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Gamma radiation induced decolorization of an aqueous textile dye solution in the presence of different additives

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ABSTRACT

Dye wastewater containing an azo dye, direct red 28 was prepared in triple distilled water and was irradiated by gamma radiation. The decoloration of dye wastewater was determined spectrophotometrically. It was found out that the wastewater containing the dye could efficiently be decolorized and degraded using the gamma radiation and in presence of different additives. Starting with the concentration of 30 mg/L, almost 100% decoloration of this dye wastewater can be achieved using the radiation dose of only 2.2 kGy.

Keywords: γ-rays irradiation; Advanced oxidation processes; Decolorization; Dye wastewater

1. Introduction

About 10,000 different types of dyes are available commercially in the world [1,2]. The worldwide production of these dyes is over 7×10^5 tons per year [3]. These dyes have been extensively used in foodstuff, leather, and textile industries [4]. About 1–15% of the total dyes used in the textile industries during the manufacturing, dyeing, and other processing operations, remain unconsumed and is released in the textile wastewater and makes the textile effluents highly colored [5]. Release of these colored effluents into the ecosystem causes aesthetic pollution, eutrofication, and perturbation in aquatic life and show resistant to aerobic degradation [6]. Therefore, different techniques have been applied to decontaminate toxic textile wastewater. Typical techniques used for decontamination of dye wastewater include filtration, ion exchange, adsorption, coagulation, flocculation, reverse osmosis, sedimentation, etc. [3,7]. Although these methods are very useful, but have proven to be non-destructive and produce secondary waste products that require further treatments. The chemical processes that are being used for treatments of textile dye wastewater require high dosages and, therefore, are not feasible economically. However, an effective and more efficient approach, called advanced oxidation process (AOPs), has been developed for degradation and decoloration of dyes wastewater. AOPs are all those techniques, which generate and utilize a powerful oxidizing species, such as hydroxyl (·OH) radicals [8]. These ·OH radicals have strong oxidation potential and can initiate a sequence of reactions to break down toxic molecules to less toxic and smaller molecules. There are many different techniques which generate ·OH radicals and among them most common are

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homogeneous photocatalysis [9], heterogeneous photocatalysis [10,11], UV photolysis [8], Photo-Fenton process [12], Fenton process [13], sonolysis, ozonolysis [14], electron beam process, and process based on radiolysis of water [7]. Among these advanced oxidation processes, the use of ionizing radiation, such as gamma radiation, seems to be very promising. The effect of radiation can be intensified during radiation treatment of textile effluents and primary products formed during radiolysis of water effectively degrade dye molecules [15]. Radiolysis of water is a complex reaction, which produces various types of species. The gross reaction of water radiolysis is shown as below [16]:

$$H_2O \xrightarrow{\gamma-\text{rays}} e^-_{aq,}\ H^\cdot,\ {\bullet}OH,\ HO^\cdot_2, H_2O_2,\ H_2,\ H_3O^+ \tag{1}$$

The radiation yield of these species in term of *G*-values per 100 eV of radiation energy absorbed is given as: e^-_{aq} (2.6), H· (0.6), ·OH (2.7), H_2O_2 (0. 7), H_2 (0.45), and H_3O^+(2.6).

Among these species, the hydrated electron (e^-_{aq}) and hydrogen radical (H·) are considered as reducing species while the hydroxyl radical (·OH) and peroxy radical ($HO^\cdot_2$) are considered as oxidizing radicals. These species can attack the dye's pollutants presents in the solution and start their degradation and decoloration. Table 1 shows the estimated concentration of different reactive species at various doses used during the irradiation of dye solutions [17].

The aim of this study was to investigate the possibility of using gamma rays to decolorize or degrade simulated textile wastewater containing direct red 28 dye at different pHs, concentrations, and in the presence of different additives. The structure of direct red 28 dye is shown in Fig. 1. This figure shows that dye has two azo groups. The formula and chemical index no. of the dye are $C_{32}N_6Na_2O_6S_2$ and C.I 22,120, respectively. The dye is quite soluble in water [18]. The absorption spectrum of unirradiated aqueous solution of direct red 28 (30 mg/L) is shown in Fig. 2. This spectrum shows that dye has two absorption bands at 498 and 346 nm and a shoulder around 240 nm. The main absorption band is due to dye chromophore and it was used to study the decoloration of the dye [19]. Previously this dye was degraded by other advanced oxidation processes like Fenton reagent [20], photocatalytically using titanium dioxide nanocatalyst [21], heterogeneous photocatalysis [22], ultrasound radiation [23], photo-assisted Fenton process using zero-valent metallic iron as a catalyst [24], and ozone [25].

