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Original Research

Ozonation and Photo-Driven Oxidation of Ciprofloxacin in Pharmaceutical Wastewater: Degradation Kinetics and Energy Requirements

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Abstract

Pharmaceutical wastewater has become an important source for emitting antibiotics into aquatic environments. However, this study aims to evaluate the potential of different advanced oxidation processes like ozonation, photolysis, and photo-catalysis for degrading a fluoroquinolone antibiotic ciprofloxacin (CIP) in real pharmaceutical wastewater. The raw wastewater contains a high concentration of organic content (COD: 603 mg/L, BOD: 116 mg/L) and significant concentration of CIP (7.91 mg/L). In ozonation, compared with the acidic and basic conditions, the degradation rate was faster under basic conditions and showed a competently degraded CIP (up to 98.7%) under the optimum pH 9 within 30 min, whereas photo-catalysis by using commercial anatase (TiO_2) is considered to be the most effective technique for decreasing the concentration of CIP up to 100% within 30 min under the optimized TiO_2 dose (1000 mg/L). The degradation rate was quicker and found to be several times faster than in direct photolysis. Furthermore, electrical energy per order was also calculated for all processes and was obvious by the results that photo-catalysis consume less energy of about 8.7 kWh/m3, for almost complete deduction of CIP.

Keywords: ciprofloxacin, electrical energy per order, ozonation, pharmaceutical wastewater, photo-catalysis, photolysis

Introduction

The occurrence of antibiotics in aquatic environments, particularly fluoroquinolones (FQs), has become an emerging issue due to their increased production, consumption, and persistence in the environment that may lead to the rapid expansion of antibiotic resistance in microbial communities [1, 2]. FQs are the most successful group of broad-spectrum synthetic drugs used in human and veterinary medicines and are frequently introduced in the environment [3], as the majority of these compounds are emitted un-metabolized or as active metabolites in wastewater via various human activities, including direct disposal of unused or expired medicines, effluent of manufacturing

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facilities, hospitals, humans and animal excrement, agricultural and land runoff, and improper disposal [4-6].

Over the last few years, numerous studies have confirmed the presence of powerful fluoroquinolone CIP in effluents of hospitals, municipal wastewater treatment plants (WWTP) and surface water [7, 8]. Due to frequent and intensive use of antibiotics, hospital effluents are generally considered a major contributor of antibiotic residues in aquatic environments. But the contamination of water bodies via pharmaceutical manufacturing facilities has not gathered much attention and their role is considered to be negligible. It is found that hospital effluents have high levels (up to µg/l) of antibiotics when compared to municipal sewage, residential units, or dairies [9]. Recently, antibiotic emissions from manufacturing industries has been detected at the mg/l level, which shows alarming significance and has become a prevalent source of antibiotic residues in water bodies [10, 11].

In the production process of FQs, wastewater is generated at several steps that must be disposed of. Therefore, most manufacturers have adopted conventional wastewater treatment techniques and technologies that minimize the waste stream, but low or partially biodegradabe antibiotics make them tough to remove through biological processes and thus are discharged as contaminants into the receiving waters [12]. In developed countries, production sites that contain high active drug residues are forbidden to dispose of their effluent in municipal or industrial wastewater treatment plants. However, these effluents are properly disposed of via incineration or similar advanced treatment technologies [13]. In under-developed countries like Pakistan, the pharma industry is making progress annually, but pharmaceutical companies do not abide by the environmental standards due to the lack of advanced treatment systems and release their untreated effluent into adjacent waterways [14]. Detected levels of antibiotics in different water bodies globally vary mainly from ng/L to the mg/L range. Though the detected levels are miniscule, their frequent presence in the aquatic environment has become of great concern to human, animal, and aquatic lives [15, 11].

