Plasma-liquid system for degradation of pharmaceutical effluent

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ABSTRACT

Surface and underground water contamination are becoming a serious concern with time. In recent years, pharmaceuticals, especially antibiotics have emerged as a serious water pollution hazard. This study is for the treatment of a pharmaceutical effluent containing the antibiotic compound ciprofloxacin (CIP). Contact glow discharge (CGD) process is used for the degradation of CIP-containing effluent of the pharmaceutical industry. The results show that CGD has a clear impact on the degradation of CIP. In 15 min, the degradation is only 2.5% and increases with exposure, reaches 84.3% in 150 min and attains a saturating trend, just 84.8% in 180 min. With the use of stainless steel (AISI 304) in CGD, iron ions are included in the solution which accelerates the degradation process. The change in the degradation rate of CIP with the addition of $FeSO_4$ (2–15 mg/L) is investigated and it becomes almost double when the salt concentration is changed from 2 to 15 mg/L. According to our knowledge, it is the first study for pharmaceutical antibiotic CIP effluent decomposition by plasma liquid system.

Keywords: Plasma-liquid system; Pharmaceutical effluent; Degradation of antibiotic solution

1. Introduction

Contamination of surface waters by the continued release of pharmaceuticals has been the subject of special attention over recent years. Particularly the existence of antibiotics has become a growing concern in the aquatic environment due to their increased production, consumption, and persistence in the environment that can lead to the quick development of antibiotic resistance in the bacteriological communities [1,2]. Among antibiotics, the fluoroquinolones (FQs) are the utmost successful set of manmade drugs that are expansively used in veterinary or human treatments and are repeatedly introduced into the aquatic environment [3] as a majority of these compounds are released un-metabolized or as an energetic metabolite in wastewaters through various anthropological activities including, discharges from manufacturing facilities or hospitals, veterinary drug use, agricultural/land runoff, and inappropriate dumping of unused/ expired medicines (the common practice of flushing down the toilet) [4].

Employing regular use of antibiotics, normally hospitals were considered as the main provider of antibacterial residues to the aquatic systems. But, the pollution of aquatic environments through antibiotic production units has not collected much attention [5]. The effluents discharged by hospitals contain high concentrations of antibiotics (up

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to µg/L) when compared to urban sewage or dairies [6]. Whereas recently, antibiotic emissions detected at mg/L concentration from manufacturing facilities also shows their alarming significance [7,8] and it became a promising source of antibacterial residues in the aquatic systems [9].

The unconstrained production and use of FQs for the control of contagions in humans and animals have increased in Pakistan, which resulted in a large number of antibiotic residues in watercourses [2,10]. Besides the severity and importance of the issue, only a few studies are available regarding the existence of these antibacterial compounds in the environment of Pakistan. Thus, detailed and targeted investigations are required to investigate the presence, sources, and fate of these compounds [10,11]. Due to the limitation of conventional treatment technologies for effective removal of these recalcitrant compounds there was a need to develop a promising, safe, efficient, and environmentally friendly method to degrade such organic persistent compounds.

Many of the researchers have used different methods for the degradation of recalcitrant compounds from wastewater. Among a massive range of treatment technologies Atmospheric pressure microplasmas over a suitable liquid surface, are very simple, low cost, and environmental friendly. Recently, Rezaei et al. [12] published a comprehensive review covering different applications in material processing, nanoscience, biomedicine, sterilization, food, and the environment. As the discharges are at atmospheric pressure and room temperature, using moderate current and voltages, one doesn't need expensive vacuum equipment and heating or cooling arrangements [13–15]. For wastewater treatment, plasma-based oxidation is becoming popular for research as it rapidly removes organic contaminants and it is environmental friendly. This type of plasma is categorized as nonthermal, as electrons' energy/temperature is much higher than the molecular ions' energy/temperature. Energetic electrons interact with the background compounds like O_2, N_2, or H_2O and produce reactive radicals which diffuse in the reaction solution and decompose different present organic compounds in the solution [16–18].

