Ibuprofen Degradation from Synthetic Wastewater Using Photo-Fenton Process

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Abstract

The removal of Ibuprofen antibiotics (IBU) by photo-degradation UV/H2O2/Fe2+ system was investigated in a batch reactor under different initial concentrations of H2O2 (100-500) mg/L, Fe2+ (10-40) mg/L, pH (3-9) and initial concentrations of IBU (10-80) mg/L, and their relationship with the degradation efficiency were studied. The result demonstrated that the maximum elimination of IBU was 85.54% achieved at 300 mg/L of H2O2, 30 mg/L of Fe2+, pH=3, and irradiation time of 150 min, for 10 mg/L of IBU. The results have shown that the oxidation reagent H2O2 plays a very important role in IBU degradation.

Keywords: Ibuprofen antibiotic; Homogeneous Process; UVC; First order model.

1- Introduction

Emerging pollutants have received a lot of attention as a cause for concern in today's water pollution crisis. Pharmaceuticals, cosmetics, and other household items, together with chemicals like pesticides and endocrine-disrupting agents, fall into this category [1]. Many industrial processes generate toxic and polluted wastewater that is difficult to degrade and requires costly physical or physico-chemical treatments [2]. Water is a critical necessity for the utilization of humanity. It is crucial for rural and modern development, and also to support developing populations that require a harmless drinking water supply [3]. Due to their widespread application in a variety of settings, including the treatment of bacterial infections in people and cattle, antibiotics are among the most ubiquitous pharmaceutical chemicals found as pollutants in aquatic habitats [4]. Antibiotics are drugs that act directly or inhibit their development, thus the alternative name antibacterial. Nevertheless, they do not work against viral illnesses like the common cold or flu. Infectious diseases in humans, animals, and plants are all being treated using antibiotics [5].

Water treatment plants often find medicines, especially nonsteroidal steroidal anti-inflammatory drugs (NSAIDs), Ibuprofen, or 2-(4-(methyl propyl) phenyl) propionic acid (IBU), is a medication of the NSAID class that is crucial to daily life [6], which is an analgesic widely used for the treatment of musculoskeletal pain, rheumatoid arthritis, and fever [7]. Because IBU is persistent, non-biodegradable, and resistant, it cannot be effectively removed using standard water treatment methods [6]. As a result, many cutting-edge techniques were used to get rid of IBUs, including advanced oxidation processes (AOPs), adsorption, electrochemical treatment, membrane filtering, chlorination disinfection, and biological therapy [8]. Advanced oxidative processes (AOPs) offer a possible solution to this problem. They allow the degradation of pollutants by highly oxidizing species, such as hydroxyl radicals, generated in the reaction medium. The most widely used techniques are Fenton and Photo-Fenton reactions [9].

Hydroxyl radicals (OH•) are produced by advanced oxidation processes (AOPs) and serve as highly reactive oxidant agents for the elimination of various non-biodegradable organic pollutants such as medicines, dyes, insecticides, and viruses and bacteria. Many AOPs need either electricity or sunlight to function. Nevertheless, they can also be utilized as a pre-treatment step to break down organic pollutants that will improve the efficacy of future biological treatment procedures [10].

When Fe2+ and H2O2 are mixed, a highly reactive oxidant called OH+ is produced. Using UV irradiation from the sun's light, the photo-Fenton method is an improved version of the conventional Fenton reaction, allowing for speedier mineralization of resistant organics at a greater rate than the dark reaction procedure [11, 12]. UV irradiation or visible light can both speed up the Fenton reaction. There are several organic compounds in aqueous solutions that can be completely mineralized with the assistance of UV irradiation [13], the Photo-Fenton reaction occurs in two steps:

\[ {\text{Fe}}^{2+} + {\text{H}}_2{\text{O}}_2 \rightarrow {\text{Fe}}^{3+} + {\text{OH}}^- + \text{HO}^\bullet \]

\[ \text{HO}^\bullet + \text{Organic Compound} \rightarrow \text{Nonionic Product} \]

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The OH radicals and Fe$^{3+}$ are created when H$_2$O$_2$ oxidizes Fe$^{2+}$ ions.

