UV Based Advanced Oxidation Process for Degradation of Ciprofloxacin: Reaction Kinetics, Effects of Interfering Substances and Degradation Product Identification

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Research Article

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**UV based advanced oxidation process for degradation of ciprofloxacin: reaction kinetics, effects of interfering substances and degradation product identification**

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**Abstract**

In the photochemical UV-H₂O₂ advanced oxidation process, H₂O₂ absorbs UV light and is decomposed to form hydroxyl radicals (OH·), which are highly excited and reactive for electron-rich organic compounds and hence can degrade organic compounds. In the present work, the UV-H₂O₂ process was investigated to degrade ciprofloxacin (CIP), one of India’s widely used antibiotics, from aqueous solutions using a batch type UV reactor having photon flux = 1.9 (± 0.1) ×10⁻⁴ Einstein L⁻¹ min⁻¹. The effects of UV irradiation time on CIP degradation were investigated for both UV and UV-H₂O₂ processes. It was found that about 75% degradation of CIP was achieved within 60 s with initial CIP concentration and peroxide concentration of 10 mg L⁻¹ and 1 mol H₂O₂/ mol CIP, respectively, at pH of 7(±0.1) and fluence dose of 113 mJ cm⁻². The experimental data were analyzed by the first-order kinetics model to find out the time- and fluence-based degradation rate constants. Under optimized experimental conditions (initial CIP concentration, pH and H₂O₂ dose of 10 mg L⁻¹, 7(±0.1) and 1.0 mol H₂O₂/ mol CIP, respectively), the fluence-based pseudo-first-order rate constant for the UV and UV-H₂O₂ processes were determined to be 1.28(±0.0) ×10⁻⁴ and 1.20(±0.04) ×10⁻² cm² mJ⁻¹ respectively. The quantum yields at various pH under direct UV were calculated. The impacts of different process parameters such as H₂O₂ concentration, solution pH, initial CIP concentration, and wastewater matrix on CIP degradation were also investigated in detail. CIP degradation was favorable in acidic conditions. Six degradation products of CIP were identified. Results clearly showed the potentiality of the UV-H₂O₂ process for the degradation of antibiotics in wastewater.

**Keywords** Antibiotics, Ciprofloxacin, Degradation, Direct Photolysis, Scavenging effect, UV-H₂O₂.

**Introduction**

Consumption of pharmaceuticals (PhCs) like antibiotics is increasing day by day throughout the world because of the advent of new diseases and the rise in the consumer population due to the enhancement of life span. After

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exerting pharmacological actions, these antibiotics and their metabolites are excreted in urine or feces, and finally, these are disposed of into the sewage treatment plant. Moreover, unconsumed antibiotics are disposed of in the environment, and these finally find wastewater as their destination. Presence of different classes of antibiotics, including quinolones (ciprofloxacin, lomefloxacin, norfloxacin, ofloxacin, levofloxacin, sparflloxacin, moxifloxacin, etc.), macrolides (e.g., clarithromycin, erythromycin, roxithromycin), tetracyclines (tetracycline, doxycycline, oxytetracycline, chlortetracycline), and sulfonamides (sulfamethoxazole, sulphasalazine) have been detected in environmental settings across the world (Lofrano et al. 2017). In general, concentrations of higher µg/L range in hospital wastewater, higher to lower µg/L range in municipal sewage, and lower µg/L range in surface water (Yan et al. 2013; Yang et al. 2011) groundwater (Hu et al. 2010) and seawater have been reported. For example, the presence of some antibiotics in municipal effluent and drinking water has been reported as 3800 ng L$^{-1}$ for ciprofloxacin (CIP) (Watkinson et al. 2007) and as 3.0-3.4 ng L$^{-1}$ for sulfonamides and 1.4-4.9 ng L$^{-1}$ of macrolides (Ye et al. 2007). Fick et al. (2009) reported 14 mg L$^{-1}$ of CIP in a pharmaceutical effluent (Fick et al. 2009). 

The persistent presence of antibiotics as emerging contaminants poses a potential threat to the ecosystem and human health. The presence of antibacterial agents in the aquatic environment has increased concerns over their potential environmental risks. Adverse effects of these pharmaceutical residues on bacteria, invertebrates, and algal populations of the aquatic ecosystem have been reported by Hernando et al. (Hernando et al. 2006). Kim et al. performed an acute toxicity test on a marine bacterium (Vibrio fischeri), a freshwater invertebrate (Daphnia magna), and Japanese Medaka fish (Oryzias latipes) (Kim et al. 2008). They reported that the lethal concentration corresponds to the 50% mortality (LC$_{50}$) value for these antibiotics on these organisms to be two orders of magnitude higher than environmentally significant concentrations.

