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DEGRADATION KINETICS OF TEXTILE AZO DYE REACTIVE ORANGE-16 BY GAMMA IRRADIATION

Fifi Nurfiana[a,c*], Rochmadi Rochmadi[a], Rochim Bakti Cahyono[a], Hendig Winarno[b], Sugili Putra[c], Waringin M. Yusmaman[c]

[a]Department Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika No. 2, Kampus UGM, Yogyakarta 55281, Indonesia
[b]Research Center for Radiation Process Technology, National Research and Innovation Agency KST B.J. Habibie, Jl. Puspiptek, Tangerang Selatan, Banten15314, Indonesia
[c]Polytechnic Institute of Nuclear Technology, National Research and Innovation Agency Jl. Babarsari Kotak POB 6101/YKKB, Yogyakarta 55281, Indonesia

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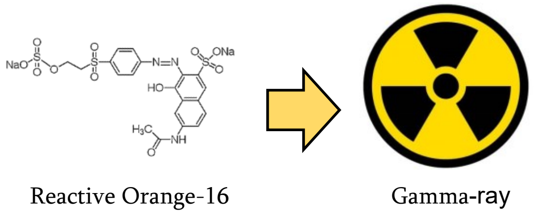
*Corresponding author
fifi004@brin.go.id

Graphical abstract



Reactive Orange-16 Gamma-ray

Abstract

Gamma radiation have become attention since their high potential for degrading compounds, especially organic pollutants. In this research, gamma radiation was studied for degrading the Reactive Orange-16 (RO-16) dye, a toxic and carcinogenic pollutant. The radiolytic degradation process was studied in a batch reactor with a gamma-ray dose rate of 2.930 kGy/h. The effect of experimental variable such as initial peroxide concentration, initial pH, initial dye concentration, and addition of inorganic anion were studied. The highest degradation rates were achieved at a peroxide concentration ranging from 2 to 4 mM. In contrast, the higher peroxide concentration indicated the slower degradation process caused by the scavenging effect of the peroxide. Degradation of 88% RO-16 dye with 0.1 mM initial concentration, was achieved at 2.0 kGy irradiation dose and 97.4% degradation in the presence of 4 mM peroxide. The dose constant (d) for those degradation processes was 1.0657 kGy^{-1} and 1.8420 kGy^{-1} respectively. The degradation was more efficient in acid pH. The degradation process increased with lower initial dye concentrations. The degradation of RO-16 dye by gamma-ray was inhibited by the presence of inorganic anions in the following sequence: NO_3^-→ CO_3^{2-} → HCO_3^- → CH_3COO^-→ Cl^-.

Keywords: Gamma radiation, Reactive Orange-16, degradation, peroxide, radiolytic

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1.0 INTRODUCTION

Reactive Orange-16 (RO-16) dye is one of the reactive azo dyes. Among all dyes, azo dyes are the most widely used. It is estimated that the amount of use of azo dyes is 60-70% of all dyes [1]. Azo dyes are identified by the presence of –N=N– bonds attached to aromatic groups [2]. This bond is known as a chromophore, which is responsible for the color of dyes and explains the degradation resistance of dyes. Despite the cost-effective use of biological processes for the treatment of some types of municipal and industrial wastewater, research has shown that conventional biological processes are not able to effectively degrade azo dyes as well as their aromatics [3]. The RO-16 dye has the potential to contribute to environmental contamination, given its highly toxic nature and hazardous mutagenic characteristics [4]. This substance is easily absorbed by the body since it dissolves in water; accordingly, this dye needs to be degraded prior to being discharged into the environment.

The combination of biological treatment (bioremediation) with advanced oxidation processes (AOPs) is one of the most well-known efficient methods for the degradation of azo dyes or decolorization in textile waste [5]. The research on the degradation of RO-16 dye that has been conducted includes photodegradation under UV irradiation [6], anodic oxidation using heavily boron-doped diamond electrodes [7], UV/H_2O_2 oxidation [8], photocatalytic with TiO_2 catalyst [9], and ozonolytic degradation [10].

In this research, a study on the degradation process of RO-16 dye by gamma radiation was carried out. To our knowledge, works dealing with the degradation of RO-16 dye using gamma radiation are not present in the literature. Out of various radiation treatments, gamma radiation has shown the most favorable outcomes. gamma radiation is more advantageous for treating dye wastewater due to its radiation effect on dye molecules in aqueous solutions, leading to effective degradation through water radiolysis [16]. Additionally, this approach is recognized as being environmentally friendly, simple, easy, and cost-effective compared to previously mentioned methods [11].

Several studies on dye degradation using gamma-ray have been conducted, including Reactive Blue-19 dye degradation [17], Congo Red dye degradation [14], Disperse Red-73 dye degradation [18], Erythrosine dye degradation [11], and Alizarin Yellow GG dye degradation [19].

