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The removal of the cefixime antibiotic from aqueous solution using an advanced oxidation process (UV/H₂O₂)

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ABSTRACT

The removal of cefixime from an aqueous solution was investigated via UV/H₂O₂ process. Aqueous solutions containing cefixime with concentrations of 9, 18, and 27 mg/L were produced. The UV/H₂O₂ process was conducted on the solutions in a laboratory reactor with a capacity of 5800 ml. The efficiency of the whole process was analyzed by comparing the concentrations of the antibiotic in the final effluents, taking into account such factors as the initial concentrations of the antibiotic (9, 18, and 27 mg/L), pH (3, 5, 7, and 9), retention time (0–180 min), different lamp voltages (12–36 W), and H₂O₂ concentrations (5–20 mg/L). The results of the study have shown that the UV/H₂O₂ process was able to remove 100% of a 9 mg/L concentration of cefixime from an aqueous solution in 3 h. The removal rates for cefixime were affected by parameters such as pH, the initial concentration of cefixime, the concentration of H₂O₂, and the intensity of UV radiations. Acidic pH (pH 3), low concentrations of cefixime (9 mg/L), low H₂O₂ concentrations (5 mg/L), and higher radiation levels (36 Watt) resulted in higher removal rates. The advanced oxidation method UV/H₂O₂ is able to effectively remove cefixime from aqueous solutions under proper environmental conditions.

Keywords: Advanced oxidation; UV/H₂O₂; Cefixime; Antibiotics

1. Introduction

Antibiotics are chemical compounds that inhibit the growth of micro-organisms and often have microbial origins and can be semi-synthetically or fully synthetically produced [1]. One of the most important antibiotics used in the treatment of infections is cefixime. Cefixime can be effectively used against various bacterial organisms and infections, including staphylococcus, hemophilic influenza, Escherichia coli, febrile streptococcus, tonsillitis, throat infections, etc. [2]. Chemically, cefixime (Fig. 1) is \((6R,7R)-7(\text{Z})-2-(\text{2-amino-4-thiazolyl})-2-(\text{carboxymethoxyimino})-acet-amido)-8\text{-oxo-3-vinyl-5-thia-1-azabicyclo-\(\text{(4,2,0)}\) octa-2-ene-2 carboxylic acid} [3].
Because antibiotics are quite widely used in medicine and veterinary medicine, they play an important role in environmental pollutions and, even in low concentrations, may lead to bacterial resistance against treatment and medications [4]. To remove antibiotics from the water stream, numerous processes may be used, including advanced oxidation processes, ion exchange, and adsorption onto activated carbon, reverse osmosis, and biological treatment. Biological treatment is not that effective in the removal of antibiotics, because antibiotics destroy the micro-organisms involved in the treatment process. Among the other processes, advanced oxidation processes used in the treatment of wastewater containing pharmaceutical products are more applicable, since these methods do not just transfer the pollutants from one phase to another, but unlike other methods, totally remove the pharmaceutical pollutants [5]. In recent years, different technologies for advanced treatment of pharmaceutical compounds have been proposed and studied, including such methods as chemical oxidation using ozone, O₃/H₂O₂, membranous filtration, and adsorption onto activated carbon [5]. Although these technologies have been available for some time, they display some weaknesses too. As an example, the ozone-based oxidation process leads to the degradation of bromide into bromate ion, which is suspected of carcinogenicity [6]. In this case, it is necessary to purify the exiting gas and float the volatile organic carbons. However, using UV radiation instead of ozone in the oxidation process (UV/H₂O₂) resolves these problems [5]. In recent years, cefixime is widely used to treat infections caused by bacteria in human and animals, leading to their presence in water and wastewater. Therefore, the main objective of the present study is the evaluation of the efficiency of the advanced oxidation process UV/H₂O₂ in the removal of cefixime from aqueous solutions. The minor objectives of the research include studying the impact of such intervening factors, such as pH, the concentration of the medication, reaction time, different intensities of UV radiation, and H₂O₂ concentrations on the removal of cefixime. If successful, this method could be used as the pre-purification stage in the treatment of pharmaceutical wastes.