More hydroxyl radicals (OH) are generated when UV radiation causes Fe$^{3+}$ to be reduced back to Fe$^{2+}$[14]. The cost-effectiveness of Fenton and Photo-Fenton reactions as AOPs has been shown by researchers [15, 16]. The hydroxyl radicals (OH') formed in these processes have a very high oxidation potential (E°) of 2.80 V and are hence very reactive, (Eq. 1): [17, 18]

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH}^+ \quad (1)$$

Exposing the reactant solutions to UV or sunlight as an irradiation source (hν) might increase the availability of OH' radicals, [19] (Eqns. 2 and 3):

$$\text{Fe}^{2+} + \text{H}_2\text{O} + \text{hν} \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{H}^+ \quad (2)$$

$$\text{H}_2\text{O}_2 + \text{hν} \rightarrow \text{OH}^- + \text{H}^+ \quad (3)$$

When OH' radicals are present during Fenton and Photo-Fenton reactions, they may react with organic molecules without being selective. [20, 21] (Eqns. 4–6): 

$$\text{OH}^- + \text{RH} \rightarrow \text{R}^+ + \text{H}_2\text{O} \quad (4)$$

$$\text{OH}^- + \text{R} \rightarrow \text{ROH} \quad (5)$$

$$\text{OH}^- + \text{RH} \rightarrow \text{RH}^- + \text{H}_2\text{O} \quad (6)$$

The synthesis of a radical cation (RH$^+$) may also occur by the transfer of an electron from an organic molecule to the OH' radical, (Eq. 7).

$$\text{OH}^- + \text{RH} \rightarrow \text{RH}^+ + \text{OH}^- \quad (7)$$

Follow-up reactions (Eq. 8) allow the resultant organic radicals and organic cation radicals to be fully mineralized:

$$\text{R}^- + \text{H}_2\text{O}_2 + \text{hν} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{inorganic ions} \quad (8)$$

Restoration of Fe$^{2+}$ ions may occur via many parallel reactions (Eqns. 9–12):

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{[Fe (HO)]}^{2+} + \text{H}^+ \quad (9)$$

$$[\text{Fe} (\text{HO})]^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{HO}_2\text{•} \quad (10)$$

$$\text{Fe}^{2+} + \text{HO}_2\text{•} \rightarrow \text{Fe}^{3+} + \text{O}_2 + \text{H}^+ \quad (11)$$

$$\text{Fe}^{2+} + \text{R}^- + \text{R}^+ \rightarrow \text{Fe}^{2+} + \text{R}^- \quad (12)$$

When assessing the effectiveness of organic compound degradation, the formed OH' radical might potentially participate in negative reactions, such as (Eqns. 13 and 14), [22, 23].

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{2+} + \text{OH}^- \quad (13)$$

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2\text{•} \quad (14)$$

This research aimed to examine the photodegradation of ibuprofen (IBU) from synthetic wastewater through the Photo-Fenton advanced oxidative process. This allowed us to develop a kinetic model of the sample and confirm the treatment’s efficacy by measuring the concentration of IBUs and organic matter mineralization.

2- Experimental Works.

2.1. Materials

In this study, ibuprofen (IBU) of 99 % purity, Fig. 1, was selected as a contaminated sample provided by the General Company for Drugs Industry (Iraq) (original manufacturer: Marck, Germany). Hydrogen peroxide (H$_2$O$_2$) (50% w/w) gotten from Merck, FeCl$_3$.6H$_2$O (99% purity), as a source of iron (II) Fe$^{2+}$. In addition, (0.1M) of Hydrochloric acid (HCl) and/ or sodium hydroxide (were used to adjust the pH and neutralize the homogeneous photocatalyst. All chemicals used were of analytical grade.

![Ibuprofen](https://example.com/ibuprofen.png)