Irradiating wastewater using gamma-ray or electron beam will break down pollutants into smaller molecules, which can then be treated and removed using conventional biological processes, such as decomposition by bacteria [12]. The breakdown of water through radiolysis is extensively documented, revealing the production of intermediate species (reaction (1)) [13], [14], [15].

$$H_2O \rightarrow {}^{\bullet}OH,\ {}^{\bullet}H,\ e_{aq}^{-},\ H_2,\ H_3O^{+},\ H_2O_2 \qquad (1)$$

The primary reducing agents generated in irradiated aqueous solutions are the hydrogen atom and the hydrated electron (e_{aq}^{-}), while the main oxidizing species produced in water radiolysis include hydroxyl radicals (${}^{\bullet}OH$), and perhydroxyl radicals (${}^{\bullet}HO_2$), which formed in subsequent reactions. The dye degradation is solely initiated by ${}^{\bullet}OH$ attacking electron-rich sites on the dye molecules [15].

In this research, the overall kinetics of degradation of RO-16 dye by gamma rays were studied, with the effects of the initial concentration of peroxide, initial pH, initial dye concentration, and the effects of the inorganic anion. These parameters influence the efficiency of radiation-induced degradation of the dyes. The investigation will highly assist in better understanding the degradation of RO-16 by gamma radiation for the successful implementation of these technologies in the treatment of dye-contaminated wastewaters.

2.0 METHODOLOGY

2.1 Materials

Reactive Orange-16 (RO-16) (dye content ≥70%, Sigma Aldrich), H_2O_2 (30% purity, Merck, Germany), $HClO_4$ (70- 72% purity, Merck, Germany), NaOH (anhydrous, Merck, Germany), $NaNO_3$ (pro analysis, Merck, Germany), NaCl (pro analysis, Merck, Germany), CH_3COONa (anhydrous for analysis, Supelco), Na_2CO_3 (anhydrous for analysis, Sigma Aldrich), $NaHCO_3$ (purity ≥95%, Merck, Germany).

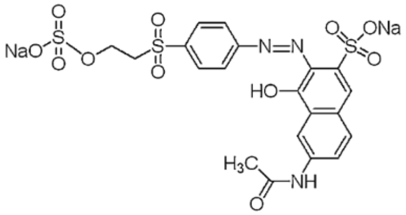


Figure 1 Molecule structure of RO-16 dye

2.2 Instrumentation

A type I gamma irradiator with a Co-60 radioactive source was used to irradiate the sample. The irradiator was installed at the Polytechnic Institute of Nuclear Technology BRIN with a dose rate of 2.930 kGy/h in November 2022. The irradiator has been calibrated with reference from Riso High Dose Reference Laboratory, Technical University - Denmark. B3 DoseStix was used as a dosimeter. A pH/C meter Hanna Instruments HI 2210 was used to monitor the pH solution. Shimadzu 1780 UV-Vis Spectrophotometer was used to analyze the color degradation.

2.3 Procedure

The amount of 250 mL of aqueous dye solution with initial concentrations of 0.05, 0.075, 0.01, and 0.15 mM; H_2O_2; and a certain initial pH value was irradiated in a gamma irradiation chamber. During the irradiation, the solution was rotated at 10 rpm constantly. At a certain irradiation dose interval, a 15 mL aliquot was taken and then analyzed by UV–Vis spectrophotometer. RO-16 concentration was calculated from the linear regression equation, which was obtained by correlating the concentration to the absorbance measured at a wavelength of 493 nm.

2.4 Determination of overall kinetics of RO-16 degradation by gamma radiation

Reaction rate is the concentration change per unit dose in a specific dose interval. In this case, the concentration of the RO-16 reactant was observed using a UV-Vis spectrophotometer at 493 nm wavelength. Degradation caused by gamma irradiation from various pollutants is known to follow a pseudo-first-order behavior [14][20][21],

$$-ln\left(\frac{C}{C_0}\right) = kt \qquad (2)$$

where C_0 and C represent the pollutant concentration before and after irradiation, k is the reaction rate constant, and t is time. In the degradation kinetics by gamma irradiation, t in equation (2) was replaced with Dose (D), where $D = t$ (hours) × irradiation dose rate (kGy/h). Meanwhile, the reaction rate constant k is replaced by the dose constant (d), thus transforming equation (2) into:

$$-ln\left(\frac{C}{C_0}\right) = dD \qquad (3)$$

Plotting $-ln(C/C_0)$ against irradiation dose (D) allowed us to determine the dose constant (d), represented by the slope of the line.

3.0 RESULTS AND DISCUSSION

3.1 The UV-Vis spectra of the RO-16 dye

The UV-Vis spectrum of RO-16 dye is characterized by two bands at maximum peaks of 493 and 387 nm (visible light region) and two bands at maximum peaks of 297 and 254 nm (ultraviolet region), as seen in Figure 2. The absorption peaks at 297 and 254 nm are attributed to the π→π* transitions of the benzene and naphthalene rings, and the absorption decrease in this region indicated the degradation of the aromatic part of the RO-16 dye [8]. The two bands at 493 and 387 nm are caused by the n→π* transitions in the azo bond and are due to the presence of azo and hydrazone forms. The 387 nm band corresponds to the azo form; meanwhile, the 493 nm band is associated with the hydrazone form of the azo dye [22]. These forms arise from the tautomeric intramolecular hydrogen bond interaction between the oxygen of the naphthyl group and the β-hydrogen of the azo bond, respectively. The loss of absorption peaks in the visible region indicated that the main chromophore (-N=N-) of the dye has been degraded; therefore, the dye solution becomes decolorized [7][8]. Hence, the concentration changes of RO-16 can be determined by using a UV-Vis spectrophotometer with a standard calibration curve at the appropriate dilutions. Figure 2 shows the spectrum of unirradiated RO-16 at various concentrations, and Table 1 provides the linear regression equations for each wavelength. The linear regression coefficients close to 1 (one) for each peak indicated that the concentration of RO-16 with respect to absorbance was linear.

