



## Removal of persistent pharmaceutical from water by oxidation process based on ionizing technologies

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### ABSTRACT

Ionizing radiation technology was applied as an innovative oxidation process for removing pharmaceutical contaminants from wastewater. This investigation was designed to study the degradation and mineralization of an anti-inflammatory drug diclofenac (DCF) in aqueous solutions treated by two irradiation processes in different conditions. Highest degradation efficiency reached after an optimization of the main parameters was 99% at 7 kGy for lower concentrations and 80% for higher concentrations. Moreover, the combination of irradiation and oxidizing agents could effectively enhance the radiolytic degradation of DCF. 60% and 85% of DCF (0.2 mM) was degraded at 1.5 kGy in the presence of H<sub>2</sub>O<sub>2</sub> (5 mM) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1 mM), respectively. The ionizing process follows pseudo-first-order kinetics. The performance of this process was followed by an exhaustive analytical study and a preliminary degradation mechanism was suggested based on electron paramagnetic resonance (EPR) and LC-MS identified products. EPR spectroscopy, used to identify fragments from main intermediates formed during ionization, confirmed the formation of an imine-quinone product characterized by a g factor = 2.00362, permitting to deduce that the electrophilic hydroxyl radical <sup>•</sup>OH has reacted with C=C double bonds of aromatic ring. All results provided that this process is effective for the degradation of persistent pharmaceutical in aqueous solutions due to strong oxidative properties of generated radicals mainly hydroxyl radical.

*Keywords:* Water radiolysis, Diclofenac, Advanced oxidation process, Gamma irradiation, Electron beam accelerator.

### 1. Introduction

A numerous variety of drugs has been detected in the water system worldwide, including analgesics, antibiotics, anti-inflammatory,  $\beta$ -blockers and lipid regulators etc. Some of them are consumed annually even in tens or hundreds of tons [1]. As consequence, pharmaceutical residues

are detected in water supply in relatively low concentrations, in the range of ng/L to  $\mu$ g/L [2–4], and then reach the water system as pollutants from the pharmaceutical industry, excretory products of medically treated human, and incomplete removal in wastewater treatment plants. Many relevant studies have proved that most existing

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conventional biological treatment process are not designed to completely remove contaminants of emerging concern including active pharmaceutical ingredients. Although they are often present in low concentration, various studies on effects on quality and toxicity of water systems show that these chemicals, considering that they do not appear individually, but as a complex mixture form a serious problem [5–7], which could lead to adverse health effects such as aquatic toxicity, resistance development in pathogenic bacteria, genotoxicity, and endocrine disruption [8,9]. For that as we have seen the potential impacts of pharmaceutical products, the application of appropriate water treatment remains essential.

Recently advanced oxidation processes (AOPs) have shown promising results as alternative processes for the treatment of effluents containing recalcitrant and toxic organic pollutants. Among these processes, irradiation by ionizing radiation using high energy ( $\gamma$  radiation from  $^{60}\text{Co}$  sources or beams of accelerated charged particles: electrons or protons) has been reported to be effective for the degradation of organic contaminants in water. Compared to other chemical techniques, these two water radiolysis processes uses a cleaner technology that minimizes the formation of hazardous by-products [10]. These radicals are formed by water radiolysis taking place during irradiation of diluted aqueous solutions [11]. Radiolysis of water typically involved the formation of hydroxyl radicals  $\text{HO}^\bullet$  as oxidizing species and either hydrated electrons  $e_{\text{aq}}^-$  as reducing species, both can be used in the degradation of organic pollutants present in drinking or wastewater depending on applied conditions. Furthermore, this process was already employed for decomposition of various pollutants in water remediation such as textile dyes [12], antibiotics [13,14], herbicides and pesticides [15,16].

In this paper, we conducted the investigation of the effectiveness of two ionizing technology gamma irradiation and electron beam accelerated for degradation of a non-steroidal anti-inflammatory drug diclofenac (DCF), to discuss its degradation efficiency and its mineralization conditions during radiolysis with ionization and to study the influence of the main parameters on irradiation process performance, namely absorbed doses, initial concentration and oxidant concentration (hydrogen peroxide and potassium persulfate). These tests will assist determining the experimental conditions for the treatment of this pharmaceutical pollutant by irradiation in aqueous solutions then in wastewater. Therefore, the evolution of DCF residual concentration was monitored by high performance liquid chromatography. The mineralization of this treated compound was evaluated by the measurement of the chemical oxygen demand (COD), the total organic carbon (TOC) and the determination of chloride ions for compounds containing chloride molecules. The influence of dose rate and of different water matrices composition on gamma radiolytic induced degradation of DCF was also studied. A comparative study between gamma and EB irradiation was realized. A sophisticated spectroscopic method was considered to identify and quantify the main intermediates during radiolysis mechanism, by using electron paramagnetic resonance (EPR) spectroscopy. In the end, a mechanism of DCF degradation was proposed.

## 2. Materials and methods

### 2.1. Chemicals and reagents

All chemicals applied were of the highest purity and analytical grade. Diclofenac noted here DCF, (2-(2-(2,6-dichlorophenylamino)phenyl)acetic acid), was purchased from Sigma-Aldrich.

### 2.2. Samples preparation and irradiation conditions

The desired concentrations of DCF at 0.1, 0.2, 0.4, 0.6, 0.8, and 1 mmol/L were prepared in ultrapure water and then placed in 50 ml vials in PET (polyethylene) followed by irradiation at the selected doses (1–20 kGy). Irradiation was performed with the semi-industrial gamma irradiator  $^{60}\text{Co}$  (C-188 MDS Nordion 'category II' facility at the National Center of Nuclear Sciences and Technologies, Tunisia) with a dose rate of 33.31 Gy/min, confirmed by a standard Fricke dosimeter, giving ranging from 1 to 20 kGy. For EB irradiation, a vertical electron beam accelerator from a LINAC society-France (CIRCE-III) was used under 10 MeV of beam energy and  $500 \times 10^{-3}$  A of average beam current (at NCNST-Tunisia). The beam is benched in 12.5  $\mu\text{s}$  periods, the electrons beam repetition rate enables the treatment of aqueous solutions with a flow reactor (depth: 1 cm; width 8.9 cm) placed under the scanned beam. The aqueous solutions of DCF were irradiated with doses in the range of 3–15 kGy. Different doses were obtained by modifying the conveyor speed under the scanned beam from 0.15 to 5 m/min. The absorbed dose was varied by controlling the average-current of the EB accelerator, the repetition rate frequency of current and the conveyor speed. All irradiation experiments were performed at ambient temperature (18°C–25°C). GEX B3 Dose Stix dosimeters (Radiochromic film dosimeters-Polyvinyl butyral (PVB) polymer film), was periodically used as dosimeter to control the calibration of the irradiation device.

### 2.3. Analytical procedures

The degradation efficiency was determined according to UV absorbance recorded with a Perkin Elmer scan-lambda spectrophotometer at 190–600 nm. The residual concentrations of DCF were detected by high-performance liquid chromatography (HPLC, Waters). Analysis was performed with UV detector at 284 nm, a C8 column (15 cm  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ ), a flow rate of 1.2 mL/min, a mobile phase methanol/acetonitrile/water (60%/20%/20%) and an injection volume of 20  $\mu\text{L}$ . The degradation efficiency  $E$  (%) of the treated compound was calculated according to Eq. (1):

$$E (\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C_0$  (mmol/L) is the initial concentration of DCF solution and  $C$  (mmol/L) is the final concentration of DCF solution after treatment with irradiation process. The pH value was measured by a pH meter (Ohaus starter 300) and COD values were released by COD analyzer (Chemetrics A7325). TOC was determined using a total organic carbon analyzer (Shimadzu TOC-VCPH analyzer), which is based

on oxidative combustion followed by infrared detection. Chloride ions appearing after DCF treatment were analyzed by ion chromatography (930 compact IC, Metrohm). EPR analysis was performed on a Bruker EMX Plus (X-band) spectrometer equipped with an ER410ST cylindrical cavity, microwave frequency 9.829 GHz, frequency amplitude (100G) and a microwave power of 0.2 mW.