In the present study, CIP was taken as a representative antibiotic as this compound is used widely in the Indian subcontinent. It is commonly used to kill the infection-causing bacteria in humans and animals by interposing with the enzymes, which helps to stop the synthesis of DNA and protein (Khaki et al. 2015). CIP has a higher solubility in aqueous solution, soil, and wastewater system at different pH (Zhuang et al. 2015). Therefore, the removal of CIP from the aquatic environment is essential. However, the present literature indicates that conventional wastewater treatment plants are not capable of removing the high load of antibiotics, including CIP in wastewater. This calls for effective and specific treatments that are required to reduce environmental impacts.

Several methods such as adsorption using nanohybrid graphene oxide (GO) cross-linked via calcium ions (Ca$^{2+}$) with oxidized carbon nanotubes (O-CNTs), Montmorillonite impregnated electrospun cellulose acetate nanofiber sorptive membrane (Fares et al. 2020; Das et al. 2020), eletro-coagulation (Malakootian et al. 2019; Parsa et al. 2016), biological treatment (Guney et al. 2016; Diaz et al. 2017) and different advanced oxidation processes like ozonation (Javida et al. 2020), photocatalytic removal from aqueous solution using nanoparticles (Imam et al. 2018), photo Fenton oxidation (Sciscenko et al. 2020), etc. have been explored for removal of antibiotics from wastewater. These methods have their own merits and demerits. The adsorption process is the most straightforward and cost-effective. However, it is based on the phase transfer of pollutants rather than providing complete elimination, and also exhausted adsorbents still contain a high concentration of antibiotics. The biological process is less expensive and environmentally friendly for the wastewater treatment process.
However, if the wastewater contains non-biodegradable substances, the biological process cannot degrade contaminated antibiotic wastewater. The ozonation process is very costly due to consuming high electric power for generating ozone. The Fenton process is suitable when the pH of the solution remains less than 3.

Over the last few years, the advanced oxidation process using UV-H₂O₂ has been proven to be very effective for removing the PhCs (Villegas-Guzman et al. 2017). In the UV-H₂O₂ process, H₂O₂ absorbs UV light and undergoes rapid decomposition to form hydroxyl radicals, which are more powerful, excited, and react with electron-rich organic compounds. It corresponds to the low-pressure UV lamps used in most wastewater treatment plants for disinfection; the hydroxyl radical yield is 1 mol HO•/mol H₂O₂ (Urbano et al. 2017). Most of the studies have reported the kinetic analysis of the process. However, the optimization of the parameters for the field application of the UV-H₂O₂ process is still unexplored. It is essential to determine the optimal peroxide dose, relationships between degradation efficiency with the process parameters like pH, initial concentration and wastewater matrix, etc. Thus, this work aimed to examine the influence of process parameters and operating conditions for CIP degradation, one of the widely used antibiotics, by the UV-H₂O₂ process. Specifically, the broad objectives of the study were: (1) to determine fluence-based reaction rate constants for CIP degradation under UV and UV-H₂O₂; (2) to optimize the dose of H₂O₂ for CIP degradation; (3) to evaluate the effects of initial CIP concentration, (4) to investigate the impact of water quality parameters, namely pH, electrolyte, and wastewater matrix on CIP degradation, and (5) to identify the degradation products. The goal of the study is to eliminate antibiotics from wastewater or other sources.

**Materials and Methods**

**Chemicals and reagents**

CIP is found as cationic and anionic form in the acidic and alkaline solution (pKₐ1 = 6.1 and pKₐ2 = 8.7) due to the presence of carboxylic and amine groups in the piperazine moiety (Xing et al. 2015). The chemical structure of ciprofloxacin has been demonstrated in Fig. 1. Technical grade CIP (C₁₇H₁₈FN₃O₃, Molecular Weight: 331.347 g mol⁻¹) (purity > 98%, w/w) and HPLC grade acetonitrile (purity 98%, v/v), 2% of acetic acid (purity 98%, w/w), water (40% purity, v/v) were purchased from Sigma Aldrich Chemical Ltd (USA). Hydrogen peroxide (H₂O₂, 30%), hydrochloric acid (HCl, 37%), and sodium hydroxide (NaOH, 99%) were purchased from Merck (India). The strength of hydrogen peroxide was determined by the potassium permanganate titration method, and it was examined every 15 days (Huchaba et al, 1948). All working stock solutions and drug solutions were prepared in deionized water.

**UV Reactor**

A batch type UV reactor (M/s. Lab Tree, Ambala, Haryana, India) emitting monochromatic light centered at 253.7 nm was used for direct photolysis and advanced oxidation (UV-H₂O₂). The reactor consists of eight UV tubes.
fitted inside a metal enclosure with a highly polished stainless-steel reflector. The photon flux and corresponding fluence rate are the most important parameters of the UV reactor. These parameters were determined by ferrioxalate actinometry (Hatchard et al. 1956). The photon flux and corresponding fluence rate were $1.81 \times 10^{-4}$ Einstein L$^{-1}$-min$^{-1}$ and $112.92$ mJ min$^{-1}$ cm$^{-2}$, respectively, at UV 253.7.