2. Methods

This study is of the interventional experimental type, in which the dependent variable (the final concentration of the antibiotic) has been pitted and analyzed against such operational parameters— independent variables—as the initial concentration of the antibiotic, pH, retention time, various voltages of the UV lamp, and different concentrations of H₂O₂. The study was performed in a non-continuous laboratory reactor and in each phase the sampling was carried out using the Grab sampling method and the concentrations were measured carefully using HPLC (Agilent 1200 HPLC, USA) [7]. This research was non-continuously carried out on a laboratory scale. The reactor used in this study was made of Plexiglas and had a total capacity of 5,800 ml. The UV/H₂O₂ reactor is shown in Fig. 2.

Fig. 1. Chemical structure of cefixime.

Fig. 2. Schematic illustration of the UV/H₂O₂ reactor.
To carry out the study, factors such as pH, the concentrations of the antibiotic, retention time, different voltages of the UV lamp, and varying concentrations of H$_2$O$_2$ were measured and taken into account. To study the effects of pH, four values were selected (pH 3, 5, 7, and 9). To adjust and set the pH, one normal NaOH and HCl was used. To measure pH, the Seven-easy pH meter made by the Swiss-based Melter Toledo Company was used. To determine how effective H$_2$O$_2$ is in removing the antibiotic, different concentrations of H$_2$O$_2$ (5, 10, 15, and 20 mg/L) were put to use. To determine the effect of the initial concentration of the antibiotic on the final result, the antibiotic removal experiment using advanced oxidation process UV/H$_2$O$_2$ was performed with three initial concentrations of cefixime (9, 18, and 27 mg/L) at optimum levels of pH, H$_2$O$_2$ concentrations, and fixed UV voltage. To examine the effect of various intensities of the UV radiations, three radiation intensities of 12, 24, and 36 watts were selected and tested. These radiation levels were cross-matched with different levels of pH, H$_2$O$_2$ concentrations, and antibiotic concentrations.

The initial concentrations and the final concentrations of the antibiotic were determined by the HPLC set at different times. By comparing the initial concentrations and the final concentrations of the antibiotic during different intervals, the removal rates were calculated. All the utilized chemicals were of analytical grade quality (Merck Company). The cefixime antibiotic used to prepare antibiotic aqueous solutions was obtained from a commercial source (Exir pharmaceutical company). Tests were conducted in triplicates, and results were expressed as means. After carrying out physical and chemical experiments on the samples, the obtained data and findings were analyzed. To analyze the data, SPSS and one-way analysis of variance were used.

3. Results

To determine the effect of the retention time on the removal of cefixime, the cefixime removal experiment was performed using the UV/H$_2$O$_2$ method, while UV radiation intensity was set at 36 W, the initial concentration of the antibiotic was 9 mg/L, the pH was fixed at three, the concentration of H$_2$O$_2$ was 5 mg/L, and the measurements were made at varying retention times. As is evident from Fig. 3, an initial concentration of 9 mg/L of cefixime was completely removed in three hours under fixed and stable experimental conditions.

The results showed that pH plays an important role in the removal of cefixime from an aqueous environment (Fig. 4) and a reduction in pH levels lead to an increase in the removal yield. In addition, the optimum removal yield is achieved at pH 3.

The results indicated that H$_2$O$_2$ concentration plays an important role in the removal of cefixime from an aqueous solution (Fig. 5) and an increase in the concentration of H$_2$O$_2$ leads to a decrease in the removal rates. The highest removal yield was obtained at H$_2$O$_2$ = 5 mg/L.

