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## Removal of ciprofloxacin by gamma irradiation: Degradation mechanism and pathways of products studies

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### ABSTRACT

Ciprofloxacin (CIP) is one of the widely detected members of fluoroquinolone family in the aquatic environment that is often excreted through urine waste due to its incomplete metabolization in the human body as documented by various previous reports. In this regards the present study is focused on the complete degradation of CIP by gamma irradiation in the aquatic system. CIP, when treated at an initial concentration of 5.5 ppm, near complete degradation of 98% was achieved at absorbed dose of 1000 Gy. Furthermore, this study is also focused on the calculation of bimolecular kinetics of  $\cdot\text{OH}$  with CIP which was observed to be  $2.84 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ . It was found that the G-values for CIP decreased with an increase in the absorbed dose and increased with increase in the initial concentration of CIP which is in complete agreement with our previous results. The important aspect of this study is the evaluation of major degradation products of CIP. Which confirm the oxidation of CIP as indicated by the UPLC - MS/MS and IC results, on the basis of which the degradation pathways were proposed.

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**Capsule Summary:** This study investigates the degradation of fluoroquinolone antibiotic, i.e. ciprofloxacin by advanced oxidation process.

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### INTRODUCTION

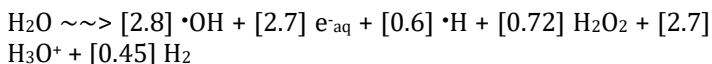
Because of quick development in populace, there has been a consistent expansion in industrialization and urbanization and in this manner new water resources are quickly diminishing and obviously the quality as well throughout different parts of the world (Ullah et al., 2009). As per public figures, just 56% of the complete nation populace approaches

clean water for drinking purposes (Farooq et al., 2008). Nonetheless, thinking about worldwide norms for protected and drinkable water, just 25.61% (country 23.5% and 30% metropolitan) of the absolute populace in Pakistan have accessibility of water for drinking purposes (Rosemann, 2005). Water that is utilized by general society for drinking designs is generally sullied with irresistible microorganisms or poisonous synthetic compounds (Azizullah et al., 2011). Different anthropogenic exercises are answerable for water

contamination in exceptionally populated urban areas like Karachi, Lahore, Rawalpindi, Peshawar, Faisalabad, Qasur, Sialkot and Gujrat (Bhutta et al., 2002). Investigation of water tests from Islamabad and its twin city Rawalpindi demonstrated that almost 94% and 34% of water tests were exceptionally dirtied with complete coliforms and fecal coliforms, separately (Jehangir, 2002).

AOPs can commonly be characterized as fluid stage oxidation methods, basically dependent on the creation of exceptionally responsive oxidative species, for example, hydroxyl extremists, in the process prompting the expulsion of the objective contamination from watery framework. It has been accounted for that customary organic techniques are not powerful enough for the total expulsion of drugs from wastewaters (Hollender et al., 2009; Suárez et al., 2008), because of the opposition of the drug mixes to biodegradation or to the restricted natural movement occurring, generally in cool atmospheres. Subsequently, new treatment approaches should be intended for effective expulsion of drugs from wastewater. AOPs indicated promising outcomes for the expulsion of follow contaminations from water bodies. Major AOPs incorporate heterogeneous and homogeneous photocatalysis utilizing bright (UV) or sun powered noticeable illumination, electrolysis, ozonation, Fenton's reagent, ultrasound and wet air oxidation. Then again, less customary however developing cycles incorporate ionizing radiation, microwaves, beat plasma and the ferrate reagent. Drugs after brought into the climate may force genuine effects on any degree of the natural progression, for example cells, organs, life forms, populace, environments, or the ecosphere.

The effective expulsion of drugs mixes from the climate has generally been examined through photolysis, ozonation, Fenton oxidation, heterogeneous photocatalysis, electrochemical oxidation and ultrasonic oxidation. Other than that, advance oxidation measures combined with other treatment measures are likewise read for the obliteration of drugs from oceanic climate (Klavarioti et al., 2009). The radiolysis of water brings about the arrangement of following dynamic species. The species are produced in times in the request for  $10^{-6}$  s.