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

	Concentration of reactive species (mM/L)			
Dose (Gy)	·OH	$H^\cdot$	e^-_{aq}	H_2O_2
183	0.051	0.011	0.051	0.015
367	0.103	0.022	0.103	0.029
733	0.205	0.044	0.205	0.059
917	0.256	0.055	0.257	0.073
1100	0.308	0.066	0.308	0.088
2200	0.616	0.132	0.616	0.176

2. Materials and methods

Reagent grade chemicals were used for solution preparation. Direct red 28 (85%) was obtained from Aldrich. Perchloric acid, Sodium hydroxide, and acetic acid were obtained from Merck. Sodium nitrate, Hydrogen peroxide (H_2O_2), and 2-propanol were obtained from BDH. Triple distilled water was used for solution preparation.

2.1. Radiation source

A Co–60 gamma ray irradiator (Issledovatel, former USSR), available at the Nuclear Institute for Food and Agriculture (NIFA), was used for irradiation. The radiation source consists of cylindrical radiation chamber having inside dimension of 0.15 m in diameter and 0.24 m in height making a total volume of $4.24 \times 10^{-3}\ m^3$. Gamma rays irradiation source was calibrated using Fricke dosimeter [26] and dose rate was found to be 1.1 kGy per hour.

2.2. pH and UV spectral measurements

A laboratory digital pH meter (WTW model-09) along with electrode (Orion) was used for pH measurement of the solutions. The pH meter was calibrated using the standard buffers. A double beam UV–Visible spectrophotometer (Varian DMS–200) was used to determine the concentration of the dye solutions at characteristic wavelength.

2.3. Preparation of solution

Simulated dye wastewater of direct red 28 was prepared by dissolving 1.18 g of the dye in 1 L of triple distilled water. The standard solutions of different concentrations were prepared by diluting this stock

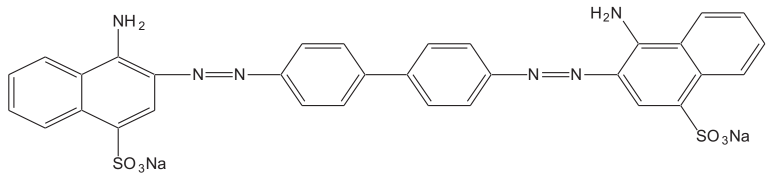

Fig. 1. Structure of direct red 28.

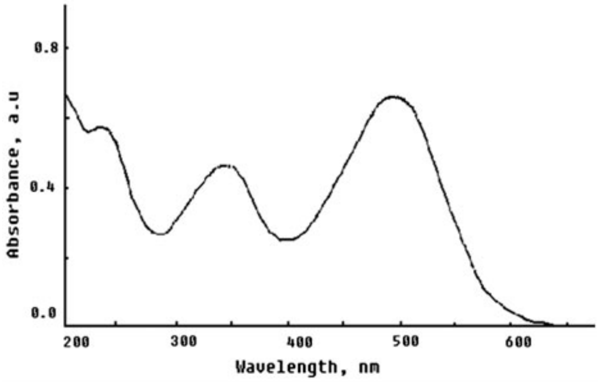

Fig. 2. Absorption spectrum of direct red 28 (30 mg/L) in aqueous solution.

solution. Standard solution of 0.5 M 2-propanol was prepared by dissolving 3.49 mL of 2-propanol in 100 mL distilled water. 5.0 M Hydrogen peroxide (H_2O_2) stock solution was prepared by diluting 18.9 mL H_2O_2 (36%) in 50 mL triple distilled water. 0.5 M perchloric acid was prepared by taking 4.31 mL of the reagent in 100 volumetric flask and the volume of the solution was made to the mark with triple distilled water. Sodium nitrate solution (0.1 M) was prepared by dissolving 2.13 g of sodium nitrate in distilled water and the solution was diluted to the 100 mL mark. Solutions of desired concentrations were prepared from these stock solutions.

2.4. Irradiation of sample solution by gamma radiation

About 10 mL of freshly prepared solutions was taken in Pyrex test tubes. The dimension of these test tubes was 0.1 cm thickness, 10.5 cm length, and 1.4 cm width. The solutions were stored in the dark and taken to the NIFA, Tarnab, Peshawar for irradiation with Cobalt–60 gamma radiation source. The solutions were irradiated for predetermined interval of times e.g. 10, 15, 20, 30, 40, 60, and 120 min at a fix position in the radiation chamber. After irradiation, the sample solutions were brought back to Radiation Chemistry Laboratory of National Center of Excellence in Physical Chemistry, University of Peshawar for spectrophotometric analysis and spectra of these solutions were recorded using UV–visible spectrophotometer.

