REMOVAL OF CRYSTAL VIOLET DYE FROM AQUEOUS SOLUTION BY GAMMA IRRADIATION

FAIZA REHMAN[1], MURTAZA SAYED[1], JAVED ALI KHAN[1], HASAN M. KHAN[1]**

[1]*Radiation and Environmental Chemistry Laboratory, National Centre of Excellence in Physical Chemistry,*
University of Peshawar, 25120, Pakistan
[2]*National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120, Pakistan*

ABSTRACT

In this study the radiation-induced degradation of crystal violet (CV) dye under various experimental conditions has been investigated. $D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ values suggests that lower doses are required for 50%, 90% and 99% removal of CV dye when the sample solution contains excessive amount of $^{\bullet}$OH radicals. The removal efficiency of CV dye in terms of G-values was also calculated under each reaction conditions. The results showed that $^{\bullet}$OH radicals are playing effective role in the degradation of CV dye as compared to e_{aq}^{-} and $^{\bullet}$H radicals. The gamma irradiation process effectively degraded CV dye at all pH values. The organic byproducts were examined and accordingly degradation pathway was proposed.

Keywords: Crystal violet dye, gamma irradiation, $^{\bullet}$OH-radicals, removal efficiency.

1. INTRODUCTION

Water pollution have gained lot of attention worldwide because wastewaters from various industrial sectors cause serious environmental and health problems. The wastewater from textile industry containing even very low concentration of dyes can cause waste streams to become intensely colored. Besides from their negative visual effects, these compounds are highly non biodegradable and mostly carcinogenic and mutagenic in nature [1].

In textile industry synthetic dyes are used as colouring material. It is estimated that annually about 1 million tons of these dyes are produced, of which 50,000 tons are lost in effluents during application and manufacturing, 5−15% of which are directly released into the environment without any adequate treatment [2]. The organic groups present in dyes results in mortality, genotoxicity, mutagenicity and carcinogenicity , so it is necessary to remove these organic pollutants from wastewaters before discharge to major water bodies (e.g., lakes, rivers or oceans). Different processes which are involve in textile production like dyeing and washing results in the production of large quantities of wastewater along with different toxic chemicals [3].

In textile industry, a major class of commercial dyes is crystal violet (CV), which is used for different purposes, such as for dermatological agent, veterinary medicine, biological staining, additive in poultry feed to reduce spread of fungus, mold and intestinal parasites and for textile dying and paper printing. However, due to poor treatment techniques for the purification of CV containing wastewater from industries it is frequently detected in surface water [4]. This dye is cationic in nature and is more toxic than anionic dye as it can easily interact with negatively charged membrane surfaces and can enter into cells and concentrate in cytoplasm [5].

Several techniques have been applied for the removal of CV from wastewater which includes physical , chemical and biological techniques [6]. Conventional methods include wet air oxidation, catalytic processes, biochemical processes, biological processes and physical adsorption for the removal of dyes from aquatic environment. Biological treatment is not a complete solution to the wastewater pollution problem because majority of dyes are non biodegradable [7]. However, a new treatment technology called Advanced Oxidation Processes (AOPs), like Fenton, electro-Fenton and photo-Fenton processes, and combinations of O_3 (or H_2O_2) with UV radiation and/or TiO_2, among others, are very effective for the treatment and elimination of textile dyes from water [8]. These processes in a very short reaction time are capable to completely decolorize and partially mineralize the textile industry dyes. AOPs involve the production of $^{\bullet}$OH radical, a powerful and non-selective oxidant that can be degrade almost all organic pollutants [9].

Gamma irradiation technology, as an advanced oxidation process, has been recognized as a promising process for hazardous organic wastewater treatment. It is well known that most colored materials undergo bleaching or color changes when exposed to ionizing radiation. Therefore, gamma and electron beam irradiation can be considered as methods for the treatment of wastewater from textile industries. Extensive research work has been carried out in literature on the radiation-induced decoloration and degradation of aqueous solutions of dyes [10].

2. MATERIALS AND METHODS

2.1. Chemicals

CV was obtained from sigma aldrich. The chemical structure of CV dye is presented in the inset of Fig. 1. *iso* - propanol, *tert* - butanol and sulphuric acid were taken from BDH. Ferrous sulphate heptahydrate was obtained from Scharlau. Sodium Chloride and potassium dichromate used in this work were of Merck. All chemicals were of analytical reagent grade and used as received without further purification. Milli-Q **(**resistivity ≥ 18.2 MΩ cm**)** water was used during preparation of all CV samples. Nitrogen and nitrous oxide gasses used in the present study were of at least 99.999 % purity.