Baloul et al. [19] investigated the degradation of paracetamol residue in water by the impact of non-thermal plasma in a multi-needle to plate reactor. Various inlet gases like air, N_2, and Ar were used. A conversion rate of 81% in the air was obtained. It was proposed that if the discharge is in the oxygenated gas, it will promote the production of O atoms and O_3 that will increase the paracetamol degradation.

In this paper, degradation of the effluent of a pharmaceutical industry containing fluoroquinolone by CGD is reported. Ciprofloxacin (CIP) a broad-spectrum fluoroquinolone antibiotic employed as the model pollutant due to high consumption, the highest production, regular detection in the effluent, and a serious risk to the environment. It has the chemical formula $C_{17}H_{18}FN_3O_3$ and a molecular weight of 331.347 g/mol.

2. Experimental system and diagnostics

CIP belongs to FQ antibiotic group was selected for analysis in this study, because of its high consumption (high prescription rate in Pakistan), high production,

regular detection in the effluents, significance, inherent cytotoxicity activity, and potential risk to the environment. The CIP of high purity > 98% was provided by Harmann Pharmaceutical Laboratories Ltd., Lahore Pakistan. All chemicals and reagents used in the study were of analytical grade or higher. Methanol used for chromatographic analysis was of high-performance liquid chromatography grade and purchased from the RCI Lab scan (Thailand). The chemical structure of CIP is given in Fig. 1.

To prevent adsorbing of antibiotics to the walls of glassware, the entire glassware used in the work was salinized with dimethyldichlorosilane solution in toluene 10% (v/v) followed by a rinse with toluene and then methanol [20]. It followed the heating of glassware for 1 h at 450°C (842°F), and then rinsed with a strong chelating agent Na_2EDTA for excluding any possible interaction with metal ions [2,21]. The samples were taken in a prewashed amber glass bottle and transported to the laboratory in ice-packed boxes. The suspended particles in the effluent were removed by filtering through Whatman glass fiber filters. Then, it was stored in dark without the addition of any chemical at 4°C for subsequent analysis [22]. The stock solution of CIP (1 mg/mL) was prepared with deionized water. The stock solution was stored in amber bottles at the cool place (4°C) for up to 2 months while working solutions were prepared on daily basis.

Fig. 2 presents the experimental arrangement. The reaction cell contained 200 mL solution. A stainless steel tube of 2 mm diameter is used as the cathode, fixed at one end, and attached with a stainless steel needle of outer diameter 0.64 and 0.34 mm inner diameter. The needle was adjusted 0.75 mm above the solution surface. The anode was also a stainless steel wire of different diameters (0.5–1.5 mm), connected to the HV power supply. A negative DC power supply is used to initiate and sustain the microplasma. The industrial-grade argon gas at 100 sccm is passed through the needle for plasma formation. The current is kept constant at 15 mA by using an 8 kΩ ballast resistor. The experiment was conducted at atmospheric pressure and room temperature (25°C; 77°F). After various time intervals (10–180 min), the samples were analyzed for CIP degradation and chemical oxygen demand (COD).

3. Results and discussion

For the analysis of CIP, a volume of 20 µL of the sample was injected into a liquid chromatography system at a wavelength of 279 nm. The degradation efficiency of CIP was calculated using the equation [23]:

$$\text{CIP}\left(\%\right) = \left(\frac{\text{CIP}_0 - \text{CIP}_t}{\text{CIP}_0}\right) \times 100 \tag{1}$$