### 3. Results and discussion

#### 3.1. Radiolytic degradation efficiency and dechlorination

The effect of initial concentration of DCF was investigated in this study. Fig. 1 depicts the evolution of UV spectra of DCF aqueous solutions at 190–400 nm following gamma irradiation at different concentrations. The spectra showed two absorption peaks, namely a typical aromatic peak which

was around 276 nm ( $\pi \rightarrow \pi^*$ ) and at 200 nm a peak relative to carboxylic group ( $n \rightarrow \pi^*$ ). For different concentrations (0.4; 0.6 and 0.8 mM), the evolution of the absorption spectra as a function of the absorbed dose shows a significant decrease of the intensity and a progressive disappearance of the characteristic band of DCF with the increase of the absorbed dose.

The influence of absorbed dose on DCF degradation yield at different initial concentrations was examined also by HPLC. This method was employed for the investigation of decomposition yield of treated DCF by quantifying residual analyte where a satisfactory resolution was obtained and recorded by HPLC chromatograms as shown by Fig. 2. As exhibited in Fig. 3a, DCF residual concentration decreased continuously with the increase of absorbed doses which is attributed to induced modifications of its chemical structure.

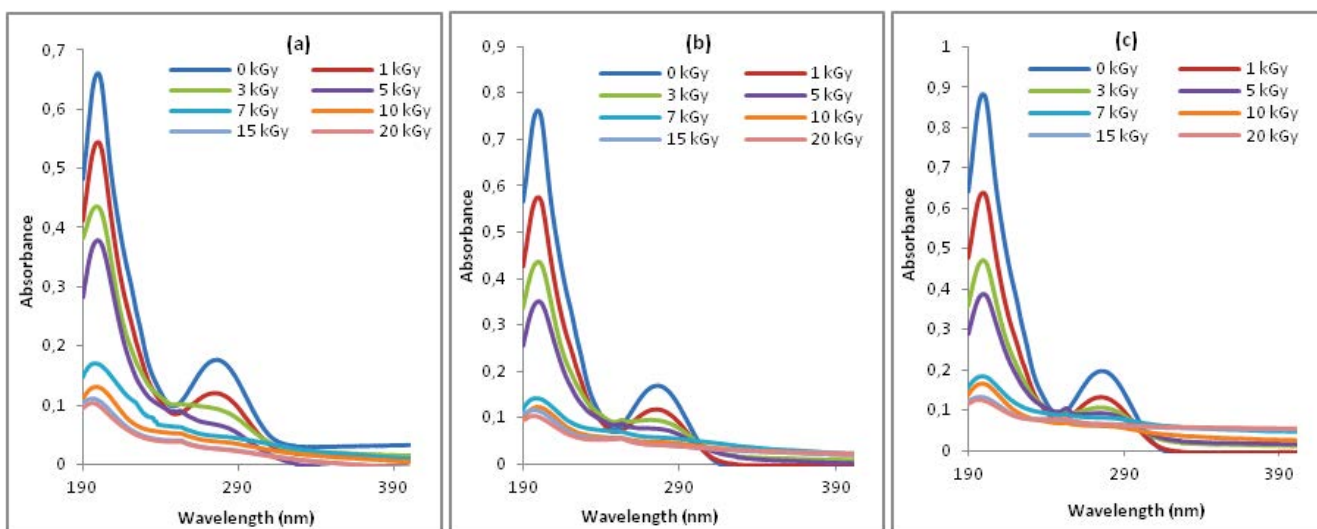


Fig. 1. UV absorption spectra of DCF before and after gamma irradiation at different concentrations (a) 0.4 mM, (b) 0.6 mM, and (c) 0.8 mM.

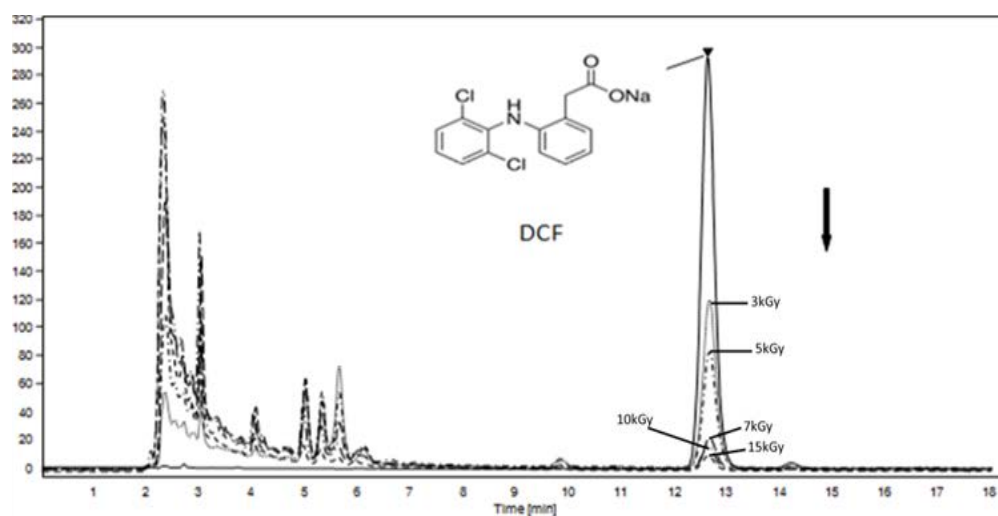


Fig. 2. HPLC chromatograms of DCF aqueous solutions irradiated at different doses.

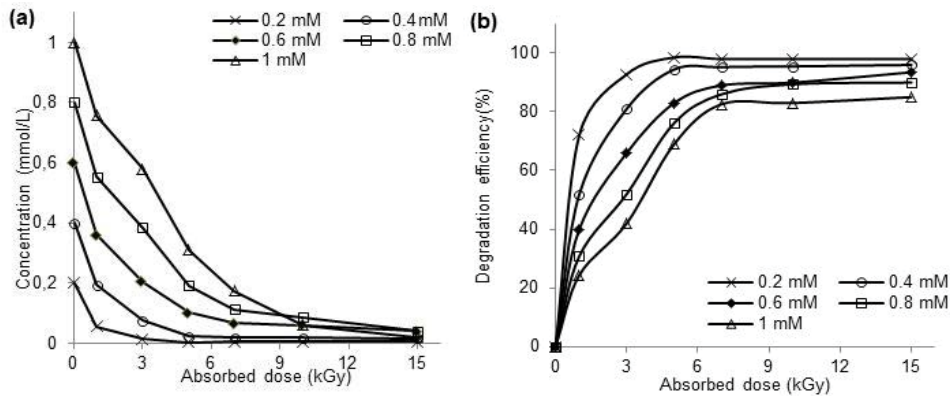


Fig. 3. DCF decomposition in aqueous solutions by gamma radiolysis according to residual concentrations (by HPLC analysis).

The DCF could be effectively degraded under low dose of irradiation, namely, DCF was almost completely degraded at 5 and 7 kGy when the initial concentration was 0.2 and 0.4 mM, respectively. The degradation was more efficient at lower concentrations (reached 99% at 7 kGy) than that at higher concentrations (80% the maxima). This can be explained by the high reactivity of DCF toward the main reactive species  $\text{HO}^\bullet$ ,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^\bullet$  generated during the irradiation process which produces numerous by-products competing for the reactive species [17]. It was found that the sufficient absorbed dose for total degradation of these compounds increases almost linearly with the initial concentration. It should be mentioned that Yu et al. [18] investigated also the degradation of DCF in aqueous solution under oxidative and reductive degradation pathways and reported that the degradation efficiency was higher under oxidative pathway.

