

HYDROXYL RADICAL BASED DEGRADATION OF CIPROFLOXACIN IN AQUEOUS SOLUTION

MURTAZA SAYED^{*1,2}, LUQMAN ALI SHAH², JAVED ALI KHAN², NOOR SAMAD SHAH^{2,3}, HASAN M. KHAN^{*2}, RAFAQAT ALI KHAN¹, ABDUR RAHMAN KHAN¹, ASAD M. KHAN¹

¹Department of Chemistry, COMSATS Institute of Information Technology, Abbotabad, 22060, Pakistan.

²Radiation Chemistry Laboratory, National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120, Peshawar.

³Department of Environmental sciences, COMSATS Institute of Information Technology, Vehari, 61100, Pakistan.

ABSTRACT

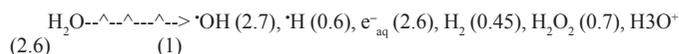
This study reports the degradation of ciprofloxacin (CIP) by means of ionizing radiations. Kinetic studies with aqueous concentrations of 4.6, 10, 15, 17.9 mg/L reveals that degradation of CIP follows *pseudo*-first order kinetics and the decay constant increased with decrease in initial concentration of CIP. The removal efficiency, represented by G-value, decreased with increasing absorbed dose and increased with higher [CIP]₀ concentration at a given absorbed dose. The effects of bubbling CIP solution with N₂, N₂O or air on CIP degradation were also studied. The influence of various radical scavengers like *tert*-butanol, *iso*-propanol, HCO₃⁻, CO₃²⁻, NO₃⁻ and NO₂⁻ as radical scavengers in N₂-saturated solutions of CIP indicated that [•]OH were more closely associated with the radiolytic decomposition of CIP than other radicals, such as e⁻_{aq} or [•]H. The pH value of aqueous media played a crucial role in the degradation of CIP. It was observed that degradation efficiency was higher under acidic condition compared to degradation in natural or alkaline media. F⁻, CH₃COO⁻ and HCOO⁻ were formed as a result of CIP degradation that were analyzed by ion-chromatography.

Keywords: Hydroxyl radical, ciprofloxacin, degradation, gamma-irradiation, kinetics

1. INTRODUCTION

The presence of antibiotics in the aquatic bodies provides a new challenge to drinking water, wastewater, and water reuse system [1-4]. Ciprofloxacin, a member from fluoroquinolone group is widely used as humans and veterinary medicine [5]. The presence of these broad spectrum antibiotics in aquatic environments, may pose serious threats to the ecosystem and human health by causing proliferation of bacterial drug resistance [6, 7]. Most fluoroquinolones are not fully metabolized in the body and thus are excreted and introduced to the environment through wastewater effluents [6, 8]. Advanced oxidation processes (AOPs), with highly reactive hydroxyl radical ([•]OH) as the main oxidative species, provide an alternate technique to transform and decontaminate these soluble human antibiotics [1, 9]. Radiation-induced decontamination of CIP and other toxic chemicals in water is a new and more promising technique [10]. This process has been found to be more economical and efficient than other waste water treatment processes [11].

The underlying principals behind gamma ray or electron beam treatment processes involve radiation chemistry of water, thoroughly studied and accepted technique. [12]. Irradiation of water using gamma ray can be explained by following equation, where the number in parenthesis represents the radiation yield (G-value) of each species per 100 eV of absorbed energy [12].



The most reactive species in Equation (1) are the oxidizing hydroxyl radicals ([•]OH) and the reducing aqueous electrons (e⁻_{aq}) and hydrogen atoms (H[•]). High concentrations of these species can be produced in a very short interval of time and can react with target contaminant. Table 1 shows an estimate of the concentration of these reactive species at different absorbed doses applied in the present study.

Table.1: Concentration of different species at various doses of gamma radiation.

Dose (Gy)	Concentration (mM)			
	OH	H	e ⁻ _{aq}	H ₂ O ₂
145	0.0406	0.0087	0.03915	0.01015
290	0.0812	0.0174	0.0783	0.0203
435	0.1218	0.0261	0.11745	0.03045
580	0.1624	0.0348	0.1566	0.0406
870	0.2436	0.0522	0.2349	0.0609

The present study focused on the use of gamma radiations as an AOP to

degrade CIP and to determine the role of [•]OH in the degradation of CIP by means of radical scavengers experiments. The main objectives of the present study were: (1) to study the decomposition of ciprofloxacin (CIP) in water using gamma radiations; (2) to investigate the decomposition kinetics of CIP; and (3) to evaluate the efficiency of [•]OH in the degradation of CIP removal using radical promoters and scavengers, often present in water.