where CIP(%) is the percentage of degradation rate, C_0 is the concentration of CIP before any treatment, C_t is the concentration after treatment process of t min. Fig. 3 shows CIP degradation with anodes of different diameters which indicates that the CGD process had a clear impact on the degradation of CIP and the initial concentration of CIP in the effluent was slightly reduced with an increase
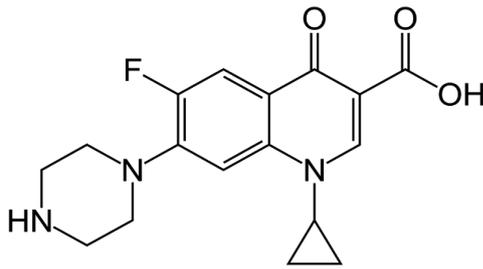
Fig. 1. Chemical structure of CIP.
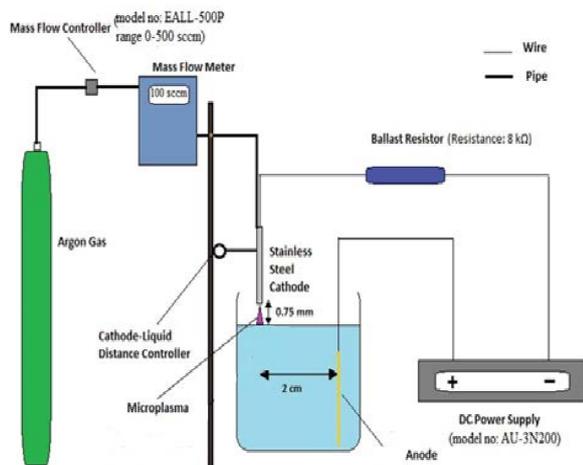
Fig. 2. Schematic arrangement of glow discharge electrolysis.
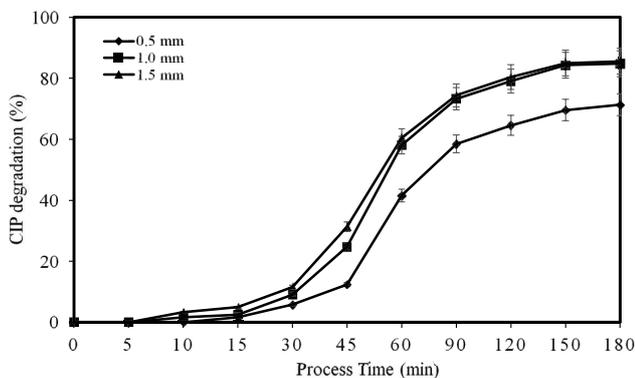
Fig. 3. Effect of anode diameter on CIP degradation.

in exposure of the plasma discharge time. Concerning the plasma exposure (1 mm = stainless steel anode) of 15 min, only 2.5% CIP was degraded which increased with exposure and reached 84.3% after 150 min. Moreover, when plasma time increased to 3 h (180 min) the 84.8% degradation was achieved with no further degradation. With the use of stainless steel anode in the CGD process, iron ions dispersed into the tested solution due to corrosion of the electrode [24] which can accelerate the degradation of CIP in the effluent. Furthermore, when changed the diameter of the anode by 0.5 and 1.5 mm, the degradation of CIP after 180 min of plasma process was 71.3%

and 85.6%, respectively, also shown in 3. The difference between the degradation degrees of CIP with different anode diameters is because with increasing the diameter of the anode, the slightly extra current passed through it which also enhanced the degradation of CIP [17]. According to Kao and Huang [25], the stainless steel wire corrodes (Fe diffused into solution) well at pH 4. However, the pH ≤ 4 value was observed in the current study during CGD treatment (45–90 min) which could be a reason behind maximum CIP degradation at this time.

Several researchers have reported that CIP degradation obeys first-order kinetics oxidative processes [26,27]. The degradation rate of CIP for each treatment is calculated by using the following first-order equation [28]:

$$-kt = \ln\left(\frac{C_t}{C_0}\right) \tag{2}$$

Here, k indicates the degradation rate constant (min^{-1}) and t is the oxidation process time. Fig. 4 depicts the variation degradation rate constant with time. The maximum rate constant for CIP degradation is observed during 45–90 min.