**Fig. 1.** Chemical Structure of IBU [24]

2.2. Photo- Fenton Procedure and Analysis

In this study, photocatalytic degradation was performed in a batch-mode reactor (Fig. 2). The irradiation source was a 6W UV lamp (TUV 6 W 4P-SE, Philips, UK), and the reactor was made of Pyrex glass (1L). The ultraviolet light source was positioned vertically inside the reactor’s core, protected by a quartz sleeve. The fluid reaction smothered the light entirely. Variations in initial solution pH (3, 5, 7, and 9), initial IBU concentration (10, 20, 30, and 40) mg/L, and H$_2$O$_2$ concentration (10, 20, 30, and 40) mg/L, and H$_2$O$_2$ concentration (100, 300, and 500) mg/L at room temperature were used to assess the rate of photocatalytic performance. The pH was adjusted by adding (0.1M) of HCl or NaOH (using pH meter type INOLAB 72, WT Co., Weilheim, Germany) and the necessary concentration of Fe$_2$O$_3$ nanoparticles was added once the proper concentration of IBU was generated. To attain primary adsorption equilibrium between IBU and Fe$_2$O$_3$, the suspension was magnetically agitated at 200 rpm (model MSH-300N, BOECO, Hamburg, Germany) in the dark for 30 minutes. After that, we got the required amount of H$_2$O$_2$ in there. It was lit up in order to start photocatalytic reactions. A specified quantity of 10 mL of the sample was taken from each reacted IBU solution at
specified intervals of irradiation, centrifuged for a period of time until the catalyst separated, and then the separated aqueous solutions were tested for the concentration of IBU using a spectrophotometer (UV-1800, SHIMADZU, Japan) using (UV Probe 4.2) software survey scan at wavelengths (200-1100 nm). The wavelength used in the analysis was 275 nm. The proportion of IBU removal was calculated by the following equation (Eq. 15):

\[
\text{IBU removal Efficiency} = \left( \frac{\text{IBU}_o - \text{IBU}}{\text{IBU}_o} \right) \times 100
\]

Where: \(\text{IBU}_o\) represents the initial concentration of the antibiotic solution, mg/L.
\(\text{IBU}\) = final concentration of the antibiotic solution, mg/L.

![Fig. 2. Schematic Diagram of a Batch Reactor](image)

### 3- Results and Discussion

#### 3.1. Comparison between different systems

IBU antibiotic solution was prepared at an initial concentration of 10mg/L, pH 3, an iron dose of 20mg/L, and \(\text{H}_2\text{O}_2\) concentration of 300 mg/L, then different techniques were tested (UV alone, Photolysis, Fenton, and Photo-Fenton) for the degradation of IBU antibiotic from aqueous solution and their results were illustrated in Fig. 3. This figure shows that after 30 min of reaction time in the absence of UV light, the degradation of IBU starting. As indicated in this figure different IBU removal rates were achieved by UV alone, photolysis, Fenton, and phot-Fenton processes, with corresponding values of (9.65, 17.68, 48.32, and 85.54) %, respectively at 150min irradiation time. Results showed that Photolysis and Fenton alone have no appreciable capacity for removing antibiotics from aqueous solution under UV alone. Because there are not enough oxidizing species to effectively degrade IBU, elimination efficiency is limited. These results show that the hybrid process (UV/\(\text{H}_2\text{O}_2/\text{Fe}_2\text{O}_3\)) performs better than the individual systems in degrading IBU (UV only, Photolysis, and Fenton). As this process is crucial to the oxidative breakdown of organic matter, the difference is due to the efficient generation of reactive species (OH radicals) in this reaction. The inclusion of UV and \(\text{Fe}_2\text{O}_3\) ions as an activator may effectively break down \(\text{H}_2\text{O}_2\) molecules into OH radicals, which may contribute to a higher removal rate for the Photo-Fenton system. This occurs because OH radicals are produced during the breakdown of \(\text{H}_2\text{O}_2\) by ferrous ions and ultraviolet light.

![Fig. 3. Removal Percentage of IBU using Different Processes](image)

#### 3.2. Effect of pH

Fig. 4 illustrates a change in the percent IBU elimination at varying pH values (3, 5, 7, and 9) utilizing the photo-Fenton reaction, which plays a significant role in the degradation of antibiotics but is not the only factor to consider (initial IBU concentration of 10mg/L, \(\text{H}_2\text{O}_2\) of 300 mg/L, iron nanoparticles of 20 mg/L, and 150min reaction time). Degradation of IBUs was 85.54, 74.42, 54.44, and 40.44 percent at pH 3, 5, 7, and 9, respectively. This graph demonstrates the gradual decline in antibiotic clearance as pH increases. IBU antibiotics were most effectively removed at a pH of 3. Above pH 3, deterioration slowed down. The pace of interaction between water and ferrous ions is slowed by an increase in pH when there is a reduction in the number of dissolved iron ions [25]. Furthermore, it was understood that the hydroxyl radical’s oxidation potential drops as the pH rises. When the pH rises over 3, \(\text{H}_2\text{O}_2\) dissociates and contributing to ineffective degradation at higher pH levels [26]. This result was similar to the finding of [27].