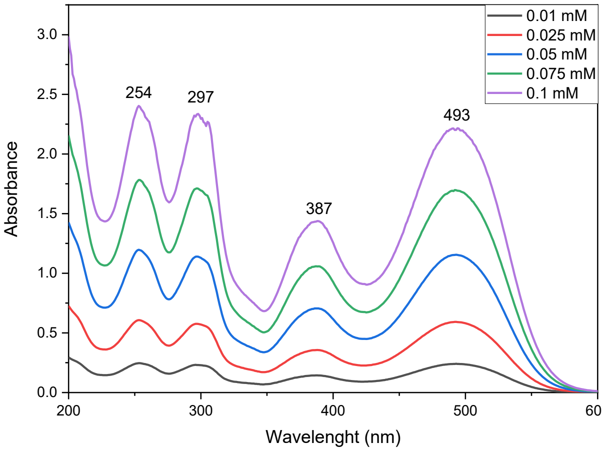


Figure 2 The unirradiated RO-16 spectra at different concentrations

Table 1 The equation of the line and linear regression of the standard curve at the spectrum peak

Wavelength (nm)	Standard curve equation	R^2
254	y= 23.802x +0.0069	0.9999
297	y= 23.223x -0.0094	0.9997
387	y= 14.272x -0.0028	0.9998
493	y= 21.818x +0.0427	0.9993

3.2 Spectra Change and Overall Kinetics of RO-16 Degradation by Gamma Irradiation

RO-16 dye samples in water solution with an initial concentration of 0.1 mM were irradiated at a dose range of 0 to 3.5 kGy. Figure 3 shows the color changes in the RO-16 dye solution due to degradation by gamma irradiation at various doses, while Figure 4 shows the absorption spectra changes of the RO-16 solution at various doses.

It was shown that the absorption peaks both in the visible and ultraviolet regions decreased rapidly with increasing the irradiation dose. The degradation of RO-16 occurred due to the breaking bonds within the RO-16 molecules by radicals and ions generated from the water radiolysis process. The most reactive species, including $^\bullet$OH, e_{aq}^-, and $^\bullet$H played a significant role in the degradation of organic compounds [15].

Figure 3 The color change in the RO-16 dye solution due to gamma irradiation (from left to right was irradiated with dose s of 0; 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5 kGy)

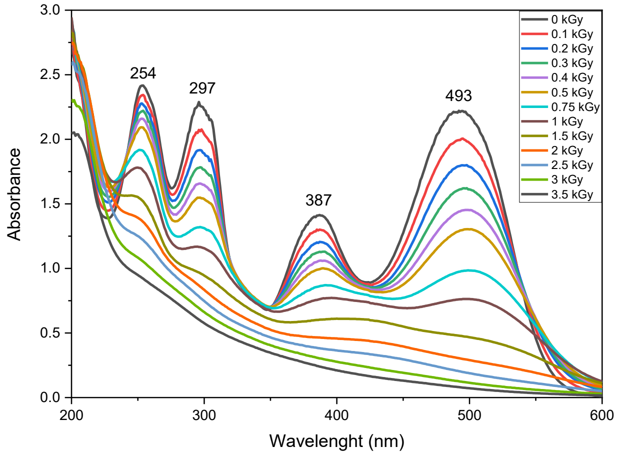


Figure 4 The change in the RO-16 spectra with increasing the irradiation dose; room temperature (29 °C); initial pH = 7.46; $[RO\text{-}16]_0 = 0.1$ mM

Figure 5 showed the comparison between the initial concentration (C_0) and the concentration after irradiation at a specific dose (C), and Table 2 provided the dose constant (d) values obtained by plotting $-ln(C/C_0)$ with irradiation dose (D).