The number in bracket shows the G-values for species, which can be characterized as the quantity of species, extremists, particles or atoms shaped by retaining 100 eV of energy (Spinks and Woods, 1990). Among the species created,  $e^{-\text{aq}}$  and  $\cdot\text{H}$  goes about as lessening specialists while  $\cdot\text{OH}$  goes about as solid oxidizing specialist. Such cycle are likewise defined as Advanced Oxidation/Reduction Processes (AO/RPs) (Mezyk et al., 2008). AOPs dependent on gamma light are more proficient and savvy for expulsion of poisons for huge scope from water bodies (Rivera-Utrilla et al., 2013). This procedure is applied in different nations yet not in like

manner use because of lacking information on its exhibition and activity (Song et al., 2008). This study investigates the degradation of fluoroquinolone antibiotic, i.e. ciprofloxacin by advanced oxidation process.

## MATERIAL AND METHODS

### Gamma irradiation source

For gamma-irradiation tests, stock CIP solution 50 ppm was prepared by dissolving 25 mg of CIP per 500 mL of Milli-Q water. To ensure the complete solubility, the prepared solutions were then ultrasonically treated for 20–30 min. In this study Co-60 gamma beam source (Issledovatel USSR), presented at the Nuclear Institute for Food and Agriculture (NIFA) was utilized for gamma treatment procedures. The gamma-beam irradiator comprises of twelve barrel shaped Co-60 bars having breadth of  $1.1 \times 10^{-2}$  m and  $2.1 \times 10^{-2}$  m in stature and was ensured by lead protecting.

### HPLC analysis

For quantitative analyses of CIP, an agilent 1200 series high Performance Liquid Chromatography (HPLC) unit, outfitted with UV-detector operated at 280 nm was maintained for the examination of ciprofloxacin (CIP). The versatile stage utilized for the investigation of CIP was water/methanol/acetonitrile/1 % acetic acid (20/25/15/40, V/V). The division was accomplished on turned around stage Eclipse XDB – C18 section (5  $\mu\text{m}$ , 4.6 x 150 mm) at stream pace of 1 mL  $\text{min}^{-1}$ . The segment temperature was set at 30  $^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

### Removal of CIP by induced gamma irradiation

To investigate the removal of CIP by gamma irradiation, aqueous solution of 5.5 ppm CIP was irradiated with dosages of 0, 150, 360, 500 and 1000 Gy. It is depicted in Figure 1, that there is a gradual decline in concentration of CIP because of gamma irradiation. It was seen that the CIP arrangement of 5.3 ppm was completely removed upon contact to  $\gamma$ -radiation of just 1kGy. The G-values for the removal of CIP from aqueous solution was calculated according to Eq. 1.

$$G = \frac{R (6.02 \times 10^{23})}{D (6.24 \times 10^{16})} \quad (1)$$

In above Equation 1, the R represents the difference in the removal of CIP (in M), D is the exposed quantity given to CIP molecule,  $6.02 \times 10^{23}$  is the Avogadro's number and  $6.24 \times 10^{16}$  the alteration aspect from Gy to 100 eV/ L.

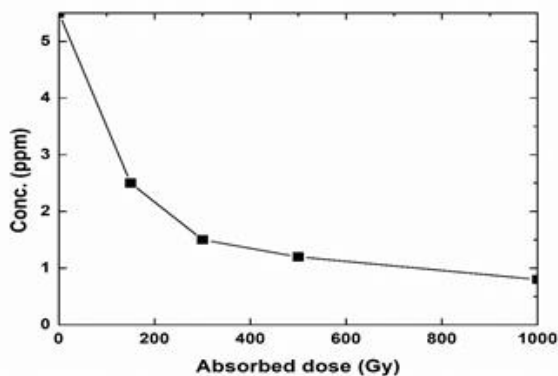


Fig. 1: Removal in concentration of CIP from aqueous solution at various absorbed doses in Gy