![Fig. 4. Effect of pH on the Removal of 10 mg/L of IBU](image)
3.3. Effect of initial H₂O₂ concentration

Since H₂O₂ is the generator of hydroxyl radicals, its concentration is crucial in the degradation of antibiotics; the impact of various starting concentrations of H₂O₂ (100, 300, and 500) mg/L on photo-oxidative degradation of erythromycin was studied. The optimal concentration of H₂O₂ for IBU degradation in an aqueous solution was established by using the Fenton process, with all other variables (including the initial concentration of Fe⁺² at 10 mg/L) remaining constant throughout the testing. At a starting dosage of 10mg/L, the pH was neutral, and no bacteria were present. As seen in Fig. 5, when the quantity of H₂O₂ was raised, so too was the percentage of IBUs removed. High concentrations of hydrogen peroxide are necessary to completely eradicate the IBU antibiotic (85.54%). An additional increase in the amount of H₂O₂ decreases the degradation rate of antibiotics to the H₂O₂ molecule can arise with OH• quickly:

\[ \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2 \]  \hspace{1cm} (16)

As a result, increased H₂O₂ in the reaction system accumulates a significant number of OH•, decreasing the likelihood of OH• damaging organic molecules [28]. These observations conform with the results of [29].

3.4. Effect of Fe (II)

Experiments were conducted with (10, 20, 30, 40) mg/L of Fe⁺² concentration while keeping other parameters constant at pH=3, H₂O₂ 300 mg/L, and 10mg/L of IBU concentration; the results are plotted in Fig. 6: it can be seen from this figure that the degradation rate of IBU increased with increasing the amounts of iron salt. With 150 minutes of irradiation, it peaked at its highest value (85.54% elimination). When Fe⁺² concentration is 40 mg/L, 60.43 percent of the contaminant is gone. Increasing the Fe⁺² concentration above this value did not influence the degradation rate but slowed down the process. There was a clear correlation between the concentration of iron salt and the pace at which organic contaminants were broken down, to a certain Fe concentration (II). Brown turbidity formed when iron salt was added in greater quantities, blocking the UV light necessary for photolysis and leading to the recombination of OH radicals. Fe⁺² worked as a scavenger by reacting with OH radicals [30]. Fe⁺² concentrations should be kept low for both financial and ecological considerations [31]. These observations conform to the results of [12].

3.5. Influence of IBU concentration and time

Results from experiments with IBU at 10, 20, 40, and 80 mg/L at 300 mg/L H₂O₂, 20 mg/L Fe⁺², and pH 3 are presented in Fig. 7. This figure shows that the degradation efficiency of IBU increases with reaction time in the photocatalytic process, reaching equilibrium after approximately 150 min. Adding more contact time has had a somewhat positive impact on degrading efficiency, which has led to more IBUs being eliminated. That find agreement between these findings [32]. This figure also shows that increased IBU concentrations do not result in higher removal percentages. When the number of molecules increases, the amount of OH• generated remains constant under constant operating conditions, thereby explaining the observed pattern. Another possible explanation for slowing the deterioration pace is as follows. Antibiotic concentration has no effect on the rate at which hydroxyl radicals are generated; (ii) however, a high concentration can prevent UV light from reaching the bottom of the solution, lowering the rate at which hydroxyl radicals are generated; (iii) the degradation rate may be further slowed due to insufficient availability of oxidizing agent. High antibiotic concentrations may also initiate additional reactions, such as dimerization, complex formation, etc., which would further complicate the reaction mechanism; (iv) at the high concentration, Fe⁺² ions are shielded from absorbing UV light, leading to the abrupt termination of the photo-oxidation reaction [33].