2.5. Percent decoloration

Percent decoloration was calculated by the following formula:

$$\%\ \text{Decoloration} = \frac{(A_o - A_i)}{A_o} \times 100 \tag{2}$$

where A_o = absorbance of aqueous dye solution at zero dose; A_i = absorbance of aqueous dye solutions at different doses.

2.6. Dose constant

Dose constant (k) was calculated from the slope of the line of natural logarithm (ln) of the dye concentration (in moles/L) versus the dose (Gy). These dose constant values were used to calculate the radiation dose required for 50% degradation of the dye (D_{50}), for 90% degradation (D_{90}), and for 99% degradation of the dye (D_{99}) using the formulas ln 2/k, ln 10/k, and ln 99/k, respectively. Where k in above formulae is dose constant and was equal to the slope of ln (concentration) vs. dose plot under pseudo-first-order conditions.

2.7. Solute G-values

The G-value is defined as the number of species (e.g. molecules, radicals, and ions) produced or destroyed per 100 eV of absorbed energy. The radiation yield in term of G-values (species/100 eV), at different doses, was calculated by the formula given below:

$$G - \text{values} = (R)/D \times 9.652 \times 10^6 \text{species}/100\,\text{eV}$$

where (R) is the change in concentration (in M) of the species (i.e. difference in concentration of dye before irradiation and after irradiation), D is the dose absorbed (in Gy), and 9.652×10^6 is conversion factor [17].

2.8. Synergistic effect studies

In this work, different additives were used to study the degradation of the aqueous dye as well as to minimize the amount of gamma radiation needed for the desired results. Nitrogen saturation of the aqueous dye was performed by bubbling the gas through the solution for 25 min in specially constructed reaction vessels. Effect of species generated in the presence of oxygen and hydrogen peroxide on degradation of dye molecules was also studied.

3. Results and discussion

3.1. Stability of direct red 28 before irradiation

The pre-irradiation stability of the aqueous dye solution was determined at 498 nm for a period of 40 d at different conditions of light, temperature, and pH. The absorbance of aqueous dye solution (70.0 mg/L) in diffused sunlight at room temperature (25˚C) was found stable for 40 d. Similarly the pre-irradiation stabilities of the dye solution were also checked in dark, fluorescence light, at different temperatures (room temperature (i.e. 25˚C), 7, 40, and –10˚C), and at different pHs (pH 6.0, 8.0, and 10.0) at 498 nm. The absorbance of dye solution was also found stable at these conditions of light, temperature, and pH. These observations are consistent with the fact that the two azo groups and benzene rings that are present in the dye structure are non-biodegradable. Therefore, the dye can remain for long period in the environment and hence can cause various problems associated with toxic compounds.

3.2. Radiolytic degradation of direct red 28 in aqueous solution

The effects of various irradiation doses of gamma rays on different concentrations of the dye were studied. For this purpose different concentration of the dye, ranging from 35 to 100 mg/L, were prepared and subjected to various doses of gamma radiation (up to 1,100 Gy) and their % decoloration was determined as shown in Fig. 3. The results in the Fig. 3 reveal that % decoloration of the dye increases with increase in radiation dose at all the concentrations. This figure also shows that highest % decoloration was observed for solution having dye concentration of 35 mg/L and when the concentration of the aqueous dye was increased then % decoloration was decreased. For instance, at radiation dose of 1,100 Gy, the % decoloration for dye solutions having concentration of 35, 80, and 100 mg/L were determined to be 83, 69, and 64%, respectively. Therefore, it can be stated that irradiation treatment of aqueous dye for their decoloration is more efficient at low-solute concentration and higher dose is required for higher solute concentrations.

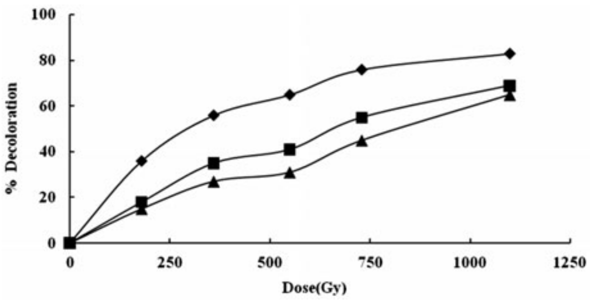

Fig. 3. Percent decoloration of aqueous dye at 35 mg/L (♦), 80 mg/L (■), and 100 mg/L (▲) concentrations.

The efficiency of irradiation process can also be determined with the help of G-values that are given in Table 2. This table shows that at all the concentrations, as dose of gamma radiation was increased, the G-values decreased. This decrease in G-values is probably due to the formation of intermediate reaction by-products and their possible competition with the parent compound for different reactive species. Basfar and coworkers also arrived to similar explanation when they investigated the removal of chloroform and methyl *tert*-butyl ether (MTB) by radiation [17].