2. EXPERIMENTAL

2.1 Chemicals and reagents

All of the chemical used (*tert*-butanol, *iso*-propanol, sodium carbonate, sodium bicarbonate, sodium nitrate, sodium nitrite, perchloric acid, sodium hydroxide) were of high-purity analytical grade reagents supplied by Sigma-Aldrich. The ultrapure water was obtained from a Milli-Q® system (Millipore). Nitrogen and nitrous oxide gases used in the present study were of at least 99.99% purity.

Ciprofloxacin (100%) used in this study was supplied by Sigma-Aldrich. The chemical structure of this compound is shown in Fig.1.

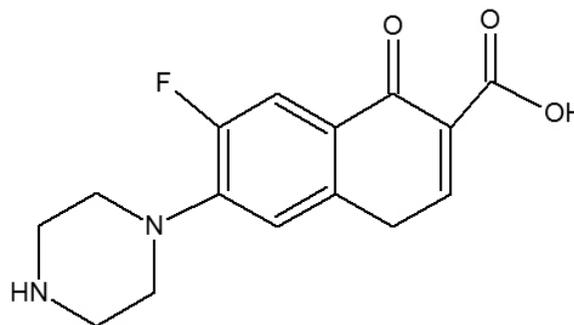


Fig. 1: Chemical Structure of Ciprofloxacin.

2.2 Experimental procedures

2.2.1 Sample preparation

CIP solution at initial concentration of 4.6 mg/L was prepared by dissolving weighted amount of solid CIP in ultrapure water. The different additives (*iso*-propanol, *tert*-butanol, CO₃²⁻, HCO₃⁻, NO₃⁻, and NO₂⁻) of different concentrations were added into CIP aqueous solution to examine their effects on CIP degradation. HClO₄ (0.05 mol/L) or NaOH (0.05 mol/L) were added into 4.6 mg/L CIP solution to make solution of desired pH and to test the effect of pH value on degradation efficiency. CIP solutions at different concentrations were also prepared to test the effect of initial concentration of CIP on degradation at the given radiation dose.

2.2.2 Irradiation procedures and bubbling of CIP solution by N₂ or N₂O gases

The irradiation source used for irradiation studies was a Co-60 gamma-ray source (Issledovatel, former USSR) available at NIFA, Tarnab, Peshawar, Pakistan. The source was calibrated by using aqueous ferrous sulfate (Fricke dosimetry) solution [12]. The dose rate was found to be 296 Gy/hr.

N₂-saturated experiments were conducted in 250 mL glass vessel, where N₂-gas was passed through CIP solution for at least 25 minutes. For N₂O saturation of CIP solution, same procedure was applied, replacing N₂ by N₂O gas. The purity of N₂ and N₂O gasses used in this study was 99.999%.

2.3 Analytical methods

Analysis of CIP was performed using high performance liquid chromatography (Agilent 1200 series HPLC, Agilent Technologies, USA), equipped with UV detector. The separation was achieved using reversed phase C-18 column, with water/methanol/acetonitrile/1% acetic acid (15/15/20/50, V/V) as mobile phase in isocratic mode at flow rate of 1ml min⁻¹. The evaluation of UV-Vis absorption spectra of CIP in aqueous solution before and after irradiation was recorded by Lambda-800 UV-Visible Spectrophotometer (Perkin Elmer Instruments, USA). For the analysis of by-products, like F⁻, CH₃COO⁻ and HCOO⁻, Metrohm Ion- Chromatograph (IC) was used. Triplicate samples were prepared and analyzed for each sample.

2.4 Calculation of G-Value and dose constants

The G-value is defined as the number of molecules of products formed or of reactant destroyed, by absorbing 100 eV of energy, it can be calculated using the following equation [13].

$$G = \frac{R}{D} \left(\frac{6.02 \times 10^{23}}{6.24 \times 10^{16}} \right) \quad (2)$$

Where R is the change in the concentration of reactant, CIP (M), D is the absorbed dose (Gy), 6.02 x 10²³ is the Avogadro's number and 6.24 x 10¹⁶ the conversion factor from Gy to 100 eV/L.

The dose constant, k, was calculated from the slope of the natural logarithm (ln) of the organic pollutant concentration in M versus dose (Gy). Dose constants were used to calculate dose required for 50% and 90% CIP degradation (D_{0.5} and D_{0.9} values) by using Eqs. (3) and (4):

$$D_{0.5} = \frac{\ln 2}{k} \quad (3)$$

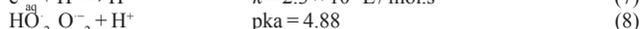
$$D_{0.9} = \frac{\ln 10}{k} \quad (4)$$

D_{0.5} and D_{0.9} were used for the analysis of solute removal [14].