In addition, for water radiolysis several reactive species were produced mainly involving hydroxyl radicals, playing the primary role in degradation of organic pollutants [16]. In aqueous medium, due to its electrophilic nature,  $\text{OH}^\bullet$  tends to abstract hydrogen or add to carbon-carbon unsaturated bonds [19]. This radical (oxidant) reacts readily with C=C and C=N double bonds, but less with C=O double bonds, which are electron-deficient at the carbon atom, where the hydroxyl radical prefer to add [11]. DCF has two aromatic rings connected with an amine group, one ring has two chlorine functional groups as a weak electron acceptor, was easy to be attacked by hydroxyl radicals. Upon irradiation of DCF aqueous solutions, its degradation takes place as a result of its reaction with the main reactive species ( $\text{HO}^\bullet$ ,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^\bullet$ ) generated by water radiolysis.

As a result of the degradation process of DCF solution, a number of final products were formed, whose chloride ion appeared as one of the major intermediates, and it was measured by ion chromatography (Fig. 4). The chloride ion concentration in the solution increased progressively with increasing the absorbed doses attributed to a cleavage of the C–Cl bond as it was confirmed by previous studies [7,20]. In fact, for 0.4 mM of DCF solutions, the chloride ion concentration measured in the solution increased from 8.6 to 15.7 mg/L by increasing the absorbed dose from 3 to 15 kGy, respectively. These results improved that the total conversion of C–Cl into  $\text{Cl}^-$  anions was not achieved

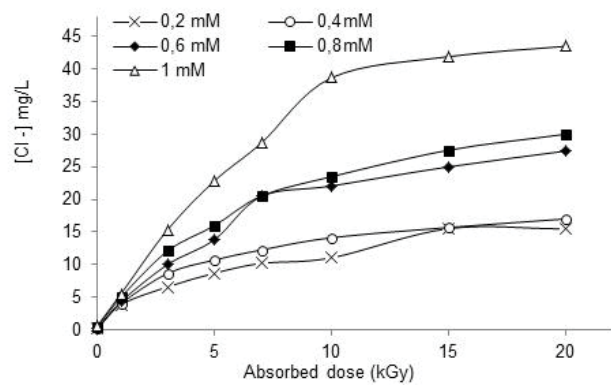


Fig. 4. Changes in chloride ions during DCF degradation vs. gamma irradiation dose at different concentrations.

when total degradation of DCF was attempt, which confirm that by-products still contain chlorine. In fact, when DCF (0.2 mM) was almost completely degraded at 5 kGy (Fig. 3a) 60% of organic chlorine was converted into chloride, while it was 45% for the highest concentration of DCF studied in this paper (1 mM).

### 3.2. Kinetic investigation

In most radiolytic degradation commonly reported in the literature, the concentration of the target component decreases exponentially with the absorbed dose and the exponential equation is analogues to a pseudo-first-order reaction. In our study, DCF concentration decreased also exponentially with absorbed dose (irradiation time) and it can be expressed according to Eq. (2), where C is DCF residual concentration,  $C_0$  is initial concentration and  $k_{\text{app}}$  ( $\text{min}^{-1}$ ) is apparent reaction constant. Therefore, if  $\ln(C/C_0)$  [Eq. (3)] is plotted vs. time (t), the slope of the line is equal to time constant [21].

$$C = C_0 e^{-k_{\text{app}} t} \quad (2)$$

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{app}} t \quad (3)$$

It can be concluded according to illustrated results that kinetic analysis of the above DCF concentration decays fit well to a pseudo-first-order reaction and the excellent straight lines thus obtained, with the correlation coefficient  $R^2$  in the range of 0.96–0.99 as depicted in Fig. 5.

The result of the above calculation showed that  $k_{app}$  varied between 0.0279 and 0.0072  $\text{min}^{-1}$  at  $[\text{DCF}]_0 = 0.1$  and 1 mM. The degradation of DCF was rapid with decreasing the initial concentration. In fact, the apparent reaction constant (that characterizes the rate of decomposition) was largest at the lowest initial concentration of DCF and it was smaller at a higher initial concentration as shown in Table 1. The relationship between the apparent constant and the initial concentration of DCF, could be expressed as a power function ( $k_{app} = 0.0076 [\text{DCF}]_0^{-0.857}$ , where  $k_{app}$  is the apparent constant,  $[\text{DCF}]_0$  is the initial concentration;  $R^2 = 0.9745$ ). This dependency of the apparent reaction constant and the initial concentration was also observed for the radiolytic degradation of other organic pollutants such as 2,4,6-trinitrotoluene [22], of endosulfan [23], of atrazine [24] and of cefador [25] where the degradation of these compounds followed pseudo-first-order model. It was reported that  $k_{app}$  can be affected by various experimental conditions such as the initial concentration of the target pollutant, its molecular structure, the pH solution and the characteristic of the solvent [14]. These data can be used to calculate the dose required for 50% and 90%

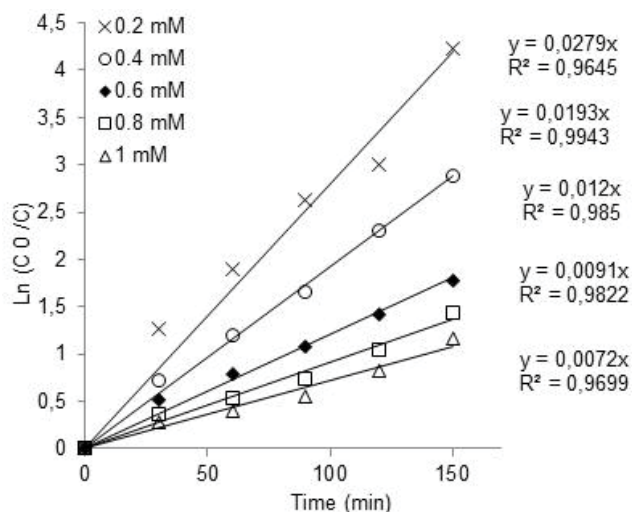


Fig. 5. Effects of DCF concentration on its degradation kinetics.

Table 1  
Dose constant ( $k_{app}$ ),  $D_{0.5}$  and  $D_{0.9}$  of DCF in aqueous solution

Residual concentration (mM)	$k_{app}$ ( $\text{min}^{-1}$ )	$t_{0.5}$ (min)	$t_{0.9}$ (min)	$D_{0.5}$ (kGy)	$D_{0.9}$ (kGy)
0.2	0.0279	24.84	82.52	0.82	2.74
0.4	0.0193	35.91	119.30	1.19	3.97
0.6	0.012	57.76	191.88	1.92	6.39
0.8	0.0091	76.17	253.03	2.53	8.42
1	0.0072	96.27	319.80	3.20	10.65

of DCF degradation ( $D_{0.5}$  and  $D_{0.9}$ ) presented in Table 3, by using Eqs. (4) and (5), respectively.

$$D_{0.5} = \frac{\ln 2}{k_{app}} \quad (4)$$

$$D_{0.9} = \frac{\ln 10}{k_{app}} \quad (5)$$

It should be noted that the in next parts of this study, the degradation efficiency was determined by UV spectrophotometry (absorbance at 276 nm characteristic to the aromatic ring as we mentioned above). The difference of degradation efficiency determined by HPLC (the residual concentration) and by UV-Vis spectrometry was also observed in the radiolytic decomposition of Gallic acid study [26].