UV radiation intensity can play an important role in the removal of cefixime, too (Fig. 6), such that higher radiation intensity levels can result in an increase in removal rates.
To study the effect of the initial concentration of the antibiotic on the removal rates (Fig. 7), the cefixime removal experiment was performed using the UV/H₂O₂ method at different retention times, a pH of three, UV radiation intensity of 36 W, H₂O₂ concentration of 5 mg/L, and varying initial concentrations of the antibiotic. The results demonstrated that the initial concentration level of the antibiotic is an important factor affecting the final removal rates of the antibiotic from an aqueous environment and as a result of an increase in the initial concentration levels, the removal yield rates decreases considerably. Maximum removal yield levels were achieved at an initial concentration of 9 mg/L. The results of these experiments indicated that cefixime removal was significantly affected by pH, H₂O₂ concentration, UV radiation intensity, and initial concentration level of the antibiotic but pH factor is the dominant one.

4. Discussion

At a retention time of three hours and an initial concentration of 9 mg/L, 100% of cefixime was removed. The cefixime removal does not change between 30 and 120 min (Fig. 3) because in UV/H₂O₂ process, the intermediates from drug photodegradation [5] may be interfered with cefixime reduction in solution. So in further research, it would be paid more attention to intermediate interface.

According to the results obtained from the present research, the recommended retention time for the completion of the oxidation reaction is three hours in order for cefixime to be removed completely. A competition mechanism may be the direct UV photolysis and the oxidation of °OH radical [5]. The reason why this amount of time is necessary might be that enough retention time is needed for the production and generation of the active radical hydroxyl and the availability of enough time for the reaction to take place and for the hydroxyl radicals to attach to the cefixime molecules. Ghalamchi and Rasouli–Fard [8] obtained a removal yield of 94% for removing cefixime trihydrate using advanced oxidation involving peroxide disulfide as the oxidant, while the active radicals were fixated using silver nanoparticles on a silica base [8].
Jung et al. [9] studied the degradation of amoxicillin by direct photolysis processes (UV and UV/H₂O₂). They concluded that 99% of the initial amoxicillin can be degraded in 80 min using an advanced oxidation process (UV/H₂O₂) [9]. Jiao et al. [10] have studied the breakdown of tetracycline using UV rays. They removed 77% of the tetracycline in an exposure time of 300 min [10].

The results obtained from the present experiments suggest that oxidation and cefixime removal percentages are affected by solution pH. Based on the one-way analysis of variance test run between the average cefixime removal rates at different pHs, significant differences were observed (P = 0.001), such that the highest removal rates were obtained at a pH of three and the lowest removal rates at pHs of seven and nine. The results obtained from this study correspond with the results obtained from the Ghalamchi and Rasouli-Fard’s 2011 study [8]. Roma et al. [11] investigated the degradation and removal of ciprofloxacin using the UV/H₂O₂ method at three different pHs of three, seven, ten in an aqueous environment. They concluded that the UV/H₂O₂ method is very successful at a pH of three. In a similar study, Naddeo et al. [12] assessed and evaluated the degradation and breakdown of diclofenac, amoxicillin, and carbamazepine effected by UV radiation in a simple solution (pure water containing just one drug) and a compound solution (made with the three drugs) and the urban sewage. They found out that with the reduction of pH (an increase in the acidity of the environment), the drug removal rates increased. Additionally, Elmolla and Chaudhuri [13] reported that at low pHs, as a result of the formation of oxonium ions (−H₂O₂⁺), hydrogen peroxide is more stable and the oxonium ions improve the stability of H₂O₂. Moreover, Bobu et al. [14] drew the conclusion that a dramatic increase in pH levels can accelerate the generation of H₅O₂⁻ ions and more OH radicals are used by carbonate and bicarbonate ions.