**Analytical Methods**

The concentration of CIP was determined by the Thermo Fisher Scientific ultra-high-performance liquid chromatography system (UHPLC) ( Dionex Ultimate 3000). A 20 µL CIP sample was inoculated directly into a C$_{18}$ (250 mm length, 4.6 mm diameter) UHPLC column at the temperature of 35°C. Acetonitrile (25%) and 2% acetic acid (75%) at the flow rate of 1 mL min$^{-1}$ were used as the mobile phase. Ortho-phosphoric acid was used to maintain a pH of 3.0 of the mobile phase. The absorbance of CIP was measured at 263 nm using a photo diode array (PDA) detector.

**Experimental procedure**

The molar absorptivity of CIP was mapped across a wide range of pH of 2-11 at wavelength 253.7 nm by UV-VIS Spectrophotometer (Model: 117, Make: Systronics India Ltd., Ahmedabad, India). The pH of the CIP solution (10 mg L$^{-1}$) was adjusted using dilute HCl and NaOH. The pH was measured using a digital pH meter (PB-11; Sartorious GmbH). The apparent molar absorptivity of CIP may be calculated as the total summation of molar absorptivity of the protonated and deprotonated species (Adak et al. 2014), as indicated by Eq 1.

$$
\varepsilon_{app, \lambda} = \sum_{i=0}^{n} \alpha_i \varepsilon_{i, \lambda}
$$

In Eq. 1, $\varepsilon_{app, \lambda}$ is the apparent molar absorptivity at wavelength $\lambda$, $\alpha_i$ is the fraction of species i at a particular pH, $\varepsilon_{i, \lambda}$ is the molar absorptivity of species i at wavelength $\lambda$, and the 0 and 1 subscripts refer to the protonated and deprotonated species, respectively. The protonated and deprotonated CIP species are the amino group in the piperazine part and carboxyl group, respectively.

Degradation of CIP under direct UV and UV-H$_2$O$_2$ AOP was conducted in batch mode, taking 100 mL of sample matrix containing 10 mg L$^{-1}$ of CIP in distilled water with desired H$_2$O$_2$ dose (0 -2.0 mol of H$_2$O$_2$/mol of CIP) at 27(±2) °C. It is to mention that direct UV experiments were conducted at various pH (2-11). The samples were irradiated for 30 for direct UV experiments and 5 min for UV-H$_2$O$_2$ experiments. Treated samples were withdrawn at pre-fixed time intervals and analyzed for remaining CIP concentrations. The experimental data were analyzed by the pseudo-first-order kinetic model (Adak et al. 2019), and the integrated form of the first-order kinetics model is given below:

$$
[CIP] = [CIP]_o \exp(k'H)
$$

In Eq. 2, [CIP] represents CIP concentration at any time t; [CIP]$_o$ is the initial CIP concentration, H is the fluence (mJ cm$^{-2}$) corresponding to time t, and $k'$ is the fluence-based pseudo-first-order rate constant (cm$^2$
The kinetics model’s fitness describing CIP degradation by the UV-H$_2$O$_2$ process was evaluated by the sum of the square of error and correlation coefficient ($r^2$), as shown below.

\[ r^2 = \frac{\sum([\text{CIP}]_c - [\text{CIP}]_{e,\text{avg}})^2}{\sum([\text{CIP}]_c - [\text{CIP}]_{e,\text{avg}})^2 + \sum([\text{CIP}]_c - [\text{CIP}]_{e})^2} \]  

(3)

Where, \([\text{CIP}]_c\) = concentration of CIP obtained from the first-order kinetics model; \([\text{CIP}]_e =\) concentration of CIP obtained from the experimental data and \([\text{CIP}]_{e,\text{avg}}\) is the average of \([\text{CIP}]_e\).

The efficiency ($E$) of degradation of CIP by UV and UV-H$_2$O$_2$ process was calculated by the following equation (Lin et al. 2016).

\[ E = \left(\frac{[\text{CIP}]_0 - [\text{CIP}]}{[\text{CIP}]_0}\right) \times 100 \]  

(4)

Apart from these, a control experiment was also performed in the dark condition with an H$_2$O$_2$ dose of 1 mol H$_2$O$_2$ / mol of CIP and CIP concentration of 10 mg L$^{-1}$. The samples were kept for 15 days in the dark, and CIP concentration was measured on alternate days.