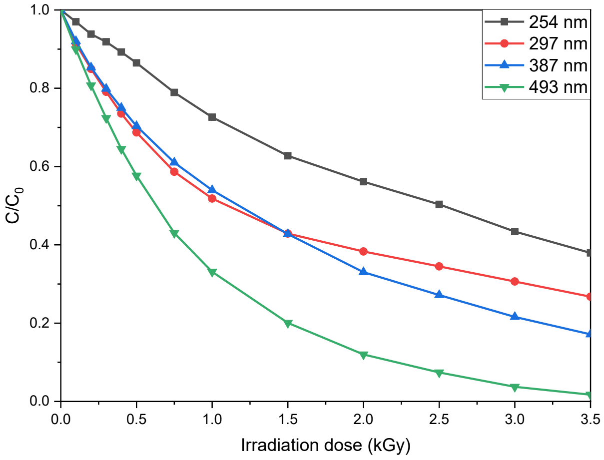
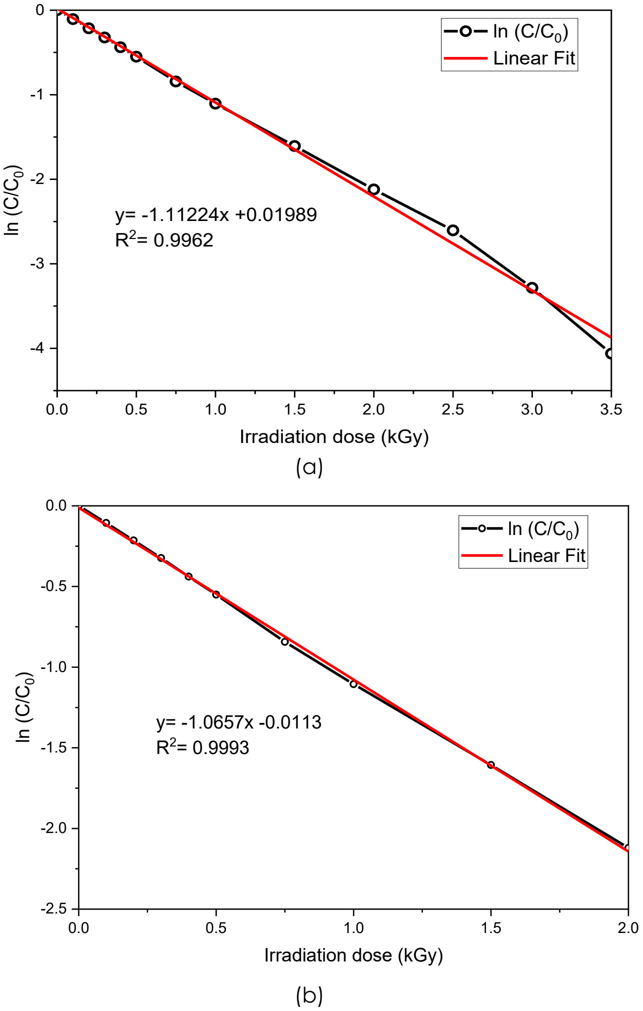


Figure 5 The change in C/C_0 RO-16 as a function of increasing irradiation dose as measured at different wavelengths; room temperature (29 °C); initial pH = 7.46; $[RO\text{-}16]_0 = 0.1$ mM

Table 2 Dose constant (d) at different wavelengths (slope of the equation of $-ln(C/C_0)$ vs irradiation dose (D) at the spectrum peak)

Wavelength (nm)	Linear Regression Equation	R^2	d (kGy^{-1})
254	y= -0.2763x -0.0136	0.9970	0.2763
297	y= -0.3651x -0.1526	0.9514	0.3651
387	y= -0.4933x -0.0773	0.9955	0.4933
493	Y= -1.1122x +0.0199	0.9965	1.1122

As seen in Table 2, the highest dose constant (d) value was at 493 nm. This wavelength is an indication of the damage to the azo chromophore group (N=N) of the RO-16 dye, leading to decolorization [7][8]. Thus, measurements of absorbance at 493 nm wavelength were used for determining the concentration changes of RO-16 in all research variables.



(a)

(b)

Figure 6 Model pseudo first order plotting at dose range (a) 0 – 3.5 kGy; (b) 0 – 2.0 kGy

Graph plotting within the dose range of 0 to 3.5 kGy provided a slightly less linear curve after the radiation dose reached 2 kGy, resulting less perfect R^2 value

(Figure 6a). Nevertheless, when the plotting was limited to 2 kGy, the R^2 value became 0.9993 with the *d* value of 1.0657 kGy^{-1} (Figure 6b). This was due to the fact that after 2 kGy of irradiation, more degradation products were formed, and the concentration of RO-16 became very low, making UV-Vis analysis less accurate for observing the remaining RO-16 concentration. This indicated the pseudo-first-order model was only suitable for the irradiation dose range of 0 - 2.0 kGy. Therefore, subsequent plotting was limited to the dose range of 0 - 2.0 kGy.

3.3 The Effect of H_2O_2 on RO-16 Degradation by Gamma Irradiation

Figure 7. presented a comparison of the degradation of RO-16 in aqueous solutions with and without peroxide and gamma irradiation. It shows significant degradation occurs in RO-16 irradiated with gamma-ray in the range of 0 to 2.0 kGy. On the other hand, adding 4 mM H_2O_2 without gamma irradiation showed almost no change in concentration or degradation, even though H_2O_2 is a strong oxidizer. This was because the concentration of added H_2O_2 was very low. Conversely, RO-16, with adding 4 mM H_2O_2 and gamma irradiation, demonstrated better degradation compared to gamma irradiation alone.