Therefore, there is a need to develop a promising, safe, efficient, and environmentally friendly method to degrade such organically persistent compounds. Oxidative degradation is expected to play an important role, through which organic pollutants can be removed from wastewater [16] based on the generation of hydroxyl radicals, which oxidize persistent, toxic, and non-biodegradable organics to inert by-products due to their high oxidation power [17]. Several researchers have applied different oxidative processes like ozonation [18], photolysis [19, 20], and TiO_2 photo-catalysis [21-23] for the degradation of fluoroquinolone antibiotics, but most of them have focused on the degradation of antibiotics in synthetic solutions rather than real matrices [24, 13]. Hence, the sole purpose of this study was to assess the efficiency of different oxidative processes for the effective degradation of CIP from real industrial wastewater, prior to its discharge to the receiving municipal wastewater. Degradation kinetics and energy requirements for oxidative processes were also evaluated. Although the target compound was selected due to their high consumption rate, huge production capacity, and its low removal by conventional treatment plants.

Experimental

Reagents and Chemicals

The titanium (IV) oxide, anatase >98% pure catalyst we used was purchased from Daejung, Korea. Ciprofloxacin (CIP) with >98% purity was obtained from Harmann Pharmaceutical Laboratories (Pvt) Limited, Lahore, Pakistan. All other chemicals, including sodium thiosulfate, triethylamine, chloroform, potassium di-hydrogen phosphate, phosphoric acid, Na_2EDTA, HCl, and NaOH were of analytical grade and obtained from Merck except for methanol (HPLC grade), purchased from RCI Labscan (Thailand). All chemicals were used without further purification.

Sample Collection, Storage, and Analysis

Our sample was collected from a local pharmaceutical production plant located at Multan Road in Lahore, Pakistan which produces antibiotics, particularly FQs, and has a collective wastewater system for the manufacturing process and for sanitation that is finally discharged to the adjacent municipal drain without any treatment. The sample was collected in pre-washed amber glass bottles, followed by the immediate addition of a small amount of Na_2EDTA, and transported to a laboratory in ice-packed boxes, filtered through a 0.45 µm filter, and stored in a refrigerator at 4ºC till analysis. General characteristics, including pH, chemical oxygen demand (COD), and biological oxygen demand (BOD), were analyzed using standard methods [25], and the pH level was examined using a pH meter (YSI /pH100). COD was determined by potassium di-chromate method and BOD_5 was measured by using the 5-day BOD test method.

However, for antibiotic analysis, the sample was concentrated by liquid-liquid extraction using chloroform as extractant, evaporated the elute to dryness with a rotary evaporator, and reconstituted with methanol to a final volume of 2 ml, and finally measured by an HPLC-PDA (Shimadzu 20A) system equipped with a C18 analytical column operated at a flow rate of 1 ml/min, with mobile phase containing methanol and phosphate buffer (3.9 pH) in the ratio of 40:60 (v/v) at 279 nm [26].

Ozonation

The ozonation experiment was conducted in a bubble column reactor (61 cm long; 2 cm internal diameter) with continuous supply of ozone through a porous diffuser placed at the bottom of the reactor at room temperature (25ºC). An ozone generator (OZ-3G) was used to produce ozone using oxygen as a feed gas. Prior to the ozone experiment the sample was filtered to remove particulate matter and then pH was adjusted to range from 3-10 through the addition of HCl and NaOH solutions. The ozone consistency was controlled by adjusting maximum percentage for O_3 generation, and the sample (1 L) was placed in the reactor to contact with 3 g of O_3/h. Samples for analytical determination of CIP degradation were taken at various intervals (0–30 min) and then sodium thiosulfate was added to block the action of the oxidant [27]. Later samples were clarified through 0.22 µm filters and stored at 4ºC until chromatographic analysis.