The effect of H$_2$O$_2$ dose on UV-H$_2$O$_2$ degradation of CIP was studied to determine the optimum quantity of the chemical. Different H$_2$O$_2$ amounts in the range of 0.125 to 2 mol H$_2$O$_2$ / mol of CIP were considered. The initial CIP concentration and pH were 10 mg L$^{-1}$ and 7.0(±0.1), respectively. Impacts of several other process parameters such as initial CIP concentration (1-20 mg L$^{-1}$), pH (3 - 11), and ionic strength (0-1000 mg of NaCl L$^{-1}$) were investigated. In all these cases, the H$_2$O$_2$ dose was taken as 0.5 mol H$_2$O$_2$ / mol CIP. The pH of experimental solutions was adjusted using concentrated aqueous HCl or NaOH. Experiments were performed to identify the degradation products of CIP using HPLC-MS/MS for 50 and 75% degraded samples. Besides, CIP degradation was studied in real wastewater. The wastewater was collected from the municipal sewer (IIEST, Shibpur, India), and it was filtered using Whatman 42 filter paper before use. The filtered wastewater was analyzed for its composition, and it was used to prepare a CIP spiked solution, which was subjected to the UV-H$_2$O$_2$ process. In all cases, the initial CIP and H$_2$O$_2$ concentrations were 10 mg L$^{-1}$ and 0.5 mol H$_2$O$_2$ / mol CIP, respectively. Also, the samples were irradiated for 5 mins, and treated samples were withdrawn at pre-fixed time intervals followed by the analysis of remaining CIP by the HPLC method.

The results reported in the present manuscript are the mean ±SD for $N = 3$ unless otherwise stated. Analysis of variance (ANOVA) of experimental data was performed by Microsoft Excel software. Significant difference was affirmed at 95% confidence intervals ($p < 0.05$).
Results and Discussion

Variation of molar absorptivity of CIP with pH at 253.7 nm

Based on the dissociation constant (pKa), the distribution of different CIP species in an aqueous solution can be illustrated by its speciation diagram as a function of pH. The species of CIP are [H4CIP3+], [H3CIP2+], [H2CIP+], [HCIP0], [CIP−], and the molar ratio of the respective protonated/deprotonated species are denoted by $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$, and $\alpha_5$ as shown in Fig. 2. The absorbance of CIP solution (10 mg L−1 in the pH range of 2-11) was measured by the UV-vis spectrophotometer at a wavelength of 253.7 nm. The corresponding apparent molar absorptivity was calculated by the Beer-Lambert law. The variation of apparent molar absorptivity at pH 2-11 is presented at a wavelength of 253.7 nm in Fig. 3. CIP's apparent molar absorptivity was high at pH 8, indicating that the neutral and deprotonated species of CIP absorb much more light than the protonated species. The molar absorptivity of individual species of CIP were determined to be 15052, 16064, 18664, 17805 and 16203 M−1 cm−1 for [H4CIP3+], [H3CIP2+], [H2CIP+], [HCIP0], and [CIP−], respectively at 253.7 nm.

Insert Fig.2 here.

Insert Fig.3 here.

Fluence-based reaction rate constant for CIP degradation

Degradation of CIP (10 mg L−1 initial concentration) under direct UV exposure at 253.7 nm was conducted at a pH of 7(±0.1). The degradation was found to be very slow, as only about 11% of degradation occurred in 2 min (Fig. 4) with a fluence of 0.226 J cm−2. Generally, fluence of 40-90 mJ cm−2 is applied in the UV disinfection of wastewater (Zheng et al. 2010). Therefore, it is impossible to treat the CIP contaminated wastewater by the UV disinfection process. The fluence base rate constant for the direct UV process was determined to be 1.28(±0.07) ×10−4 mJ−1 cm−2.

Insert Fig.4 here.

The degradation of CIP under direct UV was studied at different pH since the molar absorptivity of CIP varies with pH. The maximum molar absorptivity was obtained near pH 8.0 at 253.7 nm. It was observed that degradation of CIP was low at both acidic pH and alkaline pH. The maximum degradation was observed at pH 8.0, which agrees with the variation of molar absorptivity of CIP across pH. The pseudo-first-order degradation rate constants at various pH were also calculated. The maximum rate constant was found to be 1.40(±0.03) ×10−4 mJ−1 cm−2 (Fig 5a).

Insert Fig.5 here.
Furthermore, the apparent quantum yield was also calculated for CIP degradation under direct UV irradiation. The relation between apparent fluence-based pseudo-first-order rate constant and apparent quantum yield is given below.

\[ k_{p,app}' = \frac{\Phi_{253.7,app} \varepsilon_{253.7,app} \ln 10}{U_{253.7}} \]  

(5)