Adsorption process using various adsorbents was implied to study the removal efficiency of CIP, among them, multiwalled carbon nanotubes were successfully used as adsorbents, however, the adsorption process was slower as compared to the current investigation for the removal of CIP in water [29]. Various advanced oxidation processes (AOPs) were also successfully investigated for the removal of CIP. Mondal et al. [30] implied various AOPs for the CIP removal and found that the photocatalytic process using zerovalent iron was efficient as compared to other processes (H$_2$O$_2$/UV, UV, and H$_2$O$_2$). Moreover, the removal efficiency of CIP was found to be about 99% in 120 min at optimum conditions [31]. In the current investigation (Fig. 6) about 99% CIP removal efficiency was achieved in 40 min (FeSO$_4$ = 15 mg/L). Similarly, other findings using AOPs indicate that the studied CGD-based process is comparable to previously studied AOPs and shows better performance as compared to some of the studied AOPs [32].

The CGD can generate many chemical reactions and hence various reactive species including OH*, H*, and H$_2$O$_2$. These species are helpful for further degradation of different organic contaminants. The conductivity of the solution increases with the treatment time [24]. The increase in conductivity is due to the increase in reactive species (OH*, H*, and H$_2$O$_2$) which degrade the CIP and convert organic compounds into organic acids [18,24]. Initially, due to low conductivity, the CIP degradation was low upto 30 min. With process time, the conductivity increases and hence degradation rate of CIP increases rapidly, reaching to a maximum of 85.6% in 180 min.

During the CGD, the pH of the treated effluent decreases with the process time. It may be explained in terms of plasma water interaction that can produce short-lived OH* in a medium with a pH of more than 7 that further recombine to form long-lived reactive species like H$_2$O$_2$. The production of H* also changes the pH of the treated solutions [33–35]. The change in pH may also be due to the production of carboxylic intermediary products
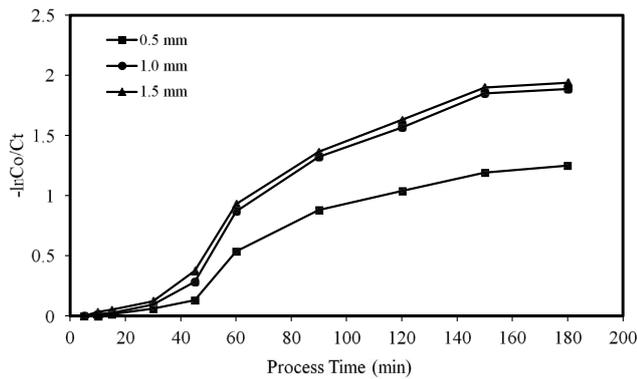
Fig. 4. Variation of degradation rate constant *k* with time.
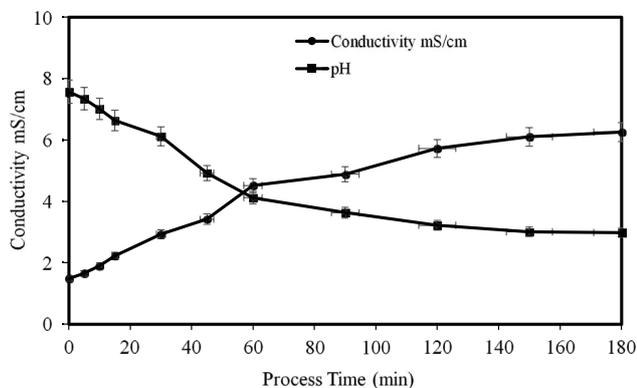
Fig. 5. Variation in conductivity and pH of the solution with time during CGD.

during the CIP degradation. The change of conductivity and the pH of the treated sample is shown in Fig. 5.