Photo-Catalytic Oxidation

The photo-catalytic experiments were carried out to degrade CIP at room temperature (25ºC) using a closed stainless steel structure comprised of 2 UV lamp with power of 36 Watt as a light source to be positioned in a quartz sleeve. Prior to the photo-catalytic reaction, the sample solution was magnetically homogenized with predetermined quantities of Anatase TiO_2 in dark for 30 min in order to ensure adequate mixing of the CIP and the TiO_2 to achieve the adsorption-desorption equilibrium. Afterward, UV lamps (emitting radiation at 254 nm) were turned on to start the photo-catalytic degradation process. During the process, samples were taken by using a syringe at the desired time intervals to 30 min, filtered through 0.22 µm filters to remove TiO_2, and stored at 4ºC until analysis. Experiments in the absence of a photo-catalyst were also carried out in order to access the degradation of CIP by direct photolysis.

Determining Degradation Rate Constants

The degradation rate constants of CIP for each treatment were calculated using the following equation [28]:

$$k = \frac{1}{t}\log Co/Ct \quad (1)$$

…where k is the rate constant (min^{-1}), t is the oxidation time in min, and C_0 stands for the concentration of CIP before treatment while C_t represents the concentration of CIP after oxidation reaction time (min).

Calculating Electrical Energy per Order (E.E/O)

The electrical energy per order was also determined as the intentional oxidative processes are electrical energy linked processes. The electrical energy per order narrates the sum of electrical energy (KWh) required to remove a contaminant by one order of magnitude in a treated volume of contaminated water, calculated by using the following equation for all oxidative processes used in this study [28, 29]:

$$E.E/O\ (kWh/m3) = \frac{P \times t \times 1000}{V \times 60 \log\ (Co/Ct)} \quad (2)$$

…where P is the power input of the system (kW), t is the oxidation time (min), V is the volume of the sample (liter), and C_0 and C_t are the initial (at time 0 min) and final concentrations of CIP at t min oxidation time. Energy calculation in this study was based on the power required by the ozone generator for the ozonation process and in case of photolysis the power input required by the UV lamp. However, this was for the photo-catalytic process power input comprised by UV lamp without energy requirements for stirring.

Results and Discussion

Quality of Pharmaceutical Wastewater

The quality parameters of the raw wastewater are summarized in Table 1, which indicates that the wastewater discharged by the pharmaceutical industry holds high organic content, as COD and BOD concentrations were higher than the permissible limits and having BOD_5/COD ratio lower than 0.4, which

Table 1. Quality of pharmaceutical wastewater.

Parameter	Unit	Value	Permitted value [a]
pH	---	6.87	6-9
Chemical oxygen demand (COD)	mg/L	603	150
Biological oxygen demand (BOD)	mg/L	116	80
BOD_5/COD ratio	---	0.19	---
CIP	mg/L	7.91	---

[a]maximum permitted values for effluents discharged in to inland waters (Punjab environmental quality standards for municipal and liquid industrial effluents, Pakistan)

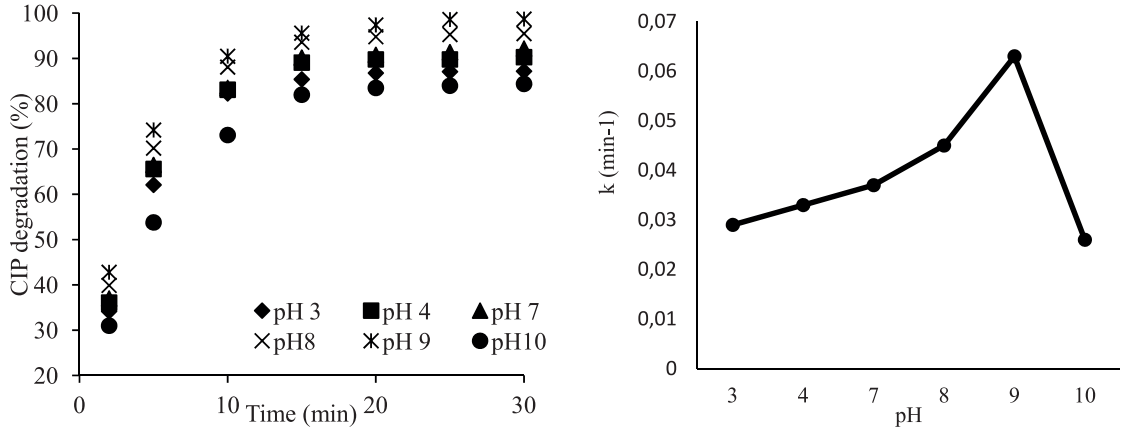

Fig. 1. a) Effect of pH on the efficiency of CIP degradation during ozonation and b) effect of initial pH on the degradation rate constant (CIP = 7.91 mg/L, oxidation reaction time = 30 min).