Hydrogen peroxide molecule can be dissociated into $^\bullet OH$ by gamma rays, which can react with $^\bullet H$ and e_{aq}^- generated by the radiolysis of water, transforming them into more reactive $^\bullet OH$ radical (Eq. (4-6)) [20]. The combination of H_2O_2 and gamma irradiation will demonstrate a good synergistic effect in degrading the RO-16 dye [14][23].

$$H_2O_2 \rightarrow 2\,{}^\bullet OH \quad (4)$$
$$H_2O_2 + e_{aq}^- \rightarrow {}^\bullet OH + OH^- \quad (5)$$
$$H_2O_2 + {}^\bullet H \rightarrow {}^\bullet OH + H_2O \quad (6)$$

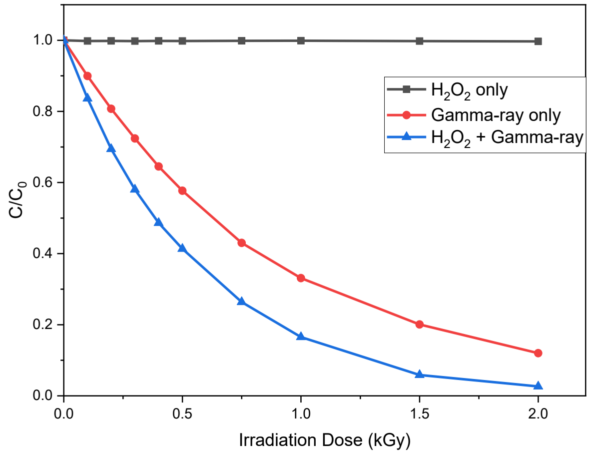


Figure 7 Removal of RO-16 with H_2O_2 only, gamma irradiation only, and combination of gamma irradiation dan H_2O_2 [RO-16]=0.1 mM, [H_2O_2]= 4 mM

This result was inline with several studies that reported the radiolytic degradation of dyes with peroxide additions. Reactive Blue-19 dye, when degraded through Cs-137 gamma irradiation, exhibited positive results with the addition of H_2O_2, and the degradation percentage increased with increasing the H_2O_2 concentration [17]. Similarly, the degradation of Congo Red dye [14] and Disperse Dye DR73 [18] through Co-60 gamma irradiation also showed positive results with the addition of oxidants H_2O_2.

Subsequently, the effect of H_2O_2 concentration was studied by observing the concentration of undegraded RO-16 after reacting with H_2O_2 at various concentrations: 1, 2, 4, 6, 8, 12, and 20 mM. Figure 8 and Table 3 showed radiolytic degradation at different concentrations of added H_2O_2, plotted on a pseudo-first-order model. The dose constant (*d*) increased with the addition of H_2O_2, reaching a maximum value at a concentration of 4 mM, where d is 1.8420 kGy^{-1} with 97% dye degradation at 2 kGy. However, with increasing on centrations of added H_2O_2, the value of d continues to decrease, as shown in Figure 9. This phenomenon leads to a reduction in the degradation percentage.

At H_2O_2 concentrations of 0-4 mM, the degradation percentage increased, reaching a maximum of 97.36% at an irradiation dose of 2 kGy and an H_2O_2 concentration of 4 mM. However, after 4 mM concentration, the degradation percentage continues to decrease, although it remains higher than without the addition of H_2O_2.

Several researchers have also reported similar findings in their studies, indicating the presence of an optimum H_2O_2 concentration in the dye degradation process. The degradation rate increased with the rising H_2O_2 concentration until it reached a critical concentration. Beyond this critical concentration, the degradation rate decreased due to an effect known as the scavenging effect [24]. Some hydroxyl radicals (•OH) can react with excess H_2O_2 through equations (7-9) [25].

$$H_2O_2 + {}^\bullet OH \rightarrow HO^\bullet_2 + H_2O \quad (7)$$
$$H_2O_2 + HO^\bullet_2 \rightarrow {}^\bullet OH + H_2O + O_2 \quad (8)$$
$$HO^\bullet_2 \text{ (or } {}^\bullet OH) + HO^\bullet_2 \rightarrow H_2O_2 \text{ (or } H_2O) + O_2 \quad (9)$$

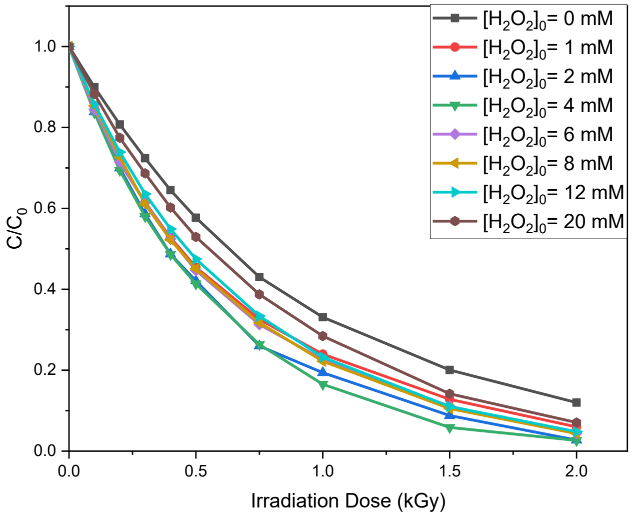


Figure 8 Removal of RO-16 with Gamma-ray/H_2O_2 at different initial concentration of H_2O_2; [RO-16] = 0.1 mM

Table 3 Dose constant (d) at different initial H_2O_2 concentrations

$[H_2O_2]_0$ (mM)	*d* (kGy^{-1})	R^2	% Degradation at 2 kGy
0	1.0657	0.9993	88%
1	1.3721	0.9983	94%
2	1.7321	0.9949	97%
4	1.8420	0.9991	97%
6	1.5164	0.9978	96%
8	1.5347	0.9989	96%
12	1.4972	0.9994	95%
20	1.3190	0.9994	93%