In the above equation, \( k_{p,app}' \) is the experimentally determined apparent fluence-based pseudo-first-order reaction rate constant (cm\(^2\) mJ\(^{-1}\)), \( \Phi_{253.7,app} \) is the apparent quantum yield at 253.7 nm (mol Einstein\(^{-1}\)), \( \varepsilon_{253.7,app} \) is the apparent molar absorptivity at 253.7 nm (M\(^{-1}\) cm\(^{-1}\)), and \( U_{253.7} \) is the molar photon energy at 253.7 nm (4.72×10\(^5\) J Einstein\(^{-1}\)). The apparent quantum yield for degradation of CIP was found to be 1.46(±0.05) ×10\(^{-3}\) mol Einstein\(^{-1}\) at pH of 7(±0.1). The quantum yields so obtained are comparable with previously reported values (Keen et al. 2013; Pereira et al. 2007). The quantum yield was found to vary with change in pH molar absorptivity of CIP varied across the pH (Fig. 5b). As the molar absorptivity of CIP at 253.7 nm was very high at near pH 8.0, it was expected that the quantum yield, as well as CIP degradation, would be more compared to the value mentioned above. The maximum quantum yield was found to be 1.51(±0.03) ×10\(^{-3}\) mol Einstein\(^{-1}\) at pH 8.0 and it decreased at both acidic and basic conditions.

Since direct UV treatment was not much effective, the UV-H\(_2\)O\(_2\) treatment was applied for the degradation of CIP. When H\(_2\)O\(_2\) was added at a concentration of 1 mol H\(_2\)O\(_2\)/mol of CIP in CIP solution (10 mg L\(^{-1}\)) at pH 7(±0.1) and irradiated under UV light, about 92% degradation was observed with the same fluence as that of direct photolysis (0.2 J cm\(^{-2}\)) dose. About 16-38 % CIP transformation could be achieved by UV disinfection with a suitable peroxide dose at a fluence of 40-90 mJ cm\(^{-2}\). The results indicate that the enhanced degradation of CIP under the UV-H\(_2\)O\(_2\) process is due to the generation of non-selective hydroxyl radicals. It is worthy of mentioning that no degradation was achieved in the presence of hydrogen peroxide in the dark.

The fluence base rate constant for UV-H\(_2\)O\(_2\) process was determined to be 1.20(±0.04) ×10\(^{-2}\) mJ\(^{-1}\) cm\(^2\). The rate constant obtained in the UV-H\(_2\)O\(_2\) process is almost two order magnitude greater than the direct photolysis case. It is to note that the determination of the true rate constant in UV-based processes is difficult as intermediate products may also absorb light and undergo degradation. Therefore, determining an apparent rate constant is preferred in the literature to understand and optimize UV-based processes and serve the necessary purpose for field applications (Adak et al. 2014; Zheng et al. 2010).

**Effect of H\(_2\)O\(_2\) concentration**

It is necessary to optimize the dose of H\(_2\)O\(_2\) to make the UV-H\(_2\)O\(_2\) process economical. To examine the effect of H\(_2\)O\(_2\) concentration on CIP degradation, the experiments were performed with an initial CIP concentration of 10 mg L\(^{-1}\) at a pH of 7(±0.1), taking different H\(_2\)O\(_2\) concentrations in the range of 0 – 2 mol H\(_2\)O\(_2\)/mol CIP. The results illustrated that degradation efficiency as well as the fluence-based rate constant increased up to a peroxide dose of 1 mol H\(_2\)O\(_2\)/mol CIP, and after that, the rate constant decreased (Fig. 6). The higher concentration of H\(_2\)O\(_2\) itself scavenges the hydroxyl radicals (Adak et al. 2014; Mondal et al. 2018). Several other studies investigating
the degradation of acid blue 25 (Ghodbane et al. 2010), chloramphenicol (Zuoorro et al. 2014), sulfonated diazo dye Reactive Green (He et al. 2011), 2,4-D-dichlorophenoxyacetic acid (Adak et al. 2019) under the UV-H₂O₂ process have reported similar trends. Furthermore, the steady-state hydroxyl radical concentration was found to be 1.33(±0.66) × 10⁻¹⁰, 2.81(±0.94) × 10⁻¹⁰, 4.05(±0.11) × 10⁻¹⁰, 5.20(±0.13) × 10⁻¹⁰, 5.35(±0.14) × 10⁻¹⁰, 5.07(±0.13) × 10⁻¹⁰, 4.67(±0.18) × 10⁻¹⁰, and 3.35(±0.17) × 10⁻¹⁰ M at 0.125, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 mol H₂O₂/mol CIP respectively. To contextualize the magnitude of treatment, consider that a UV dose of AOP typically employs a fluence of 540-2000 mJ/cm². Consequently, 28-58% transformation would be expected for CIP at AOP-level UV doses with suitable H₂O₂ addition.