shows the low biodegradability of the targeted effluent [30]. However, the most significant compound detected is CIP, an antibiotic belong to the fluoroquinolone group. The concentration of this compound in the industrial water was 7.91 mg/L, which is extremely higher than the concentration reported in other studies [1, 10, 14].

Degradation of CIP during Ozonation

In order to assess the degradability of CIP in pharmaceutical wastewater, ozonation was carried out at initial pH values ranging from 3 to 10 as pH of the solution is one of the variables that most influence the ozonation process [31]. Fig. 1 illustrates the effect of pH on the degradation of CIP in the ozonation process. It is evident from the result that the removal percentage of CIP increased rapidly as the initial pH level progressed and reached 98.7% at pH 9 within 30 min, while it was 87.2%, 90.3%, 92.2%, and 95.5% when the pH was 3, 4, 7, and 8, respectively. However, beyond pH 9 of the solution, the removal decreased to 84.4%. At lower acidic conditions, the removal can be explained due to the delayed ozone decay and by direct oxidation with ozone itself, as ozone is more stable at lower pH [32]. On the other hand, gradual increases in pH accelerate the production of more reactive hydroxyl radicals [13], which degrade the CIP more rapidly. At higher pH, the removal of CIP occurs through a combination of both ozone and hydroxyl radicals. So these results verify that basic conditions are more suitable for ozonation of CIP.

Degrading CIP during Photo-Catalytic Oxidation

The concentration of the photo-catalyst is a major factor that affects the rate of photo-catalytic oxidation. So, the effect of TiO_2 dosage was investigated under natural pH of the sample (6.87) with different TiO_2 concentrations ranging from 100 to 2000 mg/L to determine the quantity of a photo-catalyst that would lead to higher degradations of CIP. Fig. 2 reveals that the removal efficiency of CIP was found to gradually increase with increases in TiO_2 doses equal to 1000 mg/l, but additional quantities of TiO_2

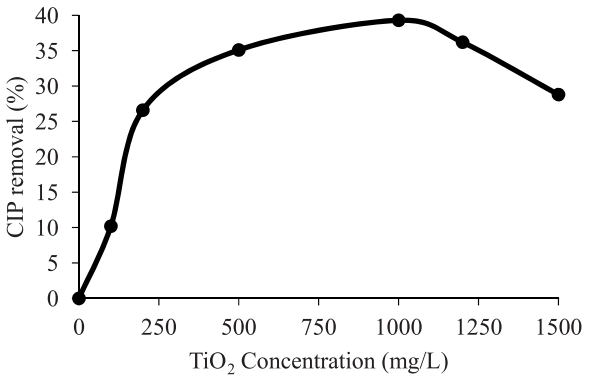

Fig. 2. Effect of initial concentration of TiO_2 on the removal of CIP in darkness (CIP = 7.91 mg/L, contact time = 30 min).

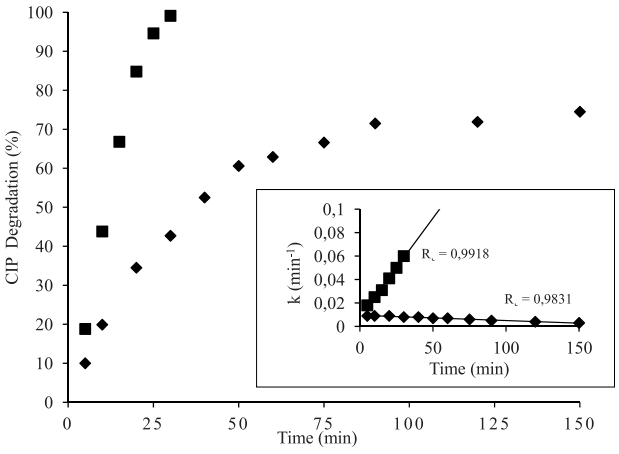

Fig. 3. Photo degradation profile of CIP during UV (photolysis) and UV/TiO_2 (photo catalysis) at inherent pH of the sample .