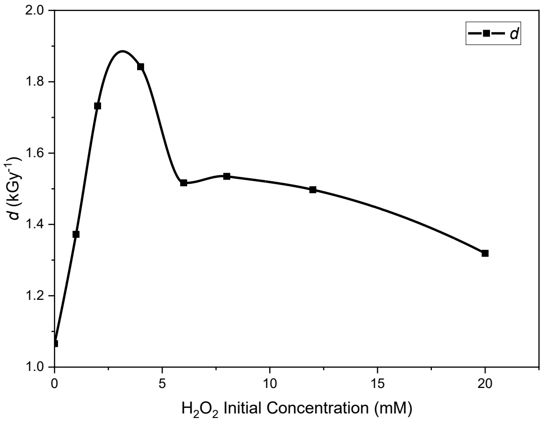


Figure 9 Dose constant (*d*) of removal RO-16 with gamma-ray/H_2O_2 at different initial concentration of H_2O_2; $[RO\text{-}16]_0$= 0.1 mM

3.4 The Effect of Initial Solution pH on RO-16 Degradation by Gamma Irradiation

pH was reported to influence the reactivity of e_{aq}^-, the percentage of •OH, and the chemical properties of the targeted contaminants [14][15][18]. Therefore, in this study, variations in the initial pH conditions of the RO-16 dye solution were conducted to understand the effects of different pH levels on the kinetics of RO-16 degradation. pH was adjusted by adding $HClO_4$ to achieve acidic conditions and adding NaOH to achieve alkaline conditions. At a solution pH of 7.46, it represented the original pH of the RO-16 dye solution without adding the acid or base.

Changes in solution pH with increasing irradiation dose under various initial pH conditions were presented in Figure 10. After irradiation at a dose of 2.0 kGy, the pH decreased from 7.46 to 3.96 in a neutral medium, from 3.98 to 3.51 in a weak acid medium, and from 8.85 to 6.84 in a weak alkaline medium. However, in strong acid (pH 2.22) and strong alkaline (pH 10.24) media, there was no notable change in pH.

The significant decrease in solution pH in neutral, weak acid, and weak alkaline media was likely attributed to the organic and inorganic acids as by-products resulting from irradiated RO-16. These degradation products at these pH conditions contributed to the observed pH decrease. Meanwhile, in a strongly alkaline medium, the weak organic acids formed may not be sufficient to neutralize the strong base, resulting in no significant change in pH.

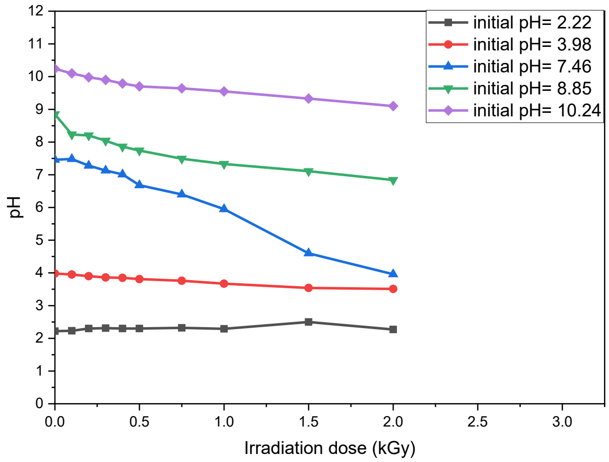


Figure 10 Changes in pH solution with increasing irradiation dose under various initial pH conditions. $[RO\text{-}16]_0$ = 0.1 mM

Figure 11 and Table 4 depict radiolytic degradation under various initial pH conditions, plotted on the pseudo-first-order model. The largest dose constant (*d*) result is at an initial pH of 2.22 with a dose constant value of 1.2825 kGy^{-1}. The dose constant found decreases with increasing initial pH. The percentage degradation observed that the highest degradation occurs at pH 2.22, corresponding to strong acidic conditions, with a degradation percentage of 92% at a radiation dose of 2.0 kGy. Meanwhile, the lowest degradation is obtained at pH 10.24, corresponding to strong alkaline conditions, with a degradation percentage of 83% at a radiation dose of 2.0 kGy.

This finding aligns with previous research indicating that the medium's pH has a promising effect on pollutant degradation. Reported in degradation of Disperse Dye DR73 [18], Congo Red [14], and Reactive

Blue-19 [17] dyes in textile wastewater are observed that dye degradation is pH-dependent, and the optimum value is obtained in acid pH conditions. The enhancement of dye degradation with a decrease in pH indicates that under acidic conditions, e_{aq}^- is likely to react with H^+, producing $^{\bullet}H$. Therefore, recombination reactions between e_{aq}^- and $^{\bullet}OH$ are limited, leading to an increased concentration of $^{\bullet}OH$ radicals[17][18]. In more alkaline solutions (higher pH), some $^{\bullet}OH$ radicals will convert to less reactive $^{\bullet}O^-$ radicals, resulting in a decreased rate of RO-16 degradation [15].