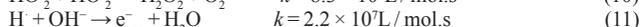
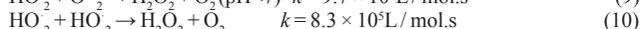
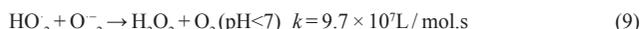
3. RESULTS AND DISCUSSION

3.1 Degradation of CIP by ionizing radiations

During ionizing irradiation, the reactions between reactive radicals ([•]OH, e_{aq}⁻, [•]H) and any additive occur in aqueous solution as follows: In aerated media, the reducing species [•]H and e_{aq}⁻ are converted into HO₂[•] and O₂^{-•} because of their fast reactions given by Eqs. (5) and (6); under acidic conditions, the H⁺ ion reacts with e_{aq}⁻ to produce H[•], as by Eq. (7); HO₂[•] and its conjugate base O₂^{-•} exist in a pH-dependent equilibrium as given by Eq. (8);



Eqs. (9)–(11) may also occur depending on experimental conditions.



Aqueous solution of 4.6 mg/L CIP was irradiated with radiation doses of 0, 145, 290, 435, 870 Gy. Fig. 2 shows the UV-absorbance spectra of CIP solution before and after irradiation at 200–400nm (Fig. 2a) and decrease in concentration of CIP as a result of after gamma ray irradiation (Fig. 2b). The results showed that the UV-absorbance and thus the conc. of CIP in the 200–400 nm region decreased with increase of radiation dose. At radiation dose of

870 Gy, 4.6 mg/L of CIP was almost completely degraded as shown in Fig. 2b.

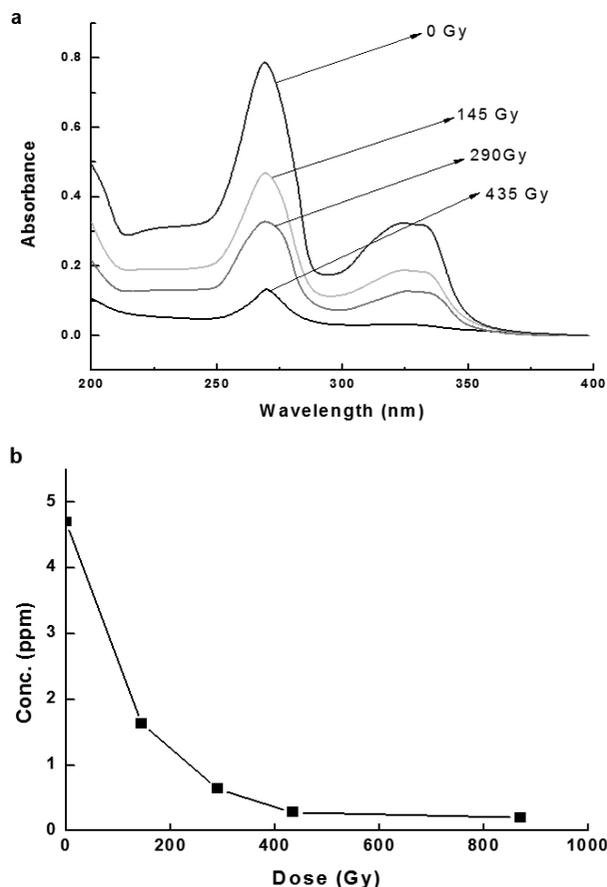
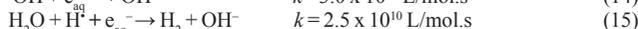
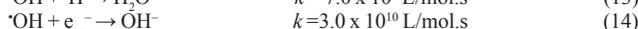
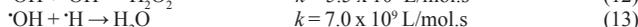
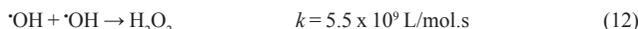


Fig. 2: The UV-absorbance spectra of CIP before and after irradiation at 200–400nm (a) and decrease in CIP concentration after gamma-ray Irradiation (b)

According to Eq. (2), the G-values of CIP (4.6 mg/L) at different radiation doses were calculated as shown in Table 2. The G-values decreased with increasing radiation dose, a trend that has been reported in several other studies [15–17]. Firstly, this trend can be explained by competition for solute molecules (CIP) between the reactive species produced during radiolysis of water. With increasing radiation dose, greater competition occurs between the reactive radicals, resulting in decrease of G-values. Secondly, there is possibility of competition for reactive radicals between the parent compound (CIP) and the reaction by-products [17]. The third possibility is the radical-radical recombination reactions, including [•]OH, e_{aq}⁻, [•]H also increases with increasing radiation dose [15] as shown by reactions such as given in Eqs. (12–15), so the radical concentration for interaction with CIP reduced.