Efficiency of the irradiation process can also be measured kinetically. The concentration of ·OH radicals, at dose of 1,100 Gy, calculated from G-values given for Eq. (1), was found to be 0.30 mM as compared with dye concentration of 35 mg/L (4.4 mM). So at all concentrations the [Dye]>>[·OH]. Thus, pseudo-first-order conditions exists i.e. the decay of the dye will be first order in

Table 2
G-values of direct red 28 solution at different concentrations determined for absorbance at 498 nm

		G-values $\left(\frac{\text{molecules}}{100\,\text{eV}}\right)$		
S. No.	Dose (Gy)	35 mg/L	80 mg/L	100 mg/L
1	0	–	–	–
2	180	1.68	1.05	1.06
3	360	0.57	0.99	0.94
4	550	0.30	0.78	0.72
5	730	0.15	0.79	0.79
6	1100	0.07	0.66	0.76

[·OH]. Therefore, –ln (Dye) vs. Dose plot will be straight line and slope of this straight line would be the dose constant "k". Fig. 4 shows the estimation of dose constants of the dye at different starting concentrations. The results in this figure show that as the concentration of dye was increased, the dose constant was decreased. This shows that dye can be removed at faster rate at low concentration.

This trend can also be verified by calculating the radiation dose required for decay of 50% (D_{50}), 90% (D_{90}), and 99% (D_{99}) of dye. These values are shown in Table 3. Results in this table reveal that less dose is required for 50, 90, and 99% decay of the dye at lower dye concentrations.

3.3. Effect of pH on the degradation of dye

Fig. 5 shows the % decoloration of the aqueous dye at pHs of 5.0, 9.0, and 12.0. The results reveal that the dye can be decolorized by radiation treatment at all the pHs i.e. from pH 5.0 to 12.0. This figure shows that the destruction of the dye was increased as we increased the dose of gamma radiation at all pH. This figure further reveals that % decoloration at pH 9.0 was higher as compared with dye degradation at pH 5.0 and 12.0. As pk_a value of ·OH radical is 11.92 and ·OH radical is in equilibrium with $O^{\cdot -}$ as given in the following equation [16]:

$$^{\cdot}OH \rightleftarrows H^+ + O^{\cdot -} \tag{3}$$

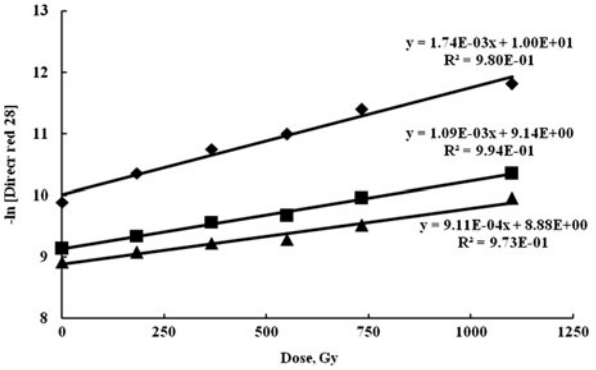

Fig. 4. Plot of –ln [direct red 28] versus dose for 35 mg/L (♦), 80 mg/L (■), and 100 mg/L (▲) direct red 28 solution at 498 nm for determination of dose constants.

At lower pH ·OH radicals predominates and at pH higher then 11.92, $O^{\cdot -}$ is the dominant species. Similarly, pk_a value of $HO_2^{\cdot}$ is 4.88 and $HO_2^{\cdot}$ is in equilibrium with $O^{\cdot -}$ as shown in the following reaction [16]:

$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^{\cdot -} \tag{4}$$

So at higher pH (pH > 5) $O_2^{\cdot -}$ is present in higher concentration and at lower pH, reactions of $HO_2^{\cdot}$ will be more significant. However, rate constants for $HO_2^{\cdot}/O_2^{\cdot -}$ reactions are very slow; therefore, OH radicals are major species that can bring about the degradation of aqueous dye pollutants [27].

Hydrated electrons at lower pH react with H^+ ions and produces H· radicals as shown in the following reaction:

$$e_{aq}^- + H_3O^+ \rightarrow H^{\cdot} + H_2O \quad k = 2.35 \times 10^{10}\ M^{-1}\,s^{-1} \tag{5}$$

Therefore, higher destruction of dye molecules at pH 9.0 may be attributed to formation of ·OH radicals. The decrease in the % destruction of aqueous dyes molecules in highly alkaline solution (such as pH 12.0) can be attributed to the conversion of highly reactive ·OH species to less reactive $O^{\cdot -}$ radicals [28]. Beside changes that occur in structure of aqueous dye molecules when pH of solution becomes acidic [18], the decrease in the % destruction of dye at low pH may also be attributed to higher concentration of H· and $HO_2^{\cdot}$ radicals, which are produced by irradiation of solution at this acidic pH [29]. Apparently, these radicals are less effective in degradation of dye. The efficiency of dye removal process at different pH can also be determined with the help of *G*-values, which are