The results obtained from the experiments suggested that oxidation rates and cefixime removal rates were affected by the concentration of H₂O₂ present in the solution. According to the one-way analysis of variance performed, there is a significant difference between cefixime removal percentages with varying concentration of H₂O₂ (P = 0.004), such that the highest removal rates were obtained at H₂O₂ concentrations of 5 mg/L. Jung et al. [9] examined the degradation and breakdown of amoxicillin by direct photolysis processes of UV and UV/H₂O₂. They concluded that the amoxicillin degradation speed considerably accelerates as the H₂O₂ concentration increases. They additionally concluded that when 10 mM H₂O₂ is added, degradation percentages increase up to six times as compared with direct photolysis with UV, i.e. when H₂O₂ is not used. Under these conditions, amoxicillin is highly degraded, up to 99% [9]. Roma et al. [11] studied the degradation and removal of ciprofloxacin using photolytic filtration alone and UV/H₂O₂ in aqueous environments. They deduced that using H₂O₂ together with UV could increase the degradation speed up to twice the rate when H₂O₂ is not used [11].

Kim et al. [15] investigated the photolytic degradation of medications and personal care products using UV and UV/H₂O₂ and deduced that adding H₂O₂ to the filtration process plus the use of UV could greatly improve the degradation of pharmaceutical and personal care products. In numerous similar studies carried out by Yuan et al. [5], Vogna et al. [16], Arsalan-Alaton and Dogruel [17], Shemer et al. [18], Pereira et al. [19], and Andreozzi et al. [20], the researchers concluded that, in general, H₂O₂ plays an important role in the oxidation of antibiotics. In other words, one of the important factors in advanced oxidation processes which affects the speed of chemical reactions is the presence of H₂O₂. A combination of photolysis and hydrogen peroxide which is a strong oxidant can lead to the production of hydroxyl radicals, and as a result facilitates the degradation process and increases the process yield. In addition, in the studies carried out by the above-mentioned researchers, H₂O₂ concentration varied in each study in correspondence with the chemical structure of the degraded medication and the properties of the aqueous matrix.

The results of the present study indicate that oxidation rates and cefixime removal rates are affected by UV radiation intensity. According to the one-way analysis of variance run, there was no significant difference between the percentage of cefixime removed at different intensities of UV radiation (P = 0.12). However, it is evident that the highest removal rates occurred at the UV intensity of 36 W and the lowest removal rates were observed at the intensity of 12 W. In a similar study, Naddeo et al. [12] evaluated the degradation of diclofenac, amoxicillin, and carbamazepine using UV radiation in different solutions. They found out that increasing radiation intensity led to a rise in the degradation levels of the medications [12]. Prados-Joya et al. [21] examined the photolysis of the antibiotic metronidazole using UV rays in aqueous environments. They found out that since, during the process low intensities of UV are used, metronidazole is not removed completely and, therefore, it is necessary to increase either the retention time or the radiation intensity [21].

One-way analysis of variance showed that there are significant differences between cefixime removal rates at various initial levels of the antibiotic (P = 0.003),
such that the highest removal rates are associated with the initial concentration of 9 mg/L and the lowest removal rates belong to the initial concentration of 27 mg/L. Behrouzi-Navid et al. [22] studied the removal of metronidazole from the effluent of a pharmaceutical factory using the UV/H₂O₂ method in a continuous cylindrical photoreactor. They concluded that a reduction in the concentration of the antibiotic resulted in a rise in the removal rates, and this can be explained by the fact that an increase in the concentration of the antibiotic means an increase in the amount of the material which is exposed to the radiation. This means that more time is necessary for the completion of the process and that the antibiotic works as a kind of filter and reduces the penetration levels of the UV rays. Consequently, the reaction completion speed and the antibiotic concentration have a reverse relationship with each other [22]. In another similar study, Jiao et al. [23] studied the degradation of tetracycline using UV. They realized that the speed of the photolysis process depends on the initial concentration of the tetracycline, such that an increase in the initial concentration of the tetracycline from 10 mg/L to 40 mg/L can cause a considerable reduction in the speed of the photolysis process [23]. In Table 1, cefixime removal from water using UV/H₂O₂ process (in the present study) compared with other studies.