Effect of initial CIP concentration on UV-H₂O₂ process

The effect of initial CIP concentration on UV-H₂O₂ degradation was studied at different initial concentrations (C₀ = 1, 5, 10, and 20 mg L⁻¹) with an H₂O₂ dose of 0.5 mol H₂O₂/mol CIP and irradiated for 1 min at pH 7(±0.1). Overall, CIP degradation decreased with increasing initial CIP concentration (Fig. 7). The degradation of CIP was achieved around 87%, 75%, 59%, and 39% for initial CIP concentrations of 1, 5, 10, and 20 mg L⁻¹, respectively. The fluence based pseudo-first-order reaction rate constants were determined to be 1.50(±0.06) × 10⁻², 1.18(±0.03) × 10⁻², 0.85(±0.0.03) × 10⁻², and 0.55(±0.02) × 10⁻² mJ⁻¹ cm² for CIP concentration of 1, 5, 10, and 20 mg L⁻¹, respectively. A similar decrease in degradation has been reported in the case of microcystin – LR using the UV/H₂O₂ process (He et al. 2011). For higher CIP concentration, the applied dose of H₂O₂ is also high. This higher amount of H₂O₂ in the matrix might act as a scavenger of hydroxyl radicals. Thus, the rate constant decreased at higher CIP concentrations. Another reason is that the increase in the initial concentration of CIP production of intermediates also increases, which can act as a scavenger of hydroxyl radicals and inhibit CIP degradation (Zuoorro et al. 2014).

Effect of pH on UV-H₂O₂ process

It has been reported that the pH of the solution is an important parameter for the degradation of any organic substances by UV-based treatment (Avisar et al. 2010). To examine the effect of pH on CIP degradation, experiments were conducted, taking an initial CIP concentration of 10 mg L⁻¹ at a peroxide concentration of 0.5 mol H₂O₂/mol CIP. The pH solution was adjusted in the range of 3 to 11 using aqueous HCl and NaOH. It was observed that the CIP degradation decreased with an increase of pH from 3 to 11 (Fig. 8). The degradation of CIP was observed ~ 76 % at pH 3 and 38 % at pH 11. The apparent fluence-based first-order rate constant was also found to decrease with increased pH. In alkaline solutions, H₂O₂ (pKa =11.8), dissociates to hydroperoxide (HO₂⁻) anion. The HO₂⁻ is dominant at pH > 10 and reacts with undissociated H₂O₂ and hydroxyl radical (Rios et al. 2017). Therefore, the hydroxyl radical concentration is lowered than expected at higher pH. The steady-state concentration of hydroxyl radical was determined to be 4.76(±0.99) × 10⁻¹⁰, 4.43(±0.80) × 10⁻¹⁰, 4.04(±0.78) × 10⁻¹⁰...
10, 2.61(±0.74) ×10⁻¹⁰, 2.61(±0.74) ×10⁻¹⁰, and 1.87(±0.54) ×10⁻¹⁰ M for pH 3, 5, 7, 9 and 11 respectively. Furthermore, it was observed that the direct photolysis was not effective at highly alkaline conditions.

Insert Fig.8 here.

Effect of ionic strength on CIP degradation

The effect of ionic strength (as sodium chloride) on CIP degradation by UV-H₂O₂ process was studied at different NaCl concentrations in the range of 0-1000 mg L⁻¹ with an H₂O₂ dose of 0.5 mol H₂O₂/mol CIP and irradiated for 1 min at pH 7(±0.1). Degradation kinetics of CIP were unchanged by the increase in NaCl concentration as there would be no change of NaCl under UV light. A similar observation has been made for the degradation of flumequine by an advanced oxidation process (Feng et al. 2015).

Degradation product of CIP

The molecular structure of CIP has been shown in Fig. 1. Quinolone moiety is present in the center, and carboxyl group, cyclopropyl group, piperazinyl ring, and fluorine are in the periphery of CIP's molecular structure. CIP can produce cleavages of these above moieties and generate different characterized intermediates. Six intermediate products of CIP degradation (50 and 75 %) by UV-H₂O₂ process have been identified by LC-MS/MS (Table 1). The CIP degradation might take place in three way: (1) reaction take place at the piperazinyl ring, (2) defluorination and hydroxyl substitution reaction occur due to oxidation of quinolone, and (3) oxidation of the cyclopropyl group leading to ring cleavage. DP3 degradation product was identified when the reaction occurred at the piperazinyl ring. DP4 and DP5 degradation product was found due to oxidation at the quinolone moiety leading to the defluorination and hydroxy substitution reaction. Several researchers have been reported that the defluorination and hydroxyl substitution on the quinolone moiety occurs by the substitution of fluorine atom by hydroxyl group (Guo et al. 2013; Paul et al. 2010; Vasconcelos et al. 2009). DP1 and DP2 were identified when the hydroxyl group might be introduced to the quinolone moiety and followed by a ring-opening elimination reaction. The formation of DP6 might be due to the loss of a keto group of the piperazinyl group.

