagent concentration by maintaining the molar ratio at 2 and increasing the molar ratio did not improve the efficiency of wastewater treatment. In addition, the subsequent addition of Fenton's reagent at regular intervals resulted in a removal percentage of more than 88% after a reaction time of 60 mins. A comparison of the amoxicillin concentration with COD indicated that reactive compounds were formed during wastewater treatment.

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