### 3.3. DCF mineralization: comparative study of DCF treated with different ionizing processes

The degradation of DCF by exposure to ionizing radiation was analyzed, in previous researches, and summarized in Table 2 along with other relevant showing the impact of different parameters on the degradation efficiency including the absorbed dose, initial concentration, pH value, the water matrix, open or closed system, the presence of other chemicals (addition of t-butanol and saturating the DCF solutions with oxygen, nitrogen, and nitrous oxide gases and  $\text{OH}^{\bullet}$  radical scavengers). The concentration of DCF influences the probability and number of effective collisions among the reactive species and DCF. It is obvious that the degradation efficiency was dependent on the employed chemical conditions during irradiation and especially on the presence of selected scavengers where the concentration of reactive species is controlled. These results show that both oxidative and reductive pathways are effective for DCF degradation. However, the most efficient DCF removal occurs as a result of a reaction with hydroxyl radicals. For example, more efficient degradation was observed [1,18] when the solution was saturated with oxygen (in aerated aqueous solution) or when  $\text{N}_2\text{O}$  was added to the solutions, an increase in hydroxyl radical is obtained providing a strong oxidizing condition. While it was reported [1] that at low doses (0.5–3 kGy) the DCF irradiation yield decreases in a deaerated solution saturated with argon and with the addition of t-butanol and these conditions have no effect above 3 kGy. Similarly, it was reported [7] that the removal of TOC

Table 2  
Degradation and mineralization of DCF by exposure to ionizing radiation in the literature

Ionizing process	Matrix	Experimental conditions	Removal efficiency (%)	Mineralization (%)	Reference
Gamma irradiation	Aqueous solution	[DCF] <sub>0</sub> = 1 mM; pH ≈ 7; DR = 7.72 krad/min	100% at 12 kGy; 75% at 4 kGy; (in N <sub>2</sub> O saturated solutions) 15% at 0.5 kGy (in N <sub>2</sub> saturated IPA solutions)	n.a.	[18]
	Aqueous solution	[DCF] <sub>0</sub> = 30 mg/L; pH = 6.37; T = 23°C–25°C	100% at 5 kGy; 86.2% at 1 kGy	n.a.	[27]
	Aqueous solution	[DCF] <sub>0</sub> = 50 mg/L; DR = 8.0 kGy/h	95% at 5 kGy	n.a.	[28]
	Natural samples of a river water	[DCF] <sub>0</sub> = 10 µg/L; DR = 4.8 kGy/h	Complete decomposition at 0.1 kGy	n.a.	[1]
	Hospital wastewater	[DCF] <sub>0</sub> = 10 µg/L; DR = 4.8 kGy/h	Complete decomposition at 0.25 kGy	n.a.	[1]
	Aqueous solution	[DCF] <sub>0</sub> = 0.5 mM; DR = 1.5 kGy/h; air saturated	Complete degradation at 1 kGy	20% of COD reduction at 20 kGy	[29]
	Aqueous solution	[DCF] <sub>0</sub> = 0.1 mM; DR = 1.5 kGy/h; air saturated	Complete degradation at 1 kGy	n.a.	[7]
	Aqueous solution	[DCF] <sub>0</sub> = 4.5 mg/L; DR = 290 Gy/h; D = 1.015 kGy	95% (In O <sub>2</sub> saturated aqueous media)	45%	[7]
	Aqueous solution	[DCF] <sub>0</sub> = 30.4 mg/L; in sealed bottle	70% (in N <sub>2</sub> saturated solutions)	32%	[30]
	Ultrapure water	[DCF] <sub>0</sub> = 0.1 mM; pH ≈ 6.1; [O <sub>2</sub> ] ≈ 7.7 mg/L; D = 0.050–25 kGy; DR = 3.9 kGy/h	99% (in N <sub>2</sub> O saturated solutions) 89.2%	5.4% at 1 kGy 29.82% at 15 kGy	[31]
Electron beam	Wastewater	[DCF] <sub>0</sub> = 5 µm; pH ≈ 7.45	>99% at 2 kGy ≈100% at 1 kGy	n.a.	[32]
	Wastewater	[DCF] <sub>0</sub> = 2.2 ng/L; pH = 7.55 ± 0.25; DR = 22.5–37.5 kGy/h	99% at 5 kGy	n.a.	[33]
	Bi-distilled water	[DCF] <sub>0</sub> = 10–40 mg/L	Almost 100% at 0.5 kGy	6.5% at 2 kGy	[34]
	Raw water	[DCF] <sub>0</sub> ≈ 10 mg/L	≈100% at 1 kGy	≈13%	[33]
	Wastewater	[DCF] <sub>0</sub> = 2.2 ng/L; pH = 7.55 ± 0.25; DR = 1,200–600 kGy/h	99% at 3 kGy	n.a.	[33]
	Ultrapure water	[DCF] <sub>0</sub> = 51.8 mg/L; pH = 6.8 ± 0.8	30% at 1 kGy	negligible	[35]

D: dose; DR = dose rate; n.a.: not available TOC was not measured by the authors.



was higher in the case of  $N_2O$ -saturated system than an aerated and  $N_2$  saturated system.

Some papers reported also the degradation of DCF by ionizing radiation where they investigated the reaction of DCF with active species ( $OH^\bullet$  and  $e_{aq}^-$ ) and their role during the radiolytic degradation of DCF [1,7,18,27,30,32]. As listed in Table 3, different values of the reaction rate constant of DCF with active radicals were obtained in other researches by competition reaction method [32] or using the pulse-radiolysis method with the spectrophotometric detection [1,18] (Table 3). The reaction rate constant of DCF with hydroxyl radical and hydrated electron was in the range of  $10^9$ – $10^{10} M^{-1} s^{-1}$ . ( $k_{OH^\bullet}$ ) was almost similar determined as  $9.0 \times 10^9$  [32] and  $9.29 \times 10^9 M^{-1} s^{-1}$  [18]. However, DCF reacts with  $e_{aq}^-$  with a rate coefficient ( $k_{e_{aq}^-}$ ) of  $(1.53 \pm 0.03) \times 10^9 M^{-1} s^{-1}$ . These values indicate that both oxidative and reductive methods can take place in DCF radiolytic degradation in aqueous solutions. It confirmed also that the degradation of DCF was dominated by hydroxyl radical followed by  $e_{aq}^-$ .

Table 1 also shows that gamma irradiation and electron beam accelerator technologies can both be adopted for water and wastewater treatment. Both radiation processes are clean and safe technology for the environment. Although the mode of interaction is similar, gamma and high energy electrons differ in several subtle ways [37]. Gamma irradiation is a type of electromagnetic radiation produced in the nuclear decay process. Gamma rays are highly energetic due to their high penetration capacity, while electron beam is a type of ionizing energy that is usually characterized by its low penetration and high dose rate. Compared

to gamma irradiation, EB is faster, safer to use, and more simple to manipulate than radioactive isotopes. It is more suitable and feasible to apply on an industrial scale.

In this paper, a comparison between gamma rays and electron beam irradiation was studied. The degradation of DCF was followed using the absorbance at 276 nm (characteristic to the aromatic ring). The spectra obtained after irradiation of DCF, using EB, showed a decrease in the intensities of the band at 276 nm as the absorbed dose increase. First, we studied the effect of initial concentration of DCF irradiated by EB in Fig. 6. As expected, the degradation of DCF decreased with increasing the applied dose (similar to the results obtained with gamma irradiation above). It was 39% and 54% was observed for an absorbed dose of 3 and 10 kGy, respectively. In a recent study, 30% of DCF degradation by EB was achieved at 1 kGy [35].