$$^{\bullet}OH \leftrightarrow H^+ + {}^{\bullet}O^- \qquad (10)$$

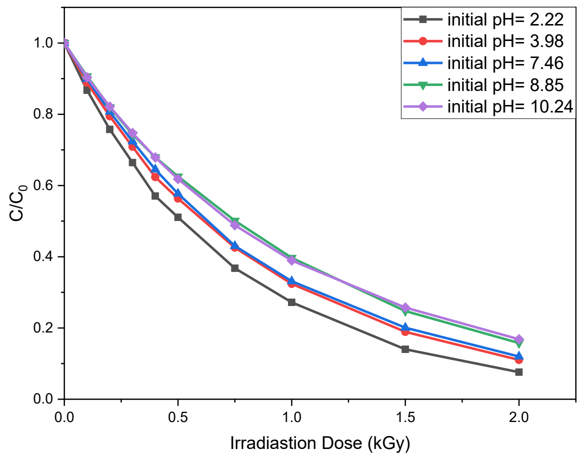


Figure 11 Removal of RO-16 with Gamma-ray at different initial pH solutions; [RO-16]= 0.1 mM

Table 4 Dose constant (*d*) at different initial pH solutions

Initial pH	*d* (kGy^{-1})	*R*^{2}	% Degradation at 2 kGy
2.22	1.2825	0.9997	92%
3.98	1.1004	0.9998	89%
7.46	1.0657	0.9993	88%
8.85	0.9199	0.9998	84%
10.24	0.8908	0.9990	83%

3.5 The Effect of Initial Concentration on RO-16 Degradation by Gamma Irradiation

Studying the optimal initial dye concentration becomes a crucial parameter in determining degradation efficiency. The influence of the initial concentration of the reactant (RO-16) on the dye degradation efficiency was investigated in the concentration range of 0.05 to 0.15 mM, with an irradiation dose range of 0 to 2.0 kGy without pH conditioning (at the original pH of 7.46).

Figure 12 and Table 5 showed radiolytic degradation under various initial concentrations of RO-16. Plotting on the pseudo-first-order model resulted in the dose constant (*d*) continuously decreasing with increasing the initial RO-16 concentrations. The highest percentage degradation of RO-16 was obtained at an initial concentration of 0.05 mM, reaching 99% at a radiation dose of 2.0 kGy. Meanwhile, the lowest degradation is observed at an initial concentration of 0.15 mM, reaching 77% at a radiation dose of 2.0 kGy.

This finding aligned with previous research that the degradation of several dyes (Congo Red, Reactive Black 5, and Reactive Blue 15) using gamma irradiation obtained similar results, indicating that at higher dye concentrations, the degradation rate was lower [14][26]. The decrease in degradation efficiency (%) and dose constant values at higher initial concentrations might be caused by a decrease in the ratio of reactive radicals to target molecule RO-16. Moreover, there was a greater reaction competition of reactive radicals with the target molecule (RO-16) and its degradation products.

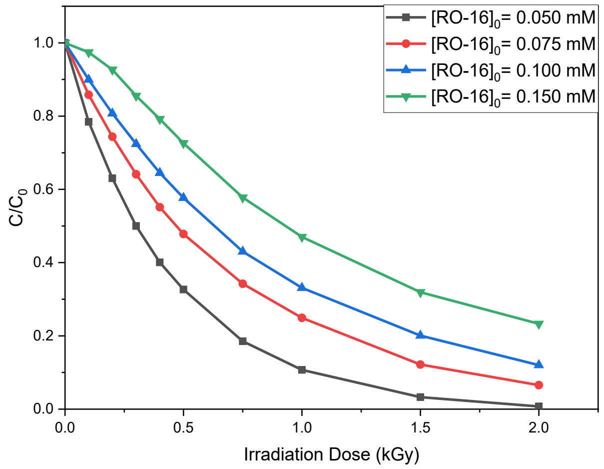


Figure 12 Removal of RO-16 with Gamma-ray at different initial RO-16 Concentrations

Table 5 Dose constant (*d*) at different initial RO-16 Concentrations

[RO-16]$_0$ (mM)	*d* (kGy^{-1})	*R*^{2}	% Degradation at 2 kGy
0.050	2.3909	0.9970	99%
0.075	1.3642	0.9994	93%
0.100	1.0657	0.9993	88%
0.150	0.7694	0.9961	77%

3.6 The Effect of Inorganic Anions on RO-16 Degradation by Gamma Irradiation

The dye degradation by conventional AOPs has shown that the presence of additives in the solution matrix also affected dye degradation. These additives are typically present in the form of ions added to the dye solution to enhance industrial processes. The presence of ions such as CO_3^{2-} and HCO_3^-, for example, which are usually added to dye baths to adjust the solution pH. The presence of inorganic anions can influence the degradation efficiency of the dye.

The study on the influence of inorganic anions presence on the dye degradation efficiency was conducted at an RO-16 concentration of 0.1 mM and without pH conditioning (recorded pH at 7.46). The ions studied include the ions: Cl^- (from NaCl), CH_3COO^- (from CH_3COONa), HCO_3^- (from $NaHCO_3$), CO_3^{2-} (from Na_2CO_3), dan NO^{3-} (from $NaNO_3$) with 1 mM initial concentrations.