Table 3
Effect of irradiation on dose constant, D_{50}, D_{90}, and D_{99} at different concentrations of direct red 28 solution

Concentration (mg/L)	Dose range (Gy)	Dose constant (k)	D_{50} (Gy)	D_{90} (Gy)	D_{99} (Gy)
35	0–1100	1.7×10^{-3}	398	1323	2647
80	0–1100	1.1×10^{-3}	630	2093	4187
100	0–1100	9.1×10^{-4}	770	2558	5117

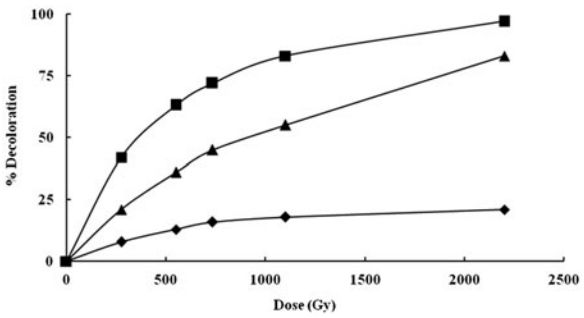

Fig. 5. Degradation of 30 mg/L direct red 28 solution at pH 5.0 (♦), 9.0 (■), and 12.0 (▲) at different radiation doses.

summarized in Table 4. The results in this table shows that at any dose, *G*-values at pH 9.0 was higher as compared with *G*-values at other pHs showing that dye removal process at pH 9.0 is more fruitful. Therefore, it can be assumed that OH radicals (produced at pH 9.0) may destroy the dye molecules more effectively. The results reveal that at lower dose of gamma radiations the *G*-values have higher values at any given pH. As dose was increased the *G*-values decreased at all pHs. It is most likely that this decrease may be due to the reaction competition between the intermediate products and reactive species produced during irradiation of the aqueous dye solution as compared with reaction of these reactive species with parent compound. Therefore, efficiency of the dye removal process increases by increasing the dose of gamma radiation.

The dose constants for decay of the dye solution at pH 5.0, 9.0, and 12.0 were calculated from plots shown in Fig. 6, for radiation doses from 0 to 2,200 Gy and were found to be $2.0 \times 10^{-4}\,\text{Gy}^{-1}$, $2.2 \times 10^{-3}\,\text{Gy}^{-1}$, and $8.8 \times 10^{-4}\,\text{Gy}^{-1}$, respectively.

Table 4
G-values (molecule/100 eV) for destruction of 30 mg/L direct red 28 solution at pH 5.0, 9.0, and 12.0 at different radiation doses

		G-values $\left(\frac{\text{molecules}}{100\,\text{eV}}\right)$		
S. No.	Dose (Gy)	pH 5.0	pH 9.0	pH 12.0
1	0	–	–	–
2	275	0.05	0.61	0.26
3	550	0.04	0.45	0.23
4	733	0.04	0.39	0.21
5	1100	0.03	0.30	0.17
6	2200	0.02	0.17	0.13

The results show that dose constant has relatively higher values at pH 9.0. While at higher or lower pH, the value of dose constant decreased. This is comparable with the results given above where % destruction and *G*-values were relatively higher for pH 9.0. Similar trends were also reported by others researchers for different dyes [7,30]. They also reported that at highly basic pH degradation of dyes reduced due to dissociation of ·OH radicals into less reactive $O^{\cdot -}$ radicals. They also suggested that OH radicals were major attacking primary species above pH 7.0 for decomposition of dyes.

Table 5 shows the doses required for 50% decay of the dye (D_{50}), 90% (D_{90}), and 99% of the dye (D_{99}) at pH 5.0, pH 9.0, and pH 12.0. The comparison of D_{50}, D_{90}, and D_{99} values at these pHs reflect that the dye solution at pH 9.0 require less dose for its 50, 90, and 99% decay as compared with the doses in relatively higher alkaline and in acidic conditions. As discussed earlier, the ·OH radicals and $O_2^{\cdot -}$ species predominates at pH 9.0. Therefore, low D_{50}, D_{90}, and D_{99} values at pH 9.0 can be attributed to formation of these species, which reacts with the dye molecules and bring about their degradation. Similarly as pk_a value of ·OH radicals is 11.9, therefore, when aqueous dye solution at high pH (pH 12.0) is irradiated, these ·OH radicals are converted to less reactive $O^{\cdot -}$ form which is less effective toward dye degradation. It is also discussed previously that pk_a value of $HO_2^{\cdot}$ radicals is 4.88. Therefore, at low pH $HO_2^{\cdot}$ radicals predominate and react with the aqueous dye molecules. However, $HO_2^{\cdot}$ radicals are also less effective in degradation of the dye molecules and results in lower % decoloration, dose constants, and higher D_{50}, D_{90}, and D_{99} values.