A ferrous salt FeSO$_4$ was added to investigate its effect on the degradation of CIP. The presence of iron in the treated effluent can enhance the degradation efficiency of CIP through the following reactions [17,36,37]. The second-order rate constants of the following reactions were with *k*-values of 63, 3.2×10^8, 8.4×10^6, 2.7×10^7 1/M S, respectively, for Eqs. (3)–(6) [38]. Following are the key reactions in such processes since they involve the formation of reactive oxygen species that reacts with pollutants leading to the degradation of pollutant:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{3}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{5}$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{6}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{7}$$
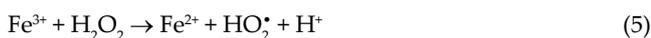
Fig. 6 presents the change in the degradation rate of CIP with the addition of FeSO$_4$ (2–15 mg/L). The addition of iron ions significantly improves the degradation of
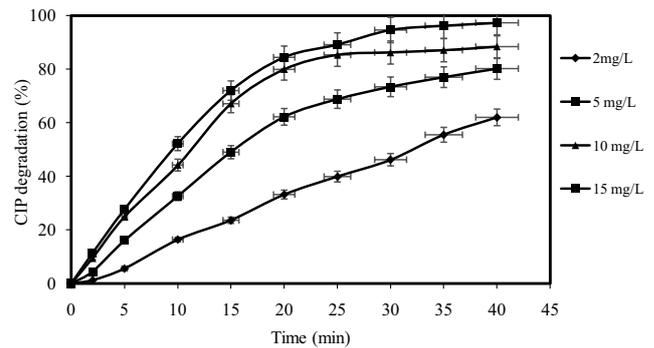
Fig. 6. For anode diameter of 1.5 mm, the effect of FeSO$_4$ concentration on the degradation of CIP.
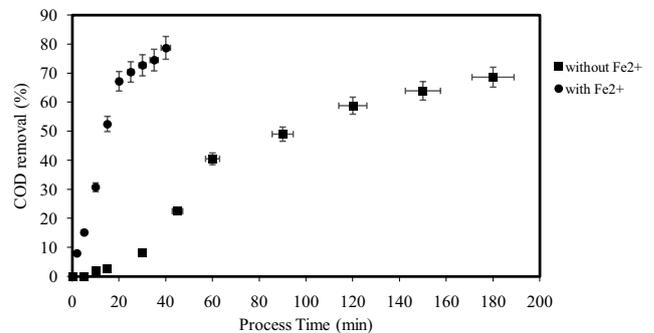
Fig. 7. For anode diameter of 1.5 mm, COD removal from CIP with and without the addition of FeSO$_4$ salt.

CIP. As the oxidation potential of HO$_2^\bullet$ is more than H$_2$O$_2$, so the addition of Fe^{2+} has improved the degradation of CIP. The degradation increases as high as 97.3% just in 40 min for FeSO$_4$ salt concentration of 15 mg/L. The degradation of the target compound is also monitored by the concentration of COD, which describes the amount of mineralization [39]. The CGD removes the COD and the removal is rapid with the addition of FeSO$_4$ salt (Fig. 7).

4. Conclusions

In recent years, pharmaceuticals, especially antibiotics have emerged as a serious pollution hazard in the surface and underground water. This study is for the treatment of a pharmaceutical effluent containing an antibiotic compound CIP. Contact glow discharge (CGD) process is used for the degradation of CIP-containing effluent of the pharmaceutical industry. The results show that CGD has a significant impact on the degradation of CIP. Initially, the degradation is slow and increases with exposure, reaches 84.3% in 150 min and attains a saturating trend, just 84.8% in 180 min. With the use of stainless steel (AISI 304) anode in CGD, iron ions are included in the solution which accelerates the degradation process. The stainless-steel anode of larger diameter proved more beneficial. The change in the degradation rate of CIP with the addition of FeSO$_4$ (2–15 mg/L) is also investigated. It is found that degradation becomes almost double when the salt concentration is increased from 2 to 15 mg/L. According

to our knowledge, it is the first study for pharmaceutical antibiotic CIP effluent decomposition by plasma liquid system. With the degradation of the effluent, the conductivity of the solution increases almost three times, and the pH decreases by the same factor of three, but both behaviors are saturated. The same behavior is recorded for the COD removal, which increases quite rapidly.

In conclusion, the CGD is found an efficient technique to remove the antibiotic compound CIP from the effluent of a pharmaceutical industry that in turn reduces the pollution hazard in the surface and underground water.

Acknowledgments

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