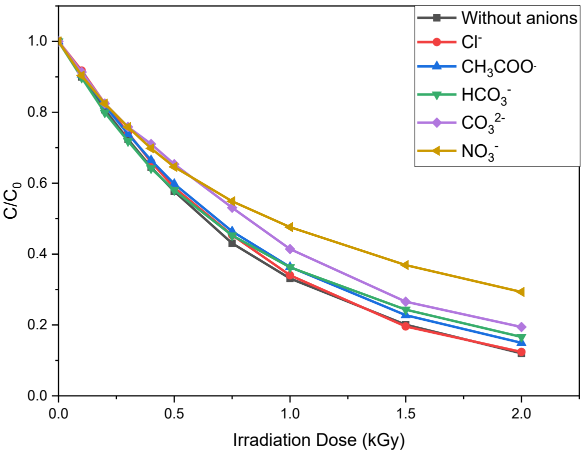


Figure 13 Effects of inorganic anions on the removal of RO-16 by gamma-ray; $[RO\text{-}16]_0$=0.1 mM, $[Cl^-]_0$= $[CH_3COONa]_0$= $[HCO_3^-]_0$= $[CO_3^{2-}]_0$= $[NO_3^-]_0$= 1 mM

Table 6 Dose constant (*d*) at different inorganic anions

$[Anions]_0$ (1 mM)	*d* (kGy^{-1})	R^2	% Degradation at 2 kGy
Without anions	1.0657	0.9993	88%
Cl^-	1.0676	0.9991	88%
CH_3COO^-	0.9612	0.9986	85%
HCO_3^-	0.8994	0.9942	83%
CO_3^{2-}	0.8363	0.9973	81%
NO_3^-	0.6058	0.9831	71%

The presence of inorganic anions inhibited the removal of the dye by gamma-ray was observed in the following order, $NO_3 \rightarrow CO_3^{2-} \rightarrow HCO_3^- \rightarrow CH_3COO^- \rightarrow Cl^-$ as seen in Figure 13 and Table 6. The presence of NO_3^- gave the largest inhibitory effect with the dose constant value was 0.6058 kGy^{-1} and 71% of dye degradation at 2.0 kGy irradiation. On the contrary, Cl^- slightly enhanced RO-16 degradation. Meanwhile, it is known that chloride ions can scavenge hydroxyl radicals and consequently inhibit dye [27][28], chlorine can also directly attack RO-16 molecules and contribute to their degradation [29][30]. In this experiment, the value of *d* in the presence of Cl^- had the same percentage of degradation as in the absence of anions, namely 88%.

This result, inline with previously reported in different dyes, indicated that the dose constant (*d*) decreases in the presence of other ions. With the presence of these ions, the efficiency of dye degradation also diminished because these ions capture the •OH radicals, leading to a decrease in the degradation percentage [15][14].

$$Cl^- + {}^\bullet OH + H^+ \rightarrow Cl^\bullet + H_2O \qquad (11)$$

$$CH_3COO^- + {}^\bullet OH \rightarrow CH3COO^\bullet + OH^- \qquad (12)$$

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^{\bullet -} + H_2O,\ k = 8.5 \times 10^6\ M^{-1}\ s^{-1} \qquad (13)$$

$$CO_3^{2-} + {}^\bullet OH \rightarrow CO_3^{\bullet -} + OH^-,\ k = 3.9 \times 10^8\ M^{-1}\ s^{-1} \qquad (14)$$

$$NO_3^- + {}^\bullet OH \rightarrow NO_3^\bullet + OH^- \qquad (15)$$

The kinetic constant values obtained from the pseudo-first-order model under experimental conditions were used to calculate the concentration of RO-16 (calculated C). The difference between the experimental concentration of RO-16 (data C) and the calculated concentration of RO-16 is determined. The average percentage error (deviation) is below 10%. This is also evident from the R^2 values, which are close to 1 (one). This demonstrates that the pseudo-first-order model adequately represents the degradation phenomenon of RO-16 under experimental conditions.

4.0 CONCLUSION

The findings presented in this manuscript demonstrate the effective application of the gamma rays for decolorizing the aqueous solution containing the azo dye Reactive Orange 16. The study revealed that the decolorization rate is notably influenced by factors such as initial concentrations of dye solution and hydrogen peroxide, initial pH, as well as the presence of inorganic anions. The decolorization process adheres to pseudo-first-order reaction kinetics, with optimal peroxide concentration in the range of 2 - 4 mM with 0.1 mM initial concentration of RO-16 dye. Degradation of 88% RO-16 dye with 0.1 mM initial concentration, was achieved at 2.0 kGy irradiation dose and 97.4% degradation in the presence of 4 mM peroxide. The dose constant (d) for those degradation processes was 1.0657 kGy^{-1} and 1.8420 kGy^{-1} respectively. Faster color removal was observed in solutions with acidic pH solutions. The pseudo-rate dose constant (*d*) exhibited a decrease with increasing initial dye concentration. The effect of hydroxyl radical scavenging by the examined inorganic anions increased in the order of chloride (Cl^-) acetate (CH_3COO^-) < bicarbonate (HCO_3^-) < carbonate (CO_3^{2-}) < nitrate (NO_3^-). The further research to be conducted on this topic involves identifying the degradation by-products of RO-16 and discovering possible degradation paths to further understand the mechanisms of the reactions occurring.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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