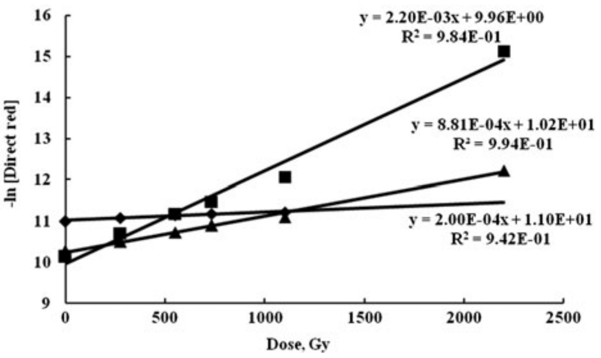

Fig. 6. Plot of –ln [direct red 28] versus dose for 30 mg/L direct red solution at pH 5.0 (♦), 9.0 (■), and 12.0 (▲) for determination of dose constant at 498 nm.

Table 5
Dose constant and dose required for 50, 90, and 99% destruction of 30 mg/L direct red 28 solution at different pH

S. No.	pH	Dose range (Gy)	Dose constant "k"	D_{50} = ln 2/k (Gy)	D_{90} = ln 10/k (Gy)	D_{99} = ln 100/k (Gy)
1	5.0	0–2200	2.0×10^{-4}	3466	11513	23026
3	9.0	0–2200	2.2×10^{-3}	315	1047	2093
4	12.0	0–2200	8.8×10^{-4}	770	2558	5117

3.4. Synergistic effect of different additives

The degradation of the aqueous dye can be amplified using gamma radiation coupled with different additives, such as nitrogen, oxygen, and hydrogen peroxide.

During the course of present study, the aqueous solution of direct red 28 (30 mg/L) was irradiated with gamma rays at dose rate of 1.1 kGy per hour, at pH of 7.9, in the presence of different additives, such as air, nitrogen, and H_2O_2; and changes in UV–visible absorption spectra were recorded. These spectra showed that the intensity of absorption bands at 498 and 346 nm (see Fig. 7) decreased as the dose of gamma rays increased. The study further revealed that on irradiation, no new peaks were formed. This trend showed that degradation of dye molecule, in the presence of these additives led to decolored or less intensely colored products than the original substances, which do not interfere with the absorption bands of the dye. Others investigators have also reported similar behavior when they studied the degradation of different dyes [31]. The relative decrease in absorbance of dye solution, in presence of N_2 was much less for the same radiation dose as compared with the air-saturated solution or in the presence of hydrogen peroxide. The percent degradation of the aqueous dye in presence of these additives is summarized in Table 6. The results show that aqueous dye can be degraded in presence of all these additives.

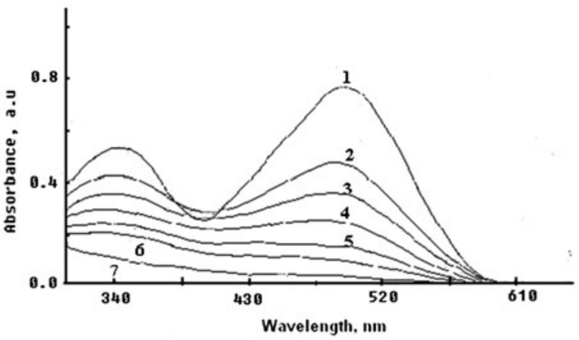

Fig. 7. Changes in absorption spectra of unirradiated and irradiated direct red 28 aqueous solution in the presence of air. Dye concentration: 30 mg/L, dose rate: 1.1 kGy/h, dose: 0 Gy (curve 1), 180 Gy (curve 2), 360 Gy (curve 3), 550 Gy (curve 4), 730 Gy (curve 5), 1,100 Gy (curve 6), 2,200 Gy (curve 7).

Aerated solution contains oxygen, therefore, both e^-_{aq} and H· radicals are rapidly scavenged by O_2 as shown in reactions 6 and 7 [16].

$$O_{2+}e^-_{aq} \rightarrow O_2^- \quad k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1} \tag{6}$$

$$O_2 + H^{\cdot} \rightarrow HO_2^{\cdot} \quad k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1} \tag{7}$$

The H_2O_2 is in very small concentration and is, therefore, negligible. The O_2^- combines with H^+ to form $HO_2^{\cdot}$ ($pk_a = 4.88$), while pk_a value of ·OH radicals is 11.92. However, the pH of the solution was 7.9, therefore, $O_2^{\cdot -}$ concentration will be significant as compared with $HO_2^{\cdot}$. Decoloration of the dye in the presence of air, at pH 7.9 is mainly attributed to the reaction of ·OH and $O_2^{\cdot -}$ radicals with parent compound. These radicals bring about the degradation of the dye molecules, similar to one suggested by Abdel–Rahim and coworker [29].