Table 2: The G-Value of CIP removal at different absorbed dose.

Absorbed dose (Gy)	145	290	435	870
G value (molecules/100 ev)	0.5635	0.3582	0.2671	0.1402



The efficiency of irradiation process for the decomposition of CIP was compared between the percentage removal (%) and G-values as shown in Fig. 3.

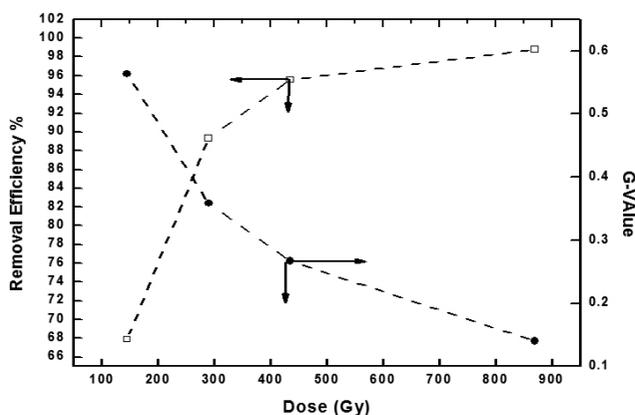


Fig. 3: Calculated G-values and Percentage removal efficiencies of CIP using gamma irradiation. The initial aqueous CIP concentration was 4.6 mg/L.

3.2 Effect of dissolved oxygen, N_2 -saturated and N_2O -saturated gases on CIP degradation.

Fig. 4 shows the effect of dissolved oxygen, N_2 -saturated and N_2O -saturated gases on CIP degradation by gamma irradiation. In this figure the fractions of CIP at a given radiation dose (C/C_0) has been plotted against radiation dose (where C is the conc. of CIP after irradiation and C_0 is the initial conc. of CIP). It is clear from Fig. 4 that CIP was degraded in all the three conditions and degradation efficiency increased with the increase in radiation dose. However, the degradation efficiency in the solution saturated with nitrous oxide was relatively higher than that in the solution saturated with air, and the latter was greater than degradation efficiency in the solution saturated with nitrogen.

Table 3: Effect of Irradiation on dose constant, $D_{0.5}$ and $D_{0.9}$ at different concentrations of CIP solution.

Concentration (mg/L)	Dose constant (k)	$D_{0.5}$ (Gy)	$D_{0.9}$ (Gy)
4.6	4.9×10^{-3}	138.62	460.51
10	2.9×10^{-3}	231.04	767.52
15	1.9×10^{-3}	346.57	1151.29
17.9	1.6×10^{-3}	433.21	1439.11

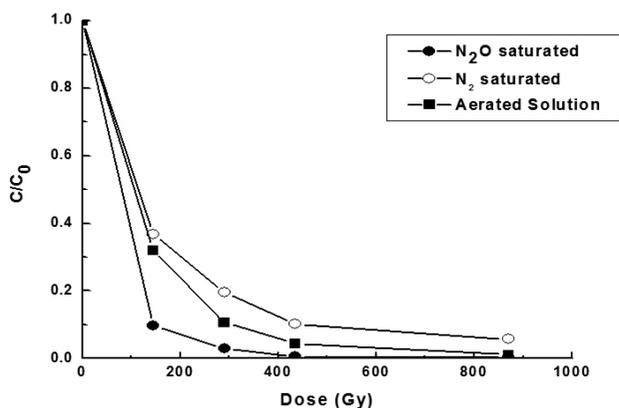


Fig. 4: Degradation of aqueous CIP solution in air, N_2 , or N_2O saturated solution by gamma irradiation.

In aqueous solution of CIP saturated with nitrogen, all of e_{aq}^- , H and OH may react with CIP. Whereas in the aqueous solution saturated with nitrous oxide, the conc. of OH is increased due to conversion of e_{aq}^- to OH as shown in Eq. (16).

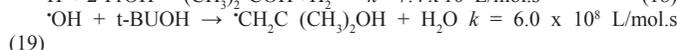
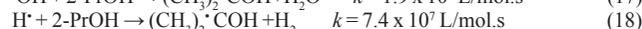


Under this condition the concentration of H is only 1/10 of that of OH and OH is the main radical that reacts with CIP.