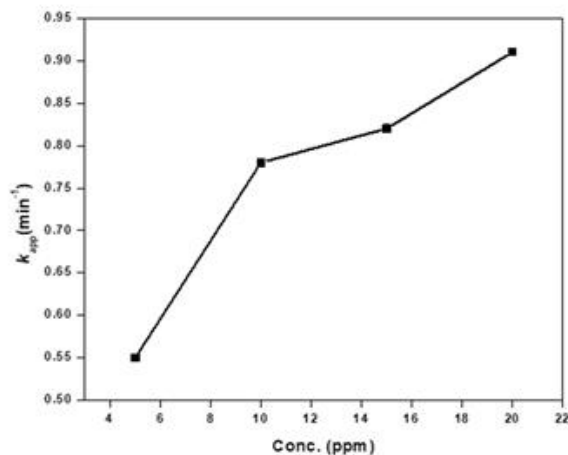


Fig. 3: Variation in varied concentration of CIP by gamma irradiation

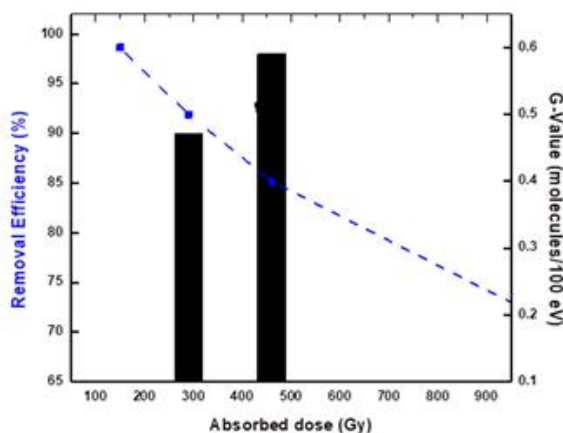


Fig. 2: G-values for removal of CIP and % removal of CIP at various absorbed doses of gamma treatment. The initial aqueous CIP concentration was 5.5 mg/L.  $N_2$ -saturate d, pH = 6.5

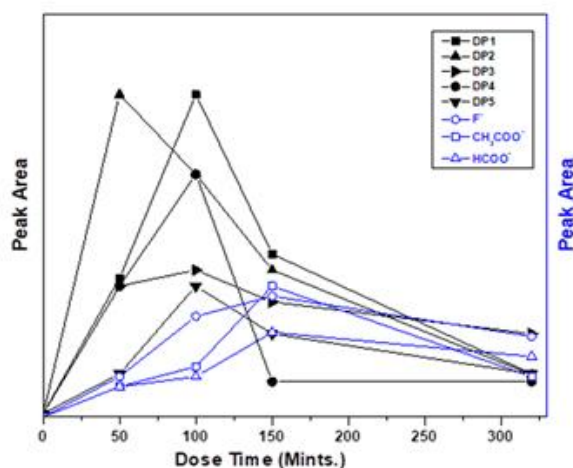


Fig. 4: Appearance and disappearance of DPS of CIP at various absorbed doses.

The most responsive reactive species in Equation (1) are the oxidizing hydroxyl species ( $\cdot OH$ ) and reducing aqueous electrons ( $e_{aq}^-$ ) and hydrogen species ( $\cdot H$ ). It is anticipated that high centralizations of these highly reactive species can be created in short time span and can be made to respond with the toxins in water. Table 1 shows the values of the reactive species generated when gamma irradiation at the specified dose are given in water. The productivity of radiation measure for the decline of CIP was additionally determined as the rate of effectiveness (%). The rate of removal efficiency can be determined using Eq. 2.

$$\% \text{ removal efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

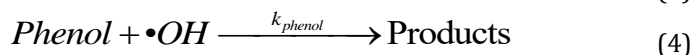
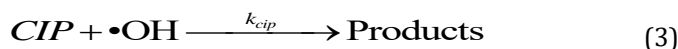
Where,  $C_0$  and  $C$  are the initial and final concentration of pollutant after absorbed dose  $D$ , respectively. Percentage removal efficiency increased with increasing absorbed dose as shown in Figure 2.

For practical application of gamma irradiation technique it is necessary to have the bimolecular kinetics of the reactive species (hydroxyl radical) with the target contaminant. Such kinetics will then be applied of the practical removal of contaminants from the aquatic systems. Pulse radiolysis is a direct removal technique for such process however, in case of developing countries like Pakistan where due to restrictions from developed countries the use of radioactive materials are not very common, a well-developed method known as competition kinetics is employed.

**Table 1:** The values of reactive species at the specified doses

Dose (Gy)	Residual Concentration (mM)			
	•OH	•H	e <sub>aq</sub> <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>
150	0.0412	0.0096	0.0395	0.01045
280	0.0892	0.0354	0.0888	0.045
490	0.1518	0.0257	0.11587	0.08056
650	0.1715	0.0578	0.1688	0.0572
1000	0.2526	0.0857	0.2456	0.069

The rate constant for response of •OH radical with CIP can be controlled by rivalry energy utilizing a test build having known rate steady with •OH radical. For assurance of hydroxyl radical with CIP, the test competitor phenol, which has second order rate steady of  $6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  with •OH was utilized (Buxton et al., 1988). The example arrangement comprising both CIP and phenol in equivalent concentration/amount were immersed with O<sub>2</sub> - gas to change hydrated electron and hydrogen radicals over to superoxide radical anions quickly (Kimura et al., 2012), which are less receptive contrasted with hydroxyl radicals.