The nitrogen-saturated solution does not contain O_2, therefore, $HO_2^{\cdot}$ radical is not formed and the main reactive species are ·OH, e^-_{aq}, and H· radicals. Among these species, the concentration of H· radical is relatively small so the important species left are e^-_{aq} and ·OH radical. These species then bring about the degradation and decoloration of the dye molecule. Therefore, the aqueous solution of dye can be degraded in non-aerobic environment. Suzuki and coworkers [32] suggested similar trends when they investigated the degradation of different azo dyes. Similar behavior was also reported by other investigators [31].

During the course of present study, aqueous solution of direct red 28, containing 1.0×10^{-2} M H_2O_2, was also irradiated by gamma radiation (0–2,200 Gy). The H_2O_2 acts as a scavenger of e^-_{aq}. The reaction by which e^-_{aq} is scavenged by H_2O_2 is shown below [16]:

$$e^-_{aq} + H_2O_2 \rightarrow \mathbf{.}OH +^- OH \quad k = 1.2 \times 10^{10}\,M^{-1}\,s^{-1} \tag{8}$$

Table 6
Degradation of 30 mg/L direct red 28 solution in the presence of oxygen, nitrogen, and hydrogen peroxide

		% Decoloration		
S. No.	Dose (Gy)	Oxygen	Nitrogen	Hydrogen peroxide
1	0	–	–	–
2	180	43	35	62
3	360	57	53	76
4	550	72	61	87
5	730	83	67	91
6	1100	88	72	96
7	2200	97	87	100

This reaction suggests that e^-_{aq} converts into ·OH radicals and hence, concentration of ·OH radical was increased. This higher concentration of OH radicals produced higher degradation of aqueous dye molecules.

The comparison of dye degradation in presence of these additives shows that dye degradation in presence of hydrogen peroxide and air was higher as compared with N_2-saturated solution. For instance, percent degradation of dye at dose of 2,200 Gy in air and H_2O_2 was determined to be 97 and 100%, respectively, while at the same dose % degradation of the dye in nitrogen-saturated solution was determined to be 87% only. As explained earlier, ·OH radicals are main reactive species produced during irradiation of aqueous dye solutions in presence of H_2O_2 and oxygen as shown in above discussions. Dessouki and Abdel–Aal [28] also found similar results when they studied the degradation of acid dyes. Wang and coworker [33] also investigated the radiation induced decomposition and decoloration of different reactive dyes in presence of H_2O_2. Their findings are also in agreement to our findings. They also found out that degradation of dyes is promoted in the presence of H_2O_2.

The rate constant of direct red 28 and OH radical is $1.2 \times 10^{10}\,M^{-1}\,s^{-1}$, which is high enough to bring about the degradation of aqueous dye molecules [33]. The low degree of dye degradation in N_2-saturated solution is due to fact that the concentration of ·OH radicals is relatively smaller and the solution contains both ·OH radicals as well as e^-_{aq}. The rate constant of reaction between e^-_{aq} and the aqueous dye is also high i.e. 1.6×10^9, which is also high enough to degrade the dye molecules. Although, the rate constant of reaction between e^-_{aq} and ·OH radicals is very high as shown in following reaction, the concentration of both radicals is very small and probability of this reaction is very low.

$$e^-{}_{aq} + {}^{\bullet}OH \rightarrow {}^{-}OH \quad k = 3.0 \times 10^{10}\,M^{-1}\,s^{-1} \tag{9}$$

Efficiency of irradiation processes in presence of different additives can be measured with the help of *G*-values also, which are summarized in Table 7. The results in this table show that as the dose of gamma radiation was increased, the *G*-values decreased. This decrease in *G*-values may be attributed to reaction of intermediate products with the reactive species produced during the irradiation of dye solution in presence of these additives. The results in this table further reveal that at any specific dose, *G*-value in presence of oxygen and hydrogen peroxide was

Table 7
G-values of 30 mg/L direct red 28 solution in the presence of oxygen, nitrogen, and hydrogen peroxide

		G-value (molecules/100 eV)		
S. No	Dose (Gy)	Oxygen	Nitrogen	Hydrogen peroxide
1	0	–	–	–
2	180	0.94	0.64	1.33
3	360	0.63	0.51	0.82
4	550	0.52	0.39	0.61
5	730	0.45	0.32	0.49
6	1100	0.32	0.23	0.33