In aerated solution, oxygen reacts with e_{aq}^- and H by fast reactions (Eqs. (5, 6)), forming $O_2^{\cdot-}$ and HO_2^{\cdot} . However OH radical still can react with CIP. These radicals can then react with CIP to increase the degradation efficiency of CIP. Therefore, it appears that among the three radicals, the OH radicals are more effective in degradation of CIP.

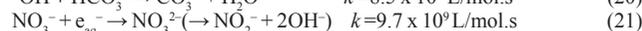
3.3 CIP degradation in the presence of OH scavengers (2-PrOH, *tert*-BuOH, CO_3^{2-} , NO_2^- , HCO_3^- and NO_3^-)

Iso-propanol (2-PrOH) can scavenge OH and H by the reactions shown in Eqs. (17) and (18) [18], whereas *tert*-BuOH can scavenge OH by the reactions shown in Eq. (20) [18]:

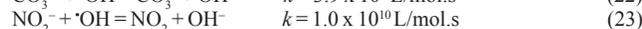
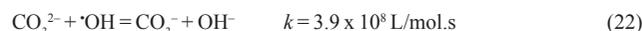


Since both $(CH_3)_2\dot{C}OH$ and $\dot{C}H_2C(CH_3)_2OH$ are relatively slow reacting species, H and e_{aq}^- play the predominant role in the presence of *tert*-butanol while e_{aq}^- plays the crucial role in the presence of *iso*-propanol. Table 4 shows the degradation efficiency at different doses for these three conditions i.e., without scavenger, with the presence of 80 mM *iso*-propanol, or 80 mM of *tert*-butanol. This shows that OH played the most important role in the degradation process while H and hydrated electron only played minor role.

Table 4 shows the effects of HCO_3^- and NO_3^- on CIP degradation. The results showed that at the same absorbed dose the degradation efficiency was lower in the presence of HCO_3^- and NO_3^- than that in the absence of them. The reason was that in the presence of HCO_3^- , OH could be rapidly scavenged by it as shown by Eq. (20). NO_3^- is a good scavenger of e_{aq}^- and it also inhibited the degradation processes of CIP [13].

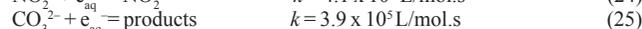
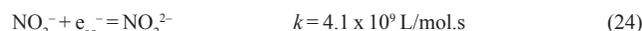


When CO_3^{2-} and NO_2^- were added, the removal efficiency of CIP was relatively lower than that in the absence of them at the same radiation dose. It might be the reason that OH was quickly scavenged by NO_2^- and CO_3^{2-} as shown by Eqs. (22, 23) [13, 18].



In the presence of these additives, there is a competition between these additives and CIP for OH . Since, the reaction between NO_2^- and OH is very fast (Eq.23), relatively small amount of OH is left to degrade CIP resulting in lower degradation as compared to degradation in presence of CO_3^{2-} or in absence of any additives (Table 4).

Both NO_2^- and CO_3^{2-} are the scavengers of e_{aq}^- also and they inhibited the degradation process of CIP as shown by Eqs. (24, 25) [18, 19].



3.4 Kinetic study for the radiolytic degradation of CIP

As shown in Fig.2b the concentration of CIP decreases exponentially with the absorbed doses, which can be represented by Eq.26 [20, 21].

$$C = C_0 e^{-kD} \quad (26)$$

Where C_0 and C represents initial and final concentrations of CIP before and after irradiation, respectively. ' k ' is the dose constant and ' D ' the absorbed dose. This Eq. (26) can be re-arranged to *pseudo*-first-order reaction as;

$$-\ln(C/C_0) = kD \quad (27)$$

Eq. (27) was used to calculate the dose constant from a linear least-squares fit of the experimental data.

Batch kinetic experiments were performed to study the dependency of Initial concentrations of 4.6, 10, 15 and 17.9 mg L⁻¹, and absorbed doses ranging from 0 to 870 Gy were used for these experiments. The aqueous CIP solutions were prepared at room temperature (ca. 25 °C) and initial pH of solution was 6.2.