For comparative study, the degradation efficiency of DCF was almost the same (39%) when irradiated with both irradiation treatments with a dose of 3 kGy. However, the degradation removal obtained with gamma irradiation was higher than the one recorded with EB irradiation when increasing the applied dose.

A similar result was observed when comparing the degradation efficiencies obtained by both of radiation process in wastewater. The authors reported that 99% of DCF (at 2.2 ng/L) degradation was obtained at EB dose of 5 kGy, while the same percentage of DCF degradation was achieved at 3 kGy of gamma irradiation dose [33]. This indicates that the degradation removal of this persistent molecule depends on the kind, the energy of ionizing radiation and the influence of irradiation parameters. Overall it was possible to conclude that both irradiation types were effective for degrading DCF in water.

Table 3  
Reaction rate constant of DCF with active radicals according to literature

$k_{OH^\bullet} (M^{-1} s^{-1})$	$k_{e_{aq}^-} (M^{-1} s^{-1})$	Process	References
$(12.4 \pm 0.02) \times 10^9$	$(3.1 \pm 0.2) \times 10^9$	$^{60}Co$	[1]
$(9.29 \pm 0.11) \times 10^9$	$(1.53 \pm 0.03) \times 10^9$	$^{60}Co$	[18]
$(13.6 \pm 0.80) \times 10^9$		UV/ $H_2O_2$	[36]
$8 \times 10^9$		$^{60}Co$	[29]
$9 \times 10^9$		$^{60}Co$	[32]

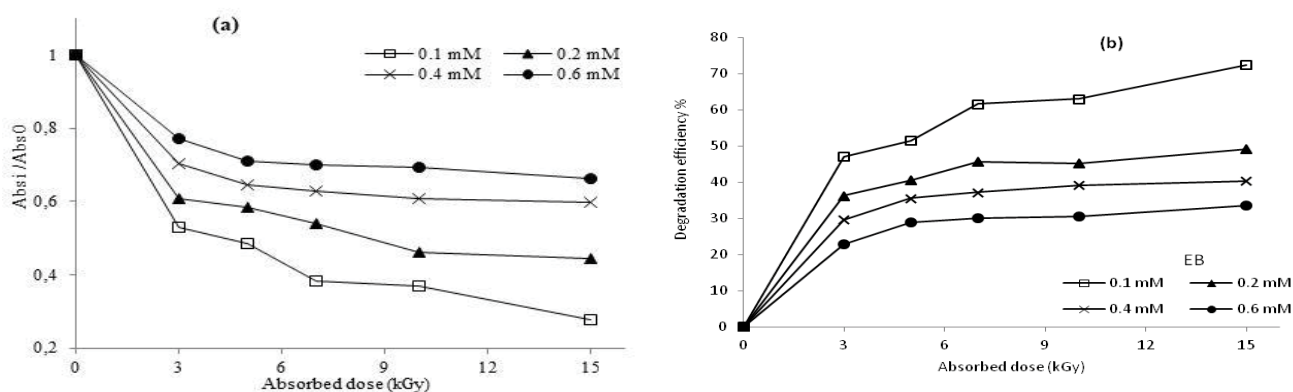


Fig. 6. (a) Absorbance decrease at 276 nm of DCF (0.1–0.6 mM) during its degradation by EB irradiation; inset: evolution of UV visible spectra of DCF solution and (b) degradation efficiency of DCF irradiated by EB at 276 nm vs. absorbed dose.

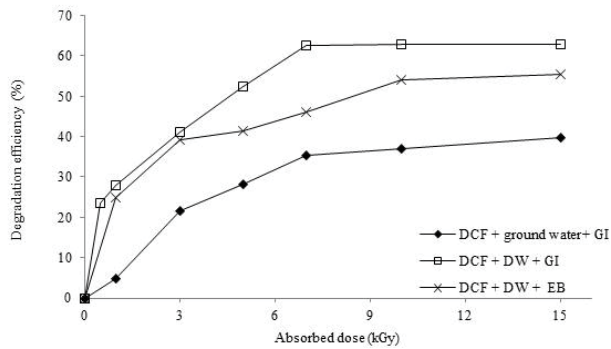
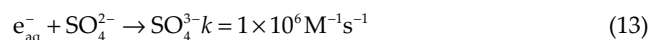
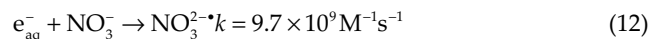
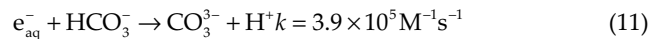
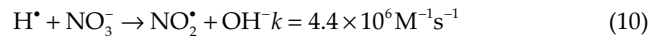
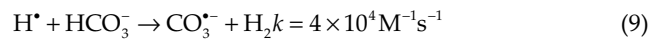
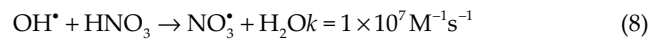
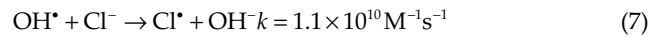
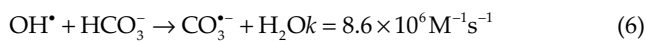


Fig. 7. Effect of dose on degradation efficiency of DCF in 0.2 mM aqueous solutions in different conditions in ground water and in distilled water (DW) by gamma irradiation (GI), and in distilled water by EB.

The degradation efficiency was about two times higher in distilled water (41.6% at 3 kGy) than in ground water (21.5% at 3 kGy). This inhibition removal rate by these anions was reported earlier for the radiolytic decomposition of pyrazinamide (antibiotic) [38], ibuprofen (anti-inflammatory drug) [39], 3-chloro-4-hydroxybenzoic acid (pharmaceutical intermediate) [20], iopromide (iodinated X-ray contrast media) [40], endosulfan (pesticide) [23] and atrazine (herbicide) [24].

In fact, these anions enter in competition with reactive radicals ( $\text{OH}^*$ ,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^*$ ) as shown by Reactions (6)–(13) [41–43]. Thereby, the collision frequency number of these reactive radicals with DCF will decrease, finally resulting in a decrease of DCF degradation rate.

Therefore, the degradation of DCF in ground water requires a higher dose compared to distilled water. However, in another study about DCF degradation reported that the presence of  $\text{OH}^*$  scavengers such as nitrate (50 mg/L), carbonate (50 mg/L) does not affect the decomposition of DCF (at 50 mg/L) [1].



### 3.5. Effect of oxidant addition on DCF degradation

#### 3.5.1. Effect of hydrogen peroxide

In order to reduce the application of high energies during the treatment, we added a selected oxidizing agent  $\text{H}_2\text{O}_2$ . In fact, the degradation can be improved by decreasing the applied dose from 10 to 1 kGy when combined with oxidant allowing the improvement of hydroxyl radicals generation. Although, it is known as an efficient oxidation agent, hydrogen peroxide is not strong enough to oxidize most pollutants by itself, but it is a perfect hydroxyl radical generator in water when exposed to gamma irradiation. This combination of ionizing radiation with hydrogen peroxide has proved to be effective for the degradation of various persistent pollutants based on the reactive activity of hydroxyl radicals [44–46].