Effect of wastewater matrix on CIP degradation

The applicability of the UV-H₂O₂ process for treating pharmaceutical compounds was studied using municipal wastewater spiked samples with an initial CIP concentration of 10 mg L⁻¹. The molar ratio of H₂O₂ to CIP was 0.5, and pH was 7(±0.1). Degradation of CIP was reasonably affected in the case of wastewater spiked samples. The composition of wastewater was determined as: pH - 7.1; total alkalinity - 221 mg L⁻¹ as CaCO₃; nitrate - 13 mg L⁻¹; five-day biochemical oxygen demand (BOD₅) - 180 mg L⁻¹; chemical oxygen demand (COD) - 420 mg L⁻¹ and UV absorbance at 253.7 nm (UV₂₅₄) - 0.496 cm⁻¹. The percentage of degradation was 85 and 64% in distilled water and wastewater, respectively, within 2 min (Fig. 9). The fluence-based rate constants of CIP degradation were determined to be 0.85(±0.03)×10⁻² cm² mJ⁻¹ and 0.48(±0.06)×10⁻² cm² mJ⁻¹ for distilled water and wastewater, respectively, which present that rate constant for the distilled water spiked sample was 2 times
higher than the wastewater-spiked sample. The slower kinetics in wastewater might be due to hydroxyl radicals' scavenging by the dissolved organic matter (DOM) present in wastewater. As the COD and UV$_{254}$ of wastewater are very high, it is expected that DOM will also be high. DOM presents in the wastewater also absorbs UV photons and reduces the quantity of hydroxyl radicals (Xu et al. 2013; Walse et al. 2004). Either the light shading effect of UV absorbance of wastewater (UV$_{254}$ = 0.496 cm$^{-1}$) at 253.7 nm or scavenging of hydroxyl radicals by dissolved organic matter may be responsible for lower kinetics of wastewater. Among them, which one is more responsible, we calculated the theoretical and observed light screening factors as given below.

$$S_{th} = \frac{1-e^{-2.3A_l}}{2.30Al}$$

(6)

$$S_{obs} = \frac{k_{WW}'}{k_{DW}'}$$

(7)

In equation 6 and 7, $S_{th}$ is the theoretical light screening factor; $S_{obs}$ is the observed light screening factor; $A$ is the absorbance of the sample; $l$ is the path length (cm); $k_{WW}'$ is the rate constant of CIP degradation in wastewater matrix and $k_{DW}'$ is rate constant of CIP degradation in distilled water. The theoretical and observed light screening factors were found to be 0.56 and 0.47, respectively. As the ratio of observed and theoretical light screening factors is less than 1, it can be concluded that the scavenging of hydroxyl radicals by dissolved organic matter in the wastewater matrix is more responsible compared to the light shading effect for reducing rate constant in wastewater. This phenomenon has been well documented by different researchers (Cater et al. 2000; Wang et al. 2006; Wasterhoff et al. 1999).

In summary, the transformation of CIP contaminated wastewater is not possible by UV disinfection treatment at 253.7 nm. It requires more photons or fluence to attain significant transformation efficiencies. More than 90% CIP (10 mg L$^{-1}$) degradation was achieved in the UV-H$_2$O$_2$ process with a fluence of 0.2 J cm$^{-2}$ and 1 mol H$_2$O$_2$/mol CIP at pH 7(±0.1). The H$_2$O$_2$ concentration played an important role in the degradation process, showing that CIP degradation decreased after some optimum H$_2$O$_2$ concentration. The apparent quantum yield for CIP degradation was calculated to be 1.46(±0.05) ×10$^{-3}$ mol Einstein$^{-1}$ at pH of 7(±0.1). The quantum yield was found to be less both in acidic and alkaline pH. The degradation of CIP decreased drastically from pH 3 to 11. It was observed that the degradation decreased with an increase in CIP concentration. The DOM and alkalinity of wastewater reduced CIP's degradation by more than 50% compared to distilled water spiked samples. The fluence-based rate constants of CIP degradation were 0.85(±0.03) ×10$^{-2}$ and 0.48(±0.06) ×10$^{-2}$ cm$^2$ mJ$^{-1}$ for distilled water and wastewater, respectively, which present that rate constant for the distilled water spiked sample was two times higher than the wastewater-spiked sample. Six products (molecular weights: 347.1289, 313.1240, 311.1279, 305.1189, 303.1397, and 262.0763) were identified for the degradation of CIP by UV-H$_2$O$_2$ process. Thus, it may be concluded that the UV-H$_2$O$_2$ process is efficient to treat concentrated CIP solutions generated in industry or
from waste streams generated from adsorption, coagulation-flocculation, and/or reverse osmosis treatment systems.

**Declarations**

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Authors' contributions:

Dr. Bijoli Mondal, Mr. Arnab Das, Mr. Shib Sankar Basak and Mrs. Sananda Sarkar have performed the experiments and drafted the paper. Dr. Asok Adak supervised the entire work and finalized the paper for submission.