Table 4: % degradation of CIP in the presence of radical scavengers (2-PrOH, *tert*-BuOH, CO_3^{2-} , NO_2^- , HCO_3^- and NO_3^-)

Absorbed dose (Gy)	Blank	% degradation in the presence of <i>tert</i> -BuOH	% degradation in the presence of iso-PrOH	% degradation in the presence of CO_3^{2-}	% degradation in the presence of NO_2^-	% degradation in the presence of HCO_3^-	% degradation in the presence of NO_3^-
0	0	0	0	0	0	0	0
145	65.41	11.44	3.89	25.14	4.55	31.43	42.95
290	86	22.57	11.8	50.89	9.85	52.56	60.47
435	93.9	32.6	23.32	73.79	12.09	67.02	69.75
870	96.3	-----	-----	90.11	14.04	80.87	81.95

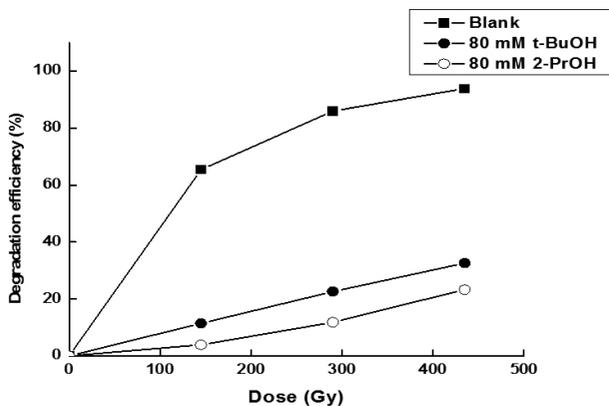


Fig. 5: Effect of 2-PrOH and t-BuOH additives on CIP degradation.

Fig.6 shows the results of the radiolytic decomposition of CIP at four different initial concentrations. At lower concentrations, the decomposition rates (based on decrease in (C/C_0)) were faster, as shown in Fig. 6A. Starting with conc. of 4.6 mg/L more than 90% CIP was degraded with less than 800 Gy. The experimental results were well fitted to the pseudo-first order reaction model given by (Eq. (27)). The value of decay constants (k) at CIP different initial concentrations of 4.6, 10, 15 and 17.9 mgL^{-1} were 0.005, 0.003, 0.002 and 0.0016 Gy^{-1} , respectively. The value of decay constant decreased as the CIP concentration increased which means that CIP can be removed at faster rate at lower concentrations, which can also be verified by calculating the radiation dose required for 50% ($D_{0.5}$) and 90% ($D_{0.9}$) removal of CIP as shown in Table 3. These results are similar with the previously reported results [21, 22].

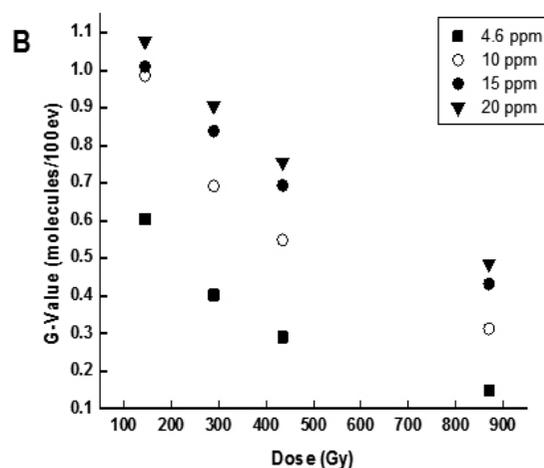
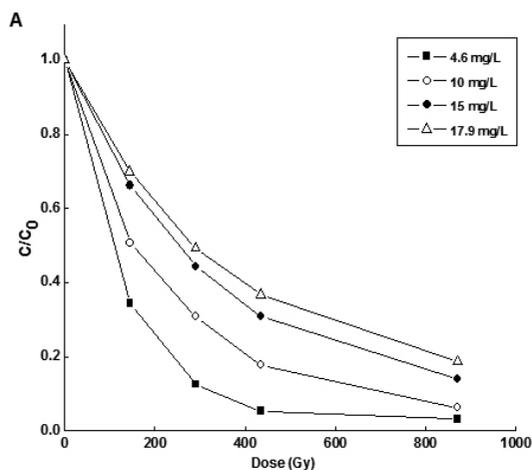


Fig. 6: Kinetic results for the radiolytic degradation of CIP at different initial concentrations. (A) Removal of CIP at different initial conc. vs. irradiation doses and (B) the G-value at different initial CIP concentrations.

The G-values calculated for four different initial CIP concentrations of CIP versus absorbed dose are presented in fig. 6B. As shown in Fig. 3, the G-values decreased with increasing radiation dose. However, for a given radiation dose, the G-values increased with the higher initial CIP concentration, which is similar to previously reported results with chloroform and MTBE [17]. This can be explained by the fact that at higher CIP concentrations, the reactive radicals have a greater chance of reacting with CIP molecules, leading to higher removal efficiency, represented by higher G-values.