4. Photodegradation Kinetics

Evaluating the degrading performance of Photo-Fenton techniques for the degeneration of IBU from synthetic wastewater necessitates an understanding of the Photo-Fenton degradation process and reaction rate, which rely on the dynamic cooperation between IBU and the nanocomposite surface. The reaction rate of heterogeneous catalytic processes is often characterized using a pseudo-first-order kinetics model under the
circumstances of the Langmuir–Hinshelwood (L-H) kinetics model [34]

\[
\ln \frac{C_t}{C_0} = k_{obs}t
\]

(17)

C and C₀ are the initial and final IBU concentrations in mg/L, respectively; k_{obs} is the measured pseudo-first-order reaction rate constant (1/min); t is the exposure period (min). A linear plot’s reversion coefficients (R²) and Kobs value findings are shown in Table 1 equations. The kinetics results were obtained by plotting \(\ln \left( \frac{C_t}{C_0} \right)\) as a function of t in the range of 0 to 150 min as shown in Fig. 8. The results demonstrate that increasing the initial concentration of IBU reduced the constant degradation rate of k_{obs}, and they also demonstrate that the high R² values (>94%) of the IBU degradation response curves at various IBU concentrations indicated that according to the results of the research, which were detailed in Section 3.5, the photodegradation of IBU followed a pseudo-first-order kinetic model.

![Fig. 7. IBU degradation percentage as a function of different IBU concentrations](image)

**Fig. 7.** IBU degradation percentage as a function of different IBU concentrations

**Table 1. Parameters Describing the Rate of IBU Degradation by the Photo-Fenton Process**

<table>
<thead>
<tr>
<th>IBU concentration</th>
<th>Removal at 150 min</th>
<th>First-order</th>
<th>K_{obs} (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mg/L</td>
<td>65.54</td>
<td>0.265</td>
<td>0.0134</td>
</tr>
<tr>
<td>20 mg/L</td>
<td>65.54</td>
<td>0.265</td>
<td>0.0134</td>
</tr>
<tr>
<td>40 mg/L</td>
<td>65.54</td>
<td>0.265</td>
<td>0.0134</td>
</tr>
<tr>
<td>80 mg/L</td>
<td>65.54</td>
<td>0.265</td>
<td>0.0134</td>
</tr>
</tbody>
</table>

![Fig. 8. Kinetic Curves for the IBU Degradation Pseudo-First-Order Equation at Various Concentrations](image)

**Fig. 8.** Kinetic Curves for the IBU Degradation Pseudo-First-Order Equation at Various Concentrations

5- Conclusion

Antibiotic IBU was degraded from an aqueous solution using the Photo-Fenton technique in this research. The reaction was affected by the iron content in the input, the amount of hydrogen peroxide, the pH, and the amount of inorganic bacterial area in the synthetic wastewater. The rate of photodegradation may be increased by adding an appropriate quantity of H₂O₂. On the other hand, H₂O₂ may be used to neutralize hydroxyl radicals at sufficiently high quantities. Using 30 mg/L Fe⁺², pH = 3, and 150 min of irradiation duration, the Photo-Fenton system used a lot of hydrogen peroxide (300mg/L) to produce 85.54% of IBU antibiotics. Not only that, but the rate constant for IBU photodegradation seems to be inversely related to the starting concentration of the pollutant, following pseudo-first-order kinetics. In most cases, the UV/H₂O₂/Fe⁺² system was a very effective method for removing IBU antibiotics from water.

**References**


تحلل البروفين من المياه الصافي المحضرة باستخدام عملية التحفيز الضوئي المتجانس باستخدام Photo–Fenton

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الخلاصة

تم في هذا البحث دراسة فعالية نظام التحفيز الضوئي المتجانس باستخدام الحمض الديفي UV / H₂O₂ / Fe⁺² / Fe₂O₃ على تحلل البروفين (IBU)، حيث تضمنت الدراسة اختبار مجموعة من المتغيرات باستخدام المفاعل الضوئي الدفعي تضمنت تغيير تركيز الابتدائي لبيروكسيد الهيدروجين (100–500) ملغ/لتر وكمية الحديد المضافة (0–400) ملم/لتر وتغيير الدالة الحامضية (3–9) والمراحل الأولية للبروفين (10–80) ملغ/لتر. أظهرت النتائج أنه عند استخدام 300 ملم/لتر من بيووكسيد الهيدروجين و300 ملم/لتر من الحديد عند دالة حامضية 3 كانت النسبة المئوية لازالة 10 ملغ/لتر من البروفين تساوي 85.54% عند 150 دقيقة فترة الإشعاع. توصلت الدراسة إلى كفاءة عملية التحفيز الضوئي المتجانس في إزالة المركبات الصيدلانية بوجود بيووكسيد الهيدروجين.

الكلمات الدالة: مضاد حيوي البروفين، تحفيز ضوئي متجانس، الأشعة فوق البنفسجية، موديل النموذج الحركي.