In this study, different amounts of hydrogen peroxide were added as shown in Fig. 8a, DCF (0.2 mM) degradation was evaluated under a wide range of  $\text{H}_2\text{O}_2$  concentration 2.5, 5, 10, and 50 mM and irradiated at 0.5, 1, and 1.5 kGy. As known,  $\text{OH}^*$ ,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^*$  have important role in the removal of organic pollutant during water treatment by ionizing radiation, permitting the initiation of radiolytic

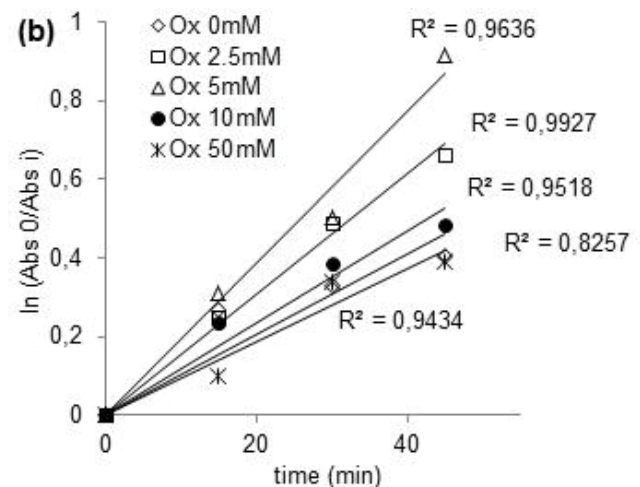
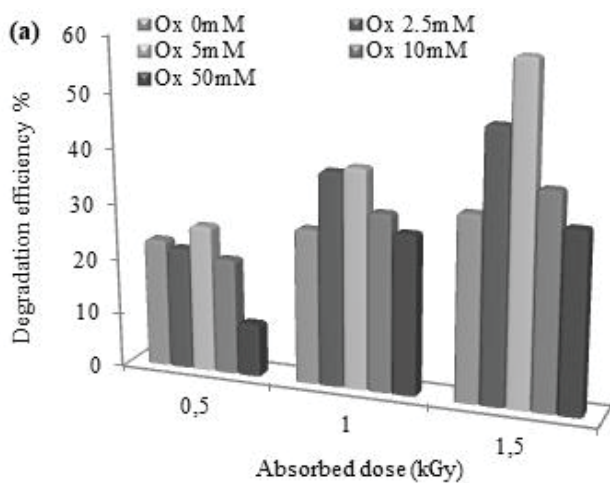
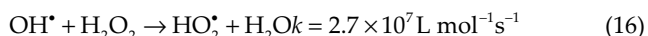
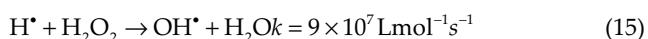
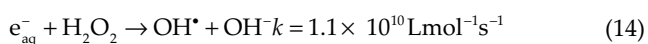


Fig. 8. (a) Effect of hydrogen peroxide concentration (2.5, 5, 10, and 50 mM) on DCF 0.2 mM degradation irradiated by gamma rays at 0.5, 1, and 1.5 kGy and (b) the related kinetics of DCF degradation.



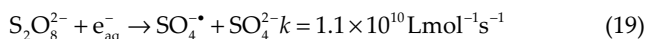
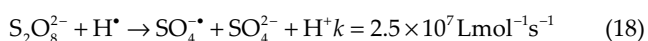
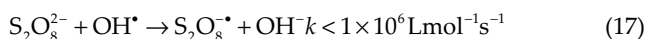
reaction. Hydrogen peroxide molecules can be split into hydroxyl radicals  $\text{HO}^\bullet$  by ionization, after reaction with  $\text{H}^\bullet$  and  $\text{e}_{\text{aq}}^-$  produced by water radiolysis, converting them into much more reactive species  $\text{HO}^\bullet$  as shown by reactions (14) and (15). However, the presence of excessive amounts of hydrogen peroxide is not effective to degrade dissolved organic compounds from water, since it scavenges hydroxyl radicals according to reaction (16):



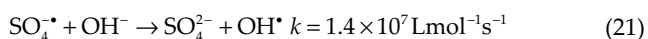
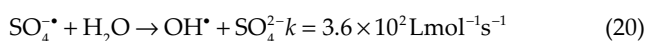
In fact, when the concentration of  $\text{H}_2\text{O}_2$  was increased from 0 to 2.5, 5, 10, and 50 mM, the degradation of DCF decreased from 23.4% to 9.6%, respectively at 0.5 kGy. These results show that 5 mM  $\text{H}_2\text{O}_2$  is an optimal concentration for 60% of DCF degradation was recorded when irradiated at 1.5 kGy. At this optimum also, the absorbed dose decreases from 10 to 1.5 kGy for 0.2 mM DCF aqueous solution. Under the applied conditions, the degradation also conformed to the pseudo-first-order kinetics as presented by Fig. 8b. These results permitted to deduce that the addition of  $\text{H}_2\text{O}_2$  during irradiation could enhance significantly the DCF degradation with very low nuclear energy.

### 3.5.2. Effect of persulfate addition on DCF degradation

In contrary to  $\text{H}_2\text{O}_2$ , the addition of higher persulfate concentrations always promote the elimination of the contaminant. In the presence of persulfate anions,  $\text{OH}^\bullet$ , and  $\text{H}^\bullet$  reacts slowly with  $\text{S}_2\text{O}_8^{2-}$  (reaction 12), whereas it reacts quickly with  $\text{e}_{\text{aq}}^-$  to produce sulfate radical ( $\text{SO}_4^{\bullet-}$ ) and more hydroxyl radicals by reaction (13) and (14) during the radiolysis of the solution [47].



Both of these radicals lead to the oxidation of DCF. As shown in Fig. 9, more than 70% of the DCF was degraded for a dose of 0.5 kGy, three times higher of the abatement obtained without  $\text{S}_2\text{O}_8^{2-}$  addition. Moreover, the radical  $\text{SO}_4^{\bullet-}$  formed can be converted to  $\text{OH}^\bullet$  by reactions (15) and (16). After the addition, the persulfate leads to a remarkable decrease of the pH due to the formation of the sulfate and hydronium ions from persulfate degradation. The pH initially set at 6.22 dropped to a pH of 3.22 for a dose of 0.5 kGy (46.3%) (Not shown).



### 3.6. Effect of gamma irradiation on pH value

The changes in pH values during treatment of DCF solutions by gamma irradiation are presented by Fig. 10. Overall, the pH values of these solutions decreased gradually with increasing the absorbed doses compared to values before irradiation. The pH decreased from 6.5 to 3.4 at 15 kGy (47.7%), and maintained constant at 20 kGy. This decrease could be attributed to the resulting formation of short-chain carboxylic acids from the cleavage of the aromatic rings such as lactic acid, glycolic acid, benzoic acid, 2-hydroxybenzoic acid, that are transformed into smaller carboxylic acids during radiolysis of treated solutions [48].

### 3.7. Effect of absorbed dose on COD and TOC values

The degree of mineralization of the target pollutant is important to follow the degradation, it does not guarantee the efficiency of the water treatment process since the by-products generated after irradiation could be more toxic. First, the oxidation rate and mineralization of organic contents in water was characterized by chemical oxygen demands. The illustrated results (Fig. 11a) showed significant modifications of COD abatement confirming the degradation efficiency of treated DCF solutions. Those obtained results showed a decrease in COD values relatively to absorbed doses. It can be seen that COD values decreased linearly with the increasing dose up to 15 kGy, indicating progressive and almost total oxidation. The degradation decreases with increasing in initial concentration of the treated compound at a fixed dose. For 0.4 and 0.8 mM of the initial values of DCF solutions, the COD values at 7 kGy are about 59% and 38%, respectively. Kinetic study presented by Fig. 11b allowed concluding about linear dependence of this parameter on absorbed dose up to 10 kGy for all DCF initial concentrations.