In the above equations, the notations  $k_{\text{CIP}}$  and  $k_{\text{phenol}}$  denote rate constants of •OH with CIP and phenol, distinctly. At a similar dose rate (DR), the pace of decline of CIP can be communicated by the rate constant and convergence of •OH (Kimura et al., 2007). Thus form the calculations it is obvious that the bimolecular kinetics of CIP with •OH was observed to be  $2.64 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

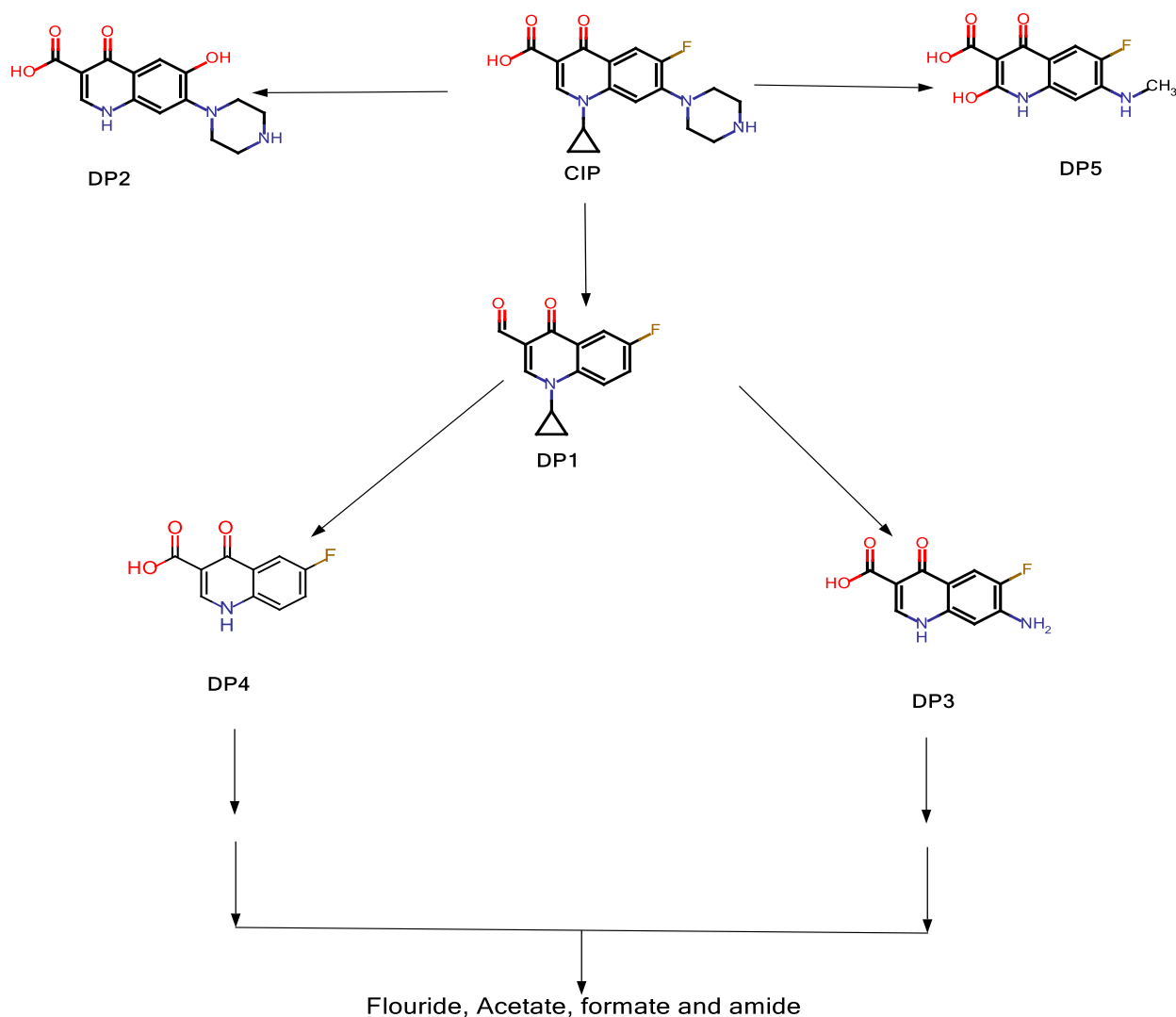
### Effect of initial concentration

The influence of initial concentration of any target contaminant on the gamma irradiation is necessary to predict the practical significance of gamma irradiation process. In this regards, the initial concentration of CIP was varied in the range of 5-20 ppm. The results in Figure 3 showed that with increase in the concentration of initial amount of the CIP, higher doses were required for its removal. The possible reason for the trend would be due to that fact that with increase in the concentration of target contaminant higher number of molecules react with gamma dose or in other words with hydroxyl radicals and thus taking higher time to degrade CIP molecules.

### Proposed degradation products and pathways

The information about the results of debasement of an objective toxin is essential to all the more likely comprehend the corruption pathways and in this manner for viable utilizations of gamma-light cycle for the tidying up of tainted water. For result investigation, watery arrangement having CIP convergence of around 10 ppm was gamma-illuminated for 3 hrs and was subsequently analyzed by UPLC - MS/MS. The illuminated arrangement was additionally investigated for various anions, for example, fluoride (F<sup>-</sup>), acetic acid derivation (CH<sub>3</sub>COO<sup>-</sup>) and formate (HCOO<sup>-</sup>) particles utilizing particle chromatography. Five debasement items (DP1 to DP5) have been recognized for CIP by utilizing UPLC-MS/MS under gamma-illumination. In view of the recognized debasement items, it very well may be recommended that corruption of CIP happens at quinolone substituent and at piperazinyl part. Intermediate specie (DP2) is the hydroxyl subsidiary of CIP. Comparable structure was likewise revealed by (Turiel et al., 2005) and (Wetzstein et al., 1999) where they proposed the replacement of fluorine specie by an OH radical as the initial phase in the defluorination of flouroquinolones. The intermediate specie (DP5) came about because of •OH assault at quinolone moiety, which