### 5. Conclusion

In recent years, a wide range of drugs has been detected in the water bodies. Many of the compounds are chemically permanent and toxic and often not be effectively removed by conventional treatment processes. So advanced oxidation process such as UV/H₂O₂ process developed for resistance compounds. This study adds to the growing literature on treatment technologies which are able to remove drug compounds from water solutions. The current research led to the following conclusions:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Target drug</th>
<th>Initial concentration</th>
<th>Matrix</th>
<th>Summary of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andreozzi et al. [20]</td>
<td>Paracetamol</td>
<td>1.0 × 10⁻⁵ moldm⁻³</td>
<td>Bi-distilled water</td>
<td>Complete degradation with mineralization degrees up to 40% H₂O₂/UV system is effective in inducing diclofenac degradation at 90 min of treatment</td>
</tr>
<tr>
<td>Vogna et al. [16]</td>
<td>Diclofenac</td>
<td>1.0 × 10⁻³ M</td>
<td>Water Solution</td>
<td>Degradation follows first-order kinetics and rate increases with increasing H₂O₂ concentration. MP irradiation more effective than LP</td>
</tr>
<tr>
<td>Shemer et al. [18]</td>
<td>Metronidazole</td>
<td>1 mg/L</td>
<td>Deionized water</td>
<td>Complete degradation at 1,700 mJ cm⁻² fluence for all drugs. Lower degradation with direct photolysis. Rates decrease in surface water compared with laboratory water</td>
</tr>
<tr>
<td>Pereira et al. [19]</td>
<td>Naproxen, Ketoprofen, Carbamazepine, Clofibric acid, Ciprofloxacin, Iohexol</td>
<td>1–3 μM</td>
<td>Laboratory grade water, surface water</td>
<td>The removal of these six pharmaceuticals varied between no observed removal and &gt;90%</td>
</tr>
<tr>
<td>Yuan et al. [5]</td>
<td>Ibuprofen, Diphenhydramine, Phenazine, and Phenytin</td>
<td>5 μM</td>
<td>Deionized water</td>
<td>The UV/H₂O₂ advanced oxidation experiments were effective for selected drugs</td>
</tr>
<tr>
<td>Rosario-Ortiz et al. [25]</td>
<td>Meprobamate, Carbamazepine, Dilantin, Atenolol, Primidone, and Trimethoprim</td>
<td>38–2,600 ng/L</td>
<td>Wastewater effluents</td>
<td>UV/H₂O₂ generally appeared to be a more efficient technology for removing pharmaceuticals from RO brines</td>
</tr>
<tr>
<td>Justo et al. [26]</td>
<td>11 Pharmaceuticals</td>
<td>Concentrations ranging from 0.2 to 1.6 μg/L</td>
<td>Reclamation osmosis brines</td>
<td>UV/H₂O₂ generally appeared to be a more efficient technology for removing pharmaceuticals from RO brines</td>
</tr>
<tr>
<td>In the present study</td>
<td>Cefixime</td>
<td>9, 18, 27 mg/L</td>
<td>Water Solution</td>
<td>100% removal of a 9 mg/L concentration of cefixime from an aqueous solution in 3 h</td>
</tr>
</tbody>
</table>

In the present study Cefixime 9, 18, 27 mg/L Water Solution 100% removal of a 9 mg/L concentration of cefixime from an aqueous solution in 3 h
• UV used along H₂O₂ is quite effective in the removal cephalosporins, especially cefixime. So, it was able to remove 9 mg/L concentration of cefixime in 3 h retention time.
• As the reaction time increases, the removal rate increases too (100% of cefixime was removed at 180 min retention time).
• An acidic environment contributes to the removal of cephalosporins more than a basic or neutral environment. The lowest pH (pH 3) had the maximum removal efficiency.
• One of the important factors in UV/H₂O₂ process for cefixime removal from water was H₂O₂ concentrations.
• With higher levels of UV lamp radiation intensity (from 12 to 36 W), removal rates increase (from 16 to 100% with initial concentration of 9 mg/L and pH 3).

A more detailed investigation of the effects of pH < 3, H₂O₂ concentration lower than 5 mg/L, and intermediates compounds on cefixime removal using UV/H₂O₂ process must be conducted by other research.

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