In addition, the TOC values of the generated products by radiolysis were examined also. Fig. 12 outlines the slow decrease of TOC values of 0.8 mM of DCF. The removal efficiency of TOC of DCF 0.8 mM varied from 4.2 to 23.9 irradiated at 1 and 15 kGy, respectively. To conclude, the TOC values confirmed the partial degradation of the DCF molecule which is due to the concentration of short-chain and stable carboxylic acids. These results are similar to previously reported results [35]. The slow reduction percentage in TOC could be due to the remaining by-products that were not

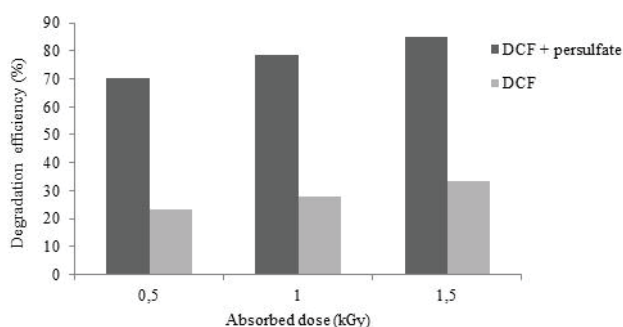


Fig. 9. Effect of persulfate [ $\text{S}_2\text{O}_8^{2-}$ ] = 1 mM on DCF (0.2 mM) degradation by gamma irradiation.

completely mineralized in this applied dose. These findings are consistent with those obtained in other works using ionizing radiation process for the mineralization of gallic acid [26], pyrazinamide [38], sulfamethazine [45], and amphetamine [49]. In fact, this behavior (weak TOC removal) for DCF mineralization was observed by other authors using other AOPs technologies such as sonolysis in presence of catalysts [50] and ozonation, photocatalysis, and non-thermal plasma [51]. In order to achieve a maximum degree of mineralization a higher dose is necessary.

### 3.8. EPR investigation of irradiated DCF

In this study, EPR analysis was considered for identification and relative quantification of free radicals generated during radiolysis of considered pharmaceutical. The EPR analytical method was used for similar compounds for other research purposes as sterilization [52–54]. In this study, EPR technique considered as an original matter in environmental control where it permitted the identification and quantification of radical species which were in accordance with the results reported in the literature [55]. Firstly, the intensities

of electron paramagnetic resonance signals of the irradiated DCF samples at highest dose (15 kGy) as a function of the microwave power were investigated at room temperature in the aim to establish saturation curve. While no signal was obtained from the non-irradiated samples, the irradiated samples exhibited significant spectra. EPR spectra of DCF irradiated at different doses (Fig. 13) are composed of two superimposed signals, namely:

- An intense and wide singlet signal characterized by a specific g factor ( $g = 2.00362$ ) which is attributed to organic radicals, mainly imine-quinones. This multiplicity of the signal confirmed that the detected radical does not interact with neighboring spins.
- A doublet characterized by a g factor  $g = 2.00140$ . This multiplicity of signal is attributed to a coupling of the free radical (electron spin  $\dot{C}$ ) with an atom of hydrogen, in  $\beta$ -position with respect to the radical ( $C-\dot{C}-CH_{\beta}$ ). This signal becomes more intense after the application of a dose of 5 kGy.

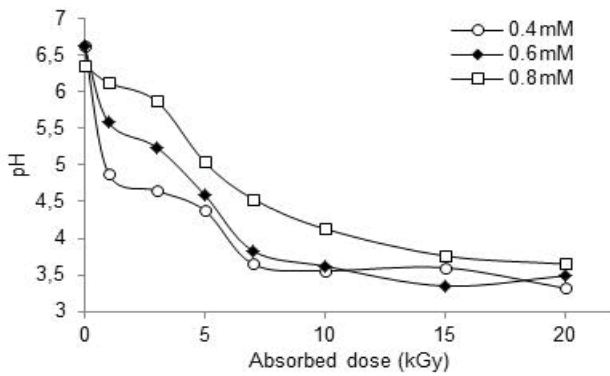


Fig. 10. Effect of gamma irradiation on pH value.

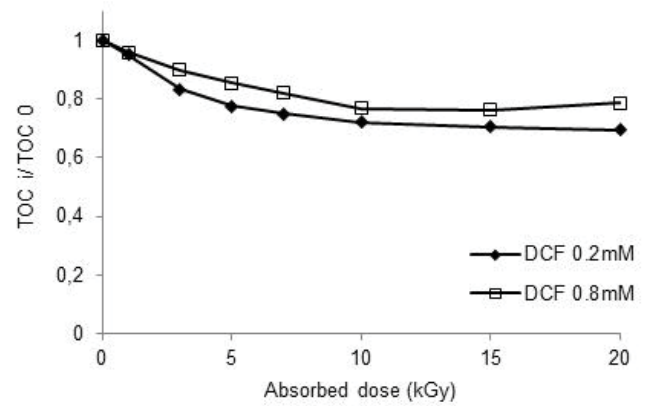


Fig. 12. Evolution of TOC values.

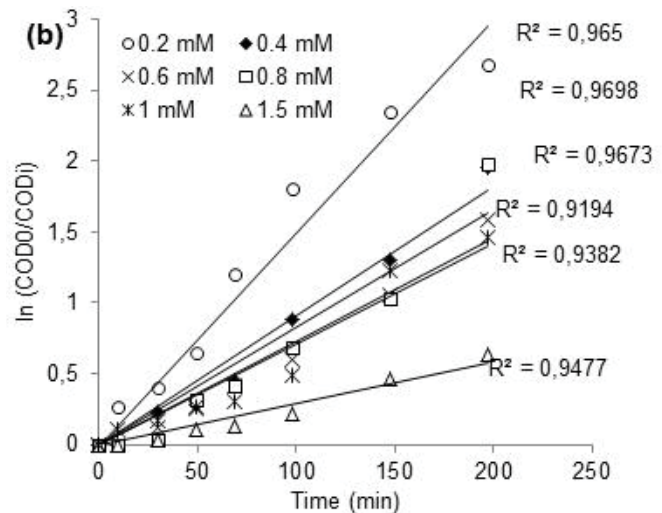
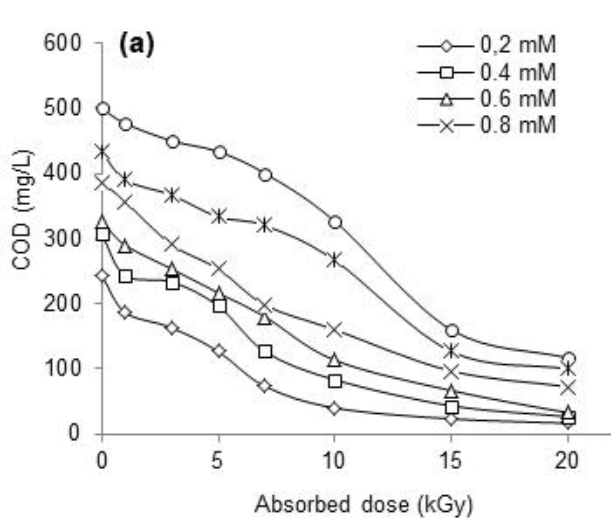


Fig. 11. (a) Evolution of COD and (b) kinetics of DCF degradation at different initial concentration according to COD values vs. irradiation time.

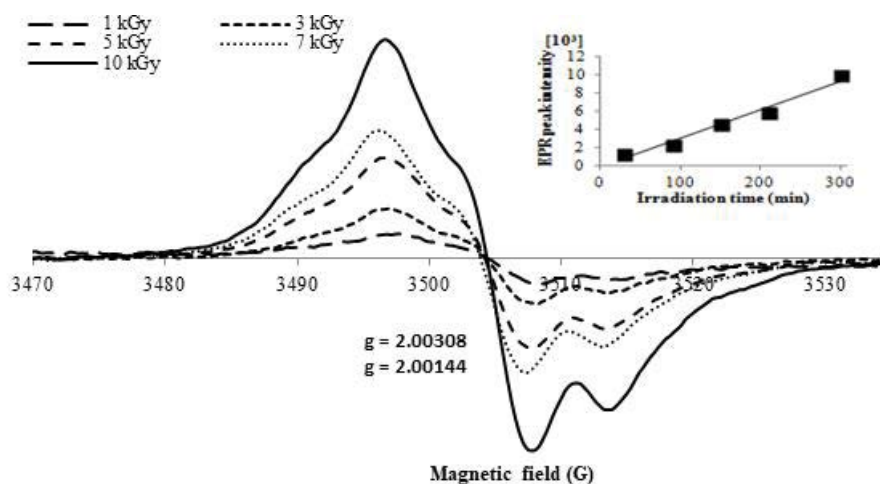


Fig. 13. EPR spectra of DCF at different absorbed doses. The inset panel represents the variation of EPR signal intensity of DCF with absorbed dose.