3.5 Effect of solution pH

Fig. 7 shows the influence of pH of aqueous medium on CIP degradation. The degradation was enhanced in acidic (pH 3.56) conditions. The reason is that, under acidic condition, hydrated electron is converted to $\cdot\text{H}$ and the relative concentration of $\cdot\text{H}$ was much higher (Eq. (7)). On the other hand in alkaline media, $\cdot\text{H}$ reacts with OH^- to generate e_{aq}^- (Eq. (12)), so increasing the concentration of e_{aq}^- and thus enhancing the probability of recombination between e_{aq}^- and $\cdot\text{OH}$ (Eq. (16)). This results in decrease of $\cdot\text{OH}$ concentration, and thus the degradation efficiency of CIP decreased at higher pH values [23].

4. By-Product Analysis

The gamma irradiation can degrade CIP effectively producing, fluoride (F^-), acetate (CH_3COO^-) and formate (HCOO^-) ions. Concentration of F^- , CH_3COO^- , HCOO^- were determined using Metrohm 800 series ion chromatograph, equipped with electrical conductivity detector. The column used was Assup-5 (250/4.0mm), with 3.2 mM Na_2CO_3 /1 mM NaHCO_3 /50 mM H_2SO_4 /water at flow rate of 1mL/min. As shown in Fig.8, with the increase in the absorb dose the CIP concentration decreased while the concentration of F^- , CH_3COO^- and HCOO^- ions increased. Acetate ion was the major product of CIP degradation while the concentration of formate ion and fluoride was relatively small. After dose of 600Gy the concentration of acetate ions are also starting to decrease, probably because of degradation of acetate ions as a result of irradiation.

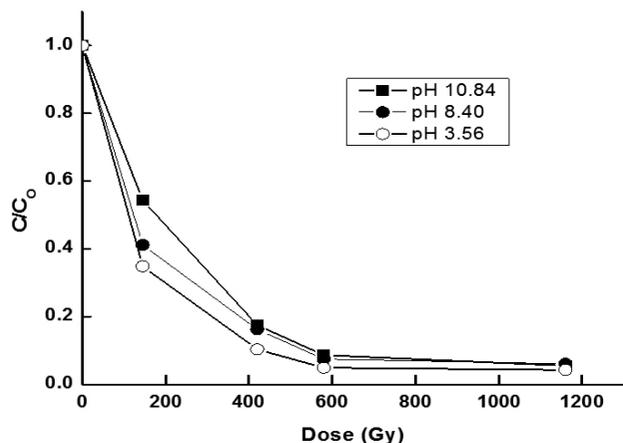


Fig. 7: Effect of pH on degradation of CIP by gamma irradiation.

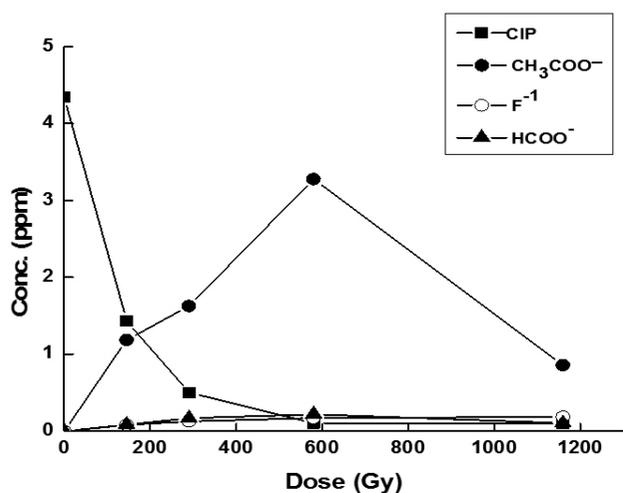


Fig. 8: Changes in the concentration of CIP, F^{-1} , CH_3COO^- , $HCOO^-$ with absorbed doses.

5. CONCLUSIONS

The results of this study showed that CIP was degraded more in N_2O -saturated solution as compared to N_2 -saturated and aerated solutions. The radical scavenger experiments indicated that $\cdot OH$ is mainly responsible for the radiolytic decomposition of CIP. The results of kinetic study showed that radiolytic oxidation of CIP followed pseudo first-order reaction. With respect to G-value, two patterns were observed in our study. The removal efficiencies as represented by G-values decreased with higher irradiation doses. At a given dose, the G-values increased with increasing aqueous CIP concentration. The pH value also affect the CIP degradation efficiency, the degradation yield was higher in acidic conditions as compared to neutral and alkaline media.

In conclusion the application of radiation technology shows promising results in the treatment of industrial and municipal effluents containing various antibiotic compounds.