Table 2. Comparison of EE/O (kWh/m^3) for CIP degradation by oxidation processes.

Oxidation process	Oxidation time (min)	Maximum Removal (%)	EE/O (kWh/ m^3)	Oxidation time (min)	Optimal Removal (%)	EE/O (kWh/ m^3)
Ozonation	30	98.7	36.8	15	95.6	25.8
Photolysis	150	74.5	151.3	90	71.5	98.9
Photo-catalysis	30	99.1	8.7	25	94.6	11.8

were found to reduce removal efficiency. Very high concentrations of TiO_2 cause turbidity in the solution, which can impair the efficiency of the photo-catalytic process by impeding the penetration of UV irradiation [33]. Thus the optimal concentration can be decided to be 1000 mg/L for subsequent experiments.

Degradation of CIP over time by direct photolysis and the photo-catalytic process is depicted in Fig. 3. It is obvious from the result that the degradation of CIP increases with irradiation time and in the case of UV irradiation alone, about half of the initial CIP concentration was reduced at a time of 40 min, which further increases with time and after 90 min removal reached 71.5%, but further than 90 min no significant removal was observed. This degradation efficiency is lower, which can be due to the occurrence of a high concentration (7.91 mg/l) of CIP in the studied wastewater as photo degradation increases with low concentrations of FQs [20]. However, when comparing the performance of UV alone (photolysis) with UV/TiO_2 (photo-catalysis), we observed that in the presence of a photo-catalyst, degradation efficiency was rapidly enhanced and more than 80% of CIP was removed within only 20 min of the process, while almost complete removal was achieved in 30 min of irradiation. Fig. 3 also shows a comparison of degradation rate of CIP with and without photo-catalyst. The result implies that the degradation proceeds much faster in the presence of a photo-catalyst due to increased production of hydroxyl radicals, and rate constant (k) was found to be several times faster than in direct photolysis, with 99.1% removal in 30 min.

Comparison of EE/O for Oxidation Processes

Electrical energy requirements per order resulting in the removal of CIP in 1 L of sample for each of the oxidation processes are presented in Table 2. It is apparent from the results that under-optimized conditions of the photo-catalytic process are proven to be a good option to give almost complete removal of CIP from pharmaceutical wastewater by consuming less energy than other processes. The ozonation process also consumes less electrical energy than UV alone for CIP removal, but the removal efficiency is slightly lower than the photo-catalytic process at the same time. So ozonation proves to be the second-best option. Hence, the electrical energy requirement for CIP removal was in the order UV/TiO_2 < O_3 < UV.

Conclusion

This study demonstrates that both ozonation and photo-catalytic oxidation processes have strong potential to remove CIP from real industrial wastewater contaminated with fluoroquinolone antibiotics. The anticipated ozonation experiments followed first-order kinetics and resulted in highest degradation of 98.7% of CIP at pH 9 within 30 min. However, 71.5% of CIP was degraded by direct photolysis after 90 min of UV irradiation, which was upgraded with the addition of TiO_2 photo-catalyst. Using 1000 mg/l of TiO_2, at 30 min of irradiation CIP was almost completely degraded. The combined process of UV/TiO_2 is more effective than UV light alone, and the rate of degradation becomes faster with the addition of a photo-catalyst. Moreover, the electrical energy requirement as calculated for each oxidation process showed that the photo-catalytic process was the most efficient process for removing CIP in real pharmaceutical wastewater by consuming less energy.

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Conflict of Interest

The authors declare no conflict of interest.

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