Based on these spectra recorded by Fig. 13, the increase of the absorbed dose caused only more intense spectra without creating any change in pattern. In fact, the EPR signal intensity, as shown in the insert of Fig. 13, increased linearly with absorbed dose (or irradiation time), relatively to the generation of radio-induced radicals. This confirmed that concentration of radio-induced species was significantly dependent on the applied dose, relatively to degradation efficiency. Moreover, the EPR results confirming the presence of imine-quinones detected at  $g = 2.00362$ , permitting to deduce that the electrophilic hydroxyl radical  $\cdot\text{OH}$  has reacted with C=C double bonds of aromatic ring.

However, the EPR analytical method is a challenging task because of the complexity of the spectra and the overlapping peaks. This study confirmed only the presence and attributions of intermediate radicals of DCF during degradation process. For this purpose, a sophisticated analytical method based on the use of EPR spin-trapping coupled to LC-MS techniques is actually processed in the aim to investigate the generated intermediates structure and the results will be presented soon by upcoming papers.

### 3.9. Oxidative degradation mechanism of DCF

The most abundant degradation products induced during the radiolysis of DCF are identified by LC-MS analysis according to many previous studies [1,18,30,32] and summarized in Fig. 14, where three different products with MW = 311 were identified, resulting of hydroxylation of the aromatic ring. In fact, the specificity of the electrophilic aromatic substitution is governed by the nature of the substituents and the addition of the electrophilic generated hydroxyl radical to the aromatic ring contribute to the appearance of resonance-stabilized carbon-centered radical with subsequent addition of oxygen and elimination of hydroperoxyl radical, yielding the phenolic products. Since the amino group is a strong electron donating group and acts generally as ortho-para directors, three main products resulting of this electrophilic substitution are presented by Fig. 14. It can be confirmed that the product with MW = 309

results of the further oxidation with the primary phenolic degradation product (a) to contribute to the formation of an imine quinone product (a') this later was confirmed also by EPR analysis, characterized by the singlet with a  $g$  factor = 2.00362 (Fig. 13). The product (b') with MW = 275, corresponding to the loss of HCL from the primary phenolic product (b) is resulting from the attack of phenol group to the chlorine substituted carbon with subsequent cyclisation to form a six-membered ring. In addition, after an iso-adduction of the hydroxyl radical to the primary product MW = 311 (c), two mono-aromatic compounds with a MW = 177 (c') and MW = 151 (c'') are formed.

## 4. Conclusions

The present investigation is a contribution to valorization of nuclear energy in environment protection and particularly in the development of AOP for wastewater treatment based on radiolysis of recalcitrant pharmaceuticals in aquatic systems. In this study, the degradation efficiency of DCF in aqueous solutions was investigated using gamma irradiation and EB irradiation. The degradation path is an oxidative decomposition which took place mainly by action of hydroxyl radical formed after radiolysis. A fraction of hydroxyl produced radical attacked DCF molecules and initiated its degradation. Here, we focused on the optimization of the absorbed doses and the initial concentrations on the degradation yield. However, the highest concentrations give a possibility to extrapolate to lower contaminants content. The results showed that the degradation efficiency of DCF and the loss of chloride  $\text{Cl}^-$  increased linearly with increasing absorbed doses. Total degradation was obtained for low concentration at 3 kGy. Based on these results, DCF can be efficiently removed from wastewater by applying irradiation technology, for total degradation doses from 3 to 10 kGy were required. However, TOC removal was not effective as DCF degradation. Lower degradation removal of DCF was reported in ground water due to the presence of natural radical scavengers (inorganic ions). The combination of irradiation process

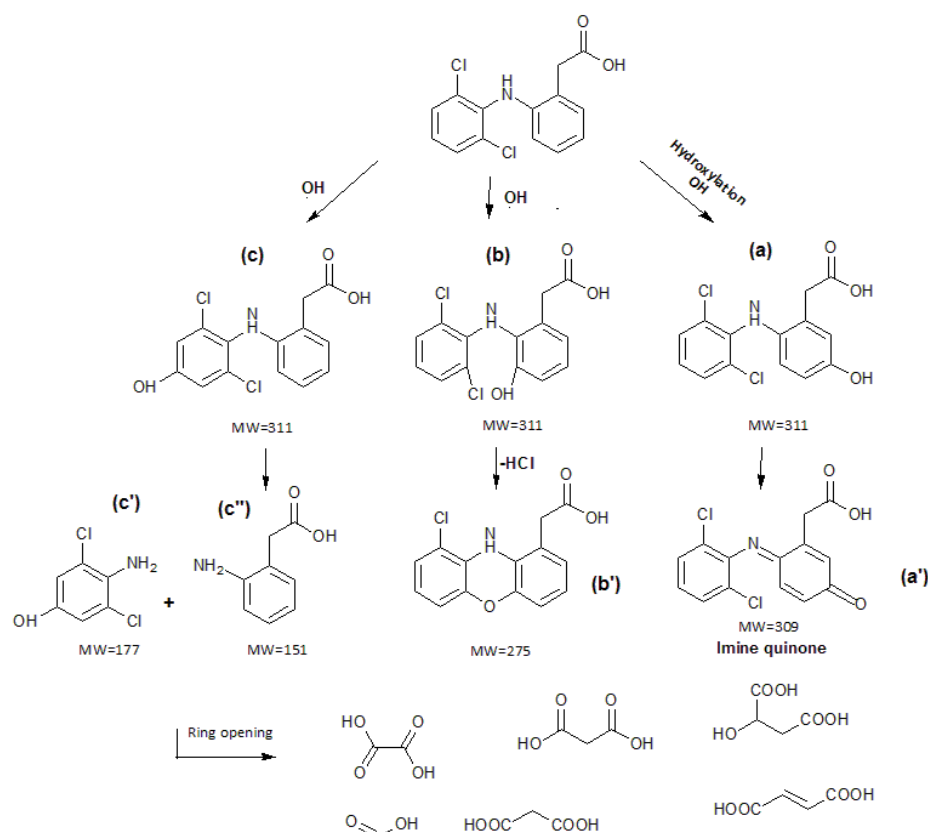


Fig. 14. Proposed oxidative degradation mechanism during radiolysis of DCF.

and oxidizing agents could effectively enhance the radiolytic degradation of DCF. 60% and 85% of DCF (0.2 mM) was degraded at 1.5 kGy in the presence of  $\text{H}_2\text{O}_2$  (5 mM) and  $\text{K}_2\text{S}_2\text{O}_8$  (1 mM), respectively. Moreover, kinetic study based on HPLC data, revealed that the DCF degradation fit the pseudo-first-order reaction. Finally, the present study underlines the use of EPR technique where the presence of free radicals after irradiation was identified and which need a deeper investigation. Overall, this process has simultaneously provided a significant pollutant removal and a lowest toxic load at lowest dose 1 kGy. These results would be used as a reference for a full-scale ionizing radiation plant to remediate real wastewater discharged by persistent pharmaceutical rejected by industries and hospitals.

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