REFERENCES

- Ikehata K, Jodeiri Naghashkar N, Gamal El-Din M. Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone-Sci Eng* **28**:353-414 (2006).
- Song W, Cooper WJ, Mezyk SP, Greaves J, Peake BM. Free radical destruction of beta-blockers in aqueous solution. *Environ Sci Technol* **42**:1256-1261 (2008).
- An T, Yang H, Song W, Li G, Luo H, Cooper WJ. Mechanistic considerations for the advanced oxidation treatment of fluoroquinolone pharmaceutical compounds using TiO_2 heterogeneous catalysis. *J Phys Chem C* **114**:2569-2575 (2010).
- An T, Yang H, Li G, Song W, Cooper WJ, Nie X. Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. *Appl Catal B-Environ* **94**:288-294 (2010).
- Zhang H, Huang C-H. Oxidative Transformation of Fluoroquinolone Antibacterial Agents and Structurally Related Amines by Manganese Oxide. *Environ Sci Technol* **39**:4474-4483 (2005).
- Watkinson AJ, Murby EJ, Costanzo SD. Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling. *Water Res* **41**:4164-4176 (2007).
- Nie X, Wang X, Chen J, Zitko V, An T. Response of the freshwater alga *Chlorella vulgaris* to trichloroisocyanuric acid and ciprofloxacin. *Environ Toxicol Chem* **27**:168-173 (2008).
- Kümmerer K, Al-Ahmad A, Mersch-Sundermann V. Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test. *Chemosphere* **40**:701-710 (2000).
- Cunningham SD, Anderson TA, Schwab AP, Hsu FC. Phytoremediation of Soils Contaminated with Organic Pollutants. In: Donald LS, ed. *Advances in Agronomy*. Academic Press (1996).
- Földváry CM, Wojnárovits L. The effect of high-energy radiation on aqueous solution of Acid Red 1 textile dye. *Radiat Phys Chem* **76**:1485-1488 (2007).
- Kurucz CN, Waite TD, Cooper WJ. The Miami Electron Beam Research Facility: a large scale wastewater treatment application. *Radiat Phys Chem* **45**:299-308 (1995).
- R.J.Woods, A.K.Pikaev. *Applied Radiation Chemistry*. New York: John Wiley & Sons, Inc.; (1994).
- Spinks JWT, Woods RJ. *An Introduction to radiation chemistry*. Third ed. ed. New York: John Wiley & Sons, Inc.; (1990).
- Cooper WJ, Cadavid E, Nickelsen MG. Removing THMs from Drinking Water Using High-Energy Electron-Beam Irradiation. *J AmWater Works Assoc* **85**:106-112 (1993).
- Lin KJ, Cooper WJ, Nickelsen MG, Kurucz CN, Waite TD. Decomposition of aqueous solutions of phenol using high energy electron beam irradiation - A large scale study. *Appl Radiat Isotopes* **46**:1307-1316 (1995).
- Mak FT, Zele SR, Cooper WJ, Kurucz CN, Waite TD, Nickelsen MG. Kinetic modeling of carbon tetrachloride, chloroform and methylene chloride removal from aqueous solution using the electron beam process. *Water Res* **31**:219-228 (1997).
- Basfar AA, Khan HM, Al-Shahrani AA, Cooper WJ. Radiation induced decomposition of methyl tert-butyl ether in water in presence of chloroform: kinetic modelling. *Water Res* **39**:2085-2095 (2005).
- Buxton G, Greenstock C, Helman W, Ross A. Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals $OH/\cdot O^-$ in aqueous-solution. *J Phys Chem Ref Data* **17**:513-886 (1988).
- Singh A, Kremers W. Radiolytic dechlorination of polychlorinated biphenyls using alkaline 2-propanol solutions. *Radiat Phys Chem* **65**:467-472 (2002).
- Mincher BJ, Curry RD. Considerations for choice of a kinetic fig. of merit in process radiation chemistry for waste treatment. *Appl Radiat Isotopes* **52**:189-193 (2000).
- Lee B, Lee M. Decomposition of 2,4,6-trinitrotoluene (TNT) by gamma irradiation. *Environ Sci Technol* **39**:9278-9285 (2005).
- Mincher BJ, Brey RR, Rodriguez RG, Pristupa S, Ruhter A. Increasing PCB radiolysis rates in transformer oil. *Radiat Phys Chem* **65**:461-465 (2002).
- Sánchez-Polo M, López-Peñalver J, Prados-Joya G, Ferro-García MA, Rivera-Utrilla J. Gamma irradiation of pharmaceutical compounds, nitroimidazoles, as a new alternative for water treatment. *Water Res* **43**:4028-4036 (2009).