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Table 1: Degradation products of ciprofloxacin by UV-$\text{H}_2\text{O}_2$ process

| Product ID | m/z     | Molecular weight | Molecular formula | Difference with CIP | Proposed structure |
|------------|---------|------------------|-------------------|---------------------|-------------------|
| DP1        | 348.1372 | 347.1289         | C17H18FN3O4       | +1O                 | ![Proposed structure](image1) |
| DP2        | 314.1311 | 313.1240         | C17H17FN3O2       | +H, -H2O            | ![Proposed structure](image2) |
| DP3        | 312.1354 | 311.1279         | C17H19N3O3        | -F, +H              | ![Proposed structure](image3) |
| DP4 | 306.1261 | 305.1189 | C15H16FN3O3 | -2C2H |
|-----|---------|---------|-------------|-------|
|     |         |         | ![Chemical Structure](image1) |       |

| DP5 | 304.1468 | 303.1397 | C15H17FN3O4 | -2C1H;+1O |
|-----|----------|---------|-------------|-----------|
|     |          |         | ![Chemical Structure](image2) |          |

| DP6 | 263.0839 | 262.0763 | C13H11FN2O3 | -4C7H1N |
|-----|---------|---------|-------------|-------|
|     |         |         | ![Chemical Structure](image3) |       |
Figure Captions

Fig. 1  Chemical structure of ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid).

Fig. 2  Speciation diagram of CIP (10 mg L\(^{-1}\)) at pH 1-12.

Fig. 3  Variation of apparent molar absorptivity of CIP at various pH at 253.7 nm.

Fig. 4  Comparison of degradation of CIP under UV and UV-H\(_2\)O\(_2\) process (initial CIP concentration =10 mg L\(^{-1}\), pH = 7(±0.1) and [H\(_2\)O\(_2\)]/[CIP] = 1).

Fig. 5  Effect of pH on first-order reaction rate constant (a) and quantum yield (b) on degradation of CIP under direct UV light (initial CIP concentration =10 mg L\(^{-1}\)).

Fig. 6  Effect of solution H\(_2\)O\(_2\) on CIP degradation by UV-H\(_2\)O\(_2\) process having initial concentration 10 mg L\(^{-1}\) and pH 7 (±0.1).

Fig. 7  Effect of initial CIP concentration on the UV-H\(_2\)O\(_2\) process having initial pH 7 and [H\(_2\)O\(_2\)]/[CIP] =0.5.

Fig. 8  Effect of solution pH on CIP degradation by UV-H\(_2\)O\(_2\) process with an initial concentration of 10 mg L\(^{-1}\) and [H\(_2\)O\(_2\)]/[CIP] =0.5.

Fig. 9  Transformation of CIP (10 mg L\(^{-1}\)) containing in distilled water and wastewater by UV-H\(_2\)O\(_2\) process with [H\(_2\)O\(_2\)]/[CIP] = 0.5 at pH 7.0(±0.1).
Fig. 1
Fig. 2

The figure illustrates the molar ratio of CIP species across different pH values. The molar ratio is represented on the y-axis, ranging from 0.0 to 1.0. The pH values range from 0 to 14 along the x-axis. Five different species, denoted as $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$, and $\alpha_5$, are shown with varying peak heights and positions depending on the pH.
Fig. 3

Molar absorption of CIP (M$^{-1}$cm$^{-1}$) vs pH

- pH values range from 2 to 11.
- Molar absorption values range from 10,000 to 22,000.

Bar graph showing increasing molar absorption with increasing pH.
Fig. 4
Fig. 5

(a) First-order rate constant (mJ^{-1} cm^{2})

(b) Quantum yield (mol Einstein^{-1})

pH

First-order rate constant (mJ^{-1} cm^{2})

0.0E+00 5.0E-05 1.0E-04 1.5E-04 2.0E-04
2 3 4 5 6 7 8 9 10 11

Quantum yield (mol Einstein^{-1})

0.0E+00 5.0E-04 1.0E-03 1.5E-03 2.0E-03
2 3 4 5 6 7 8 9 10 11
Fig. 6

Fluence-based rate constant (cm$^2$ mJ$^{-1}$) vs. $\left[\text{H}_2\text{O}_2\right]/[\text{CIP}]$.

- Triangles: Rate constant
- Orange circles: Percent removal
Fig. 7

**Fluence-based reaction rate constant (mJ cm⁻²)**

**Percentage removal of CIP**

**Initial CIP concentration (mg L⁻¹)**

![Graph showing percentage removal and reaction rate constant vs. initial CIP concentration]
Fig. 8

- Fluence-based reaction rate constant (mJ/cm²)
- Percentage removal of CIP
- Initial pH of CIP solution (mg L⁻¹)
Fig. 9