Table 8
Dose constant and dose required for 50, 90, and 99% destruction of 30 mg/L direct red 28 dye solution in the presence of Oxygen, Nitrogen, and Hydrogen peroxide

Additive	Dose range (Gy)	R^2	Dose constant (k)	D_{50} (Gy)	D_{90} (Gy)	D_{99} (Gy)
O_2	0–2200	1.00	2.2×10^{-3}	315	1046	2093
N_2	0–2200	0.90	1.0×10^{-3}	693	2303	4605
H_2O_2	0–2200	0.99	3.9×10^{-3}	178	590	1181

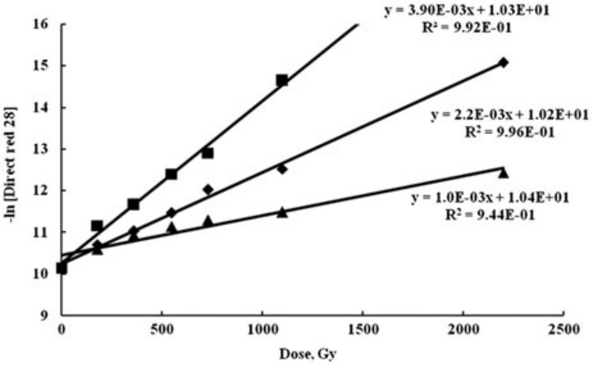

Fig. 8. Plot of –ln [direct red 28] versus dose for 30 mg/L direct red solution in presence of N_2(▲),in presence of O_2 (♦), and in presence of H_2O_2 (■) for determination of dose constant at 498 nm.

higher as compared with N_2-saturated solution. As explained above, relative concentration of ·OH radical is expected higher in H_2O_2 solution as compared with O_2 and N_2-saturated solutions.

The removal efficiency of the aqueous dye molecules in presence of different additives can also be determined kinetically by calculating the dose constant (k) values. These values are shown in Fig. 8. The results show that irradiation of aqueous dye molecules in presence of H_2O_2 (which produced relatively higher concentrations of ·OH radicals) has high-dose constant value. So it can be predicted that destruction of aqueous dye molecules in presence of H_2O_2 occurred at a higher rate as compared with N_2-saturated solution because of the reasons as discussed above.

Table 8 describes the doses required for 50, 90, and 99% destruction (D_{50}, D_{90}, and D_{99}) of the dye molecules in presence of N_2, O_2, and H_2O_2. From the results in this table it was found out that the destruction of aqueous dye molecules during irradiation in presence of H_2O_2 require less doses for 50, 90, and 99% destruction of the dye molecule as compared with other additives. Again this trend may be attributable to increased concentration of ·OH radicals produced by irradiating the aqueous dye molecule in presence of H_2O_2. As explained earlier in Eq. (8), these H_2O_2 molecules acts as scavenger for e_{aq}^{-} and convert them to OH radicals and hence the concentration of ·OH radicals is increased. In another study, it was found out that ·OH radicals react with benzene and azo groups with high rate constant i.e. $1 \times 10^{10}\ M^{-1}\ s^{-1}$ [34]. In this way, it first oxidize into fatty acids and finally to CO_2. Ma and coworker [35] proposed a mechanism for degradation of this dye by ·OH radicals that were generated in the presence of N_2O stating that when ·OH radicals react in the presence of oxygen, peroxide was formed. Most of the destruction was produced by this peroxide resulting in the formation of alcohol, aldehyde, and acids and finally leading to evolution of CO_2.

4. Conclusions

The present study revealed that simulated dye wastewater can remain for long period in the environment and can cause various problems associated with toxic compounds. The % decolorization decreased as the concentration of the dyes increased at a given dose. At all the concentrations, as dose of gamma radiation was increased, *G*-values decreased. It was concluded that the decay of the dye follows pseudo-first-order kinetics in [·OH]. The dose required for decay of 50, 90, and 99% the dye was increased as concentration of a dye increased. It was also concluded that the dye molecules can be decolorized by gamma radiation at wide range of pHs. At any dose % decoloration, *G*-values and dose constant values at pH 9.0 was higher as compared with dye degradation at pH 5.0 and 12.0. The intensity of corresponding absorbance band of the dye decreased as increased the dose of gamma radiation in the presence of different additives and dyes molecules degrade into decolored intermediate products. Irradiation of aqueous dye solution in the presence of additive, which leads to Advance Oxidation Processes, showed higher percent decolorization of aqueous dyes molecules, high-dose constant values and low D_{50}, D_{90}, and D_{99} values. It is suggested that Advance Oxidation Processes such as gamma radiation, can be used for decontamination of organic dye pollutants.

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