is the considerable site for the expansion of •OH (An et al., 2010). CIP atom after overall deficit of C<sub>2</sub>H<sub>2</sub> at the piperazinyl group forms degradation specie (DP1) that is desethylene ciprofloxacin. The development of another removal product (DP3) shows oxidation at the piperazinyl group of desethylene ciprofloxacin with the loss of nitrogen atom (Turiel et al., 2005). Degradation product (DP4) may be formed because of progressive oxidation by •OH extremist.

The appearance and disappearance of DPs of CIP in Figure 4 shows that with increase in the concentration of •OH as the absorbed gamma dose increase high removal of DPs are achieved. Also it suggest that higher doses of gamma irradiation is necessary to achieved the complete mineralization of target contaminant, which is CIP in the present case. These organic intermediates might be additionally changed over to low sub-atomic weight natural acids, for example, formic acid and acidic byproducts. Fluoride particles and ammonium particle are come about by arrival of F-gathering and nitrogen iotas from CIP (Fig. 4).



**Fig. 5:** Scheme for the degradation pathway of CIP

In light of the distinguished results corruption pathway of CIP is proposed as appeared in Figure 5. Moreover, the evaluation profile of CIP suggests that whatever the type of degradation product is formed. All these byproducts are untimely then decreasing at higher dose.

## CONCLUSIONS

It was concluded from the present study that the selected pharmaceuticals ciprofloxacin (CIP) can effectively be degraded in aquatic system by the applied AOP. The removal of selected pharmaceuticals was found to increase with increase in the absorbed gamma ray dose or UV- and VUV-

irradiation times. The degradation kinetics of CIP was found to follow pseudo-first-order kinetics under all the studied conditions. Gamma irradiation process showed promising results for the degradation of CIP from aqueous solution. CIP is the antibacterial from the flouroquinolone family, where  $\bullet\text{OH}$  radical played major role in degradation and, therefore the highest degradation of CIP. Although, there is enough to go to develop the field of gamma irradiation, yet gamma radiolysis can be considered as one of the most ground-breaking methods in green chemistry. Finally, the use of peroxides for providing mechanistic information will continue to make momentous contributions in promoting the understanding of gamma irradiation induced process.



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