2.2. Irradiation experiments

CV containing aqueous sample solutions were placed into 15 mL pyrex glass tubes and irradiated with a ^{60}Co gamma-irradiation source (National Institute for Food and Agriculture, Peshawar) with dose rate of 294 Gy/min. The dose rate was calculated by Frickie dosimetry [11]. All the experiments were performed at natural pH of the sample solution (pH = 5.8) in triplicate.

2.3. Analyses of gamma-irradiated samples

The CV samples obtained after gamma irradiation procedures were then analyzed by double beam UV-Visible spectrophotometer (Perkin Elmer, Lambda 650). The UV-Visible spectrophotometer was calibrated for absorbance scale by $K_2Cr_2O_7$ and wavelength scale by holmium oxide filter in the wavelength range of 260 - 800 nm. The UV-absorption spectrum of 3.5 × 10^{-5} M CV dye gives strong absorption peak at 588 nm as shown in Fig.1.

2.4. Calculation of dose constant

The removal of CV dye by gamma irradiation can usually be expressed by equation 1 [12] . The dose constant, *k*, is the slope of natural logarithm (ln) of the compound concentration versus absorbed dose.

$$\ln(C/C_0)=-kD \qquad (1)$$

where *C* is the concentration after gamma irradiation (M), C_0 the initial concentration (M), *k* the dose constant (Gy^{-1}) and D is the absorbed dose (Gy).

Dose constants were used to calculate the absorbed doses required for 50%, 90% and 99% degradation of CV ($D_{0.5,\ D0.9 \text{ and } D0.99}$ values) by using equations (3), (4) and (5), respectively [12].

$$D_{0.5} = (\ln 2) / k \qquad (2)$$
$$D_{0.9} = \ln(10) / k \qquad (3)$$
$$D_{0.99} = \ln(100) / k \qquad (4)$$

2.5. Calculation of G-Value

G value is defined as the number of molecules formed or destroyed by absorbing 100 eV of energy [13]**.** The degradation efficiency of pollutant removal can be described by G-value during ionizing radiation calculated by equation (5) [14].

$$G = 6.023\times10^{23}\Delta R/6.24\times10^{16}D \qquad (5)$$

e-mail: hmkhan@upesh.edu.pk

where ΔR is defined as change in concentration of the CV (M); D is the absorbed dose (Gy); 6.24×10^{16} is the conversion factor from "Gy" to "100 eV/L"; and 6.023×10^{23} is the Avogadro's constant.

2.6. Probability calculations for the determination of concentration of added scavenger

Competition kinetics was applied to determine the concentration of added scavenger (*tert*-BUOH/ *iso*-PrOH) that can effectively compete with CV dye for $^{\bullet}$OH radicals.

When water sample is gamma - irradiated $^{\bullet}$OH radicals are produced that rapidly reacts with the CV dye and added scavenger (*tert*-BUOH or *iso* -PrOH in the present case) at rate constants K_1 and K_2 , respectively.

$$^{\bullet}\mathrm{OH} + \mathrm{CV} \xrightarrow{k_1} \mathrm{Products}$$

$$^{\bullet}\mathrm{OH} + \text{tert-BUOH / iso - PrOH} \xrightarrow{k_2} \mathrm{Pr}\,oducts$$

The probability that the added scavenger effectively scavenges the amount of OH radicals from aqueous solution can be represented by equation (6) [15].

$$P_{(^{\bullet}OH\rightarrow tert-BUOH/iso-\mathrm{Pr}OH)} = \frac{k_1[^{\bullet}OH][\text{tert}-\text{BUOH/ iso}-\text{PrOH}]}{k_1[^{\bullet}OH][\text{tert}-\text{BUOH/ iso}-\text{PrOH}]+\mathrm{k}_2[^{\bullet}\,\mathrm{OH}][\mathrm{CV}]} \quad (6)$$

OR,

$$P_{(^{\bullet}OH\rightarrow tert-BUOH/iso-\mathrm{Pr}OH)} = \frac{k_1[\text{tert}-\text{BUOH/ iso}-\text{PrOH}]}{k_1[\text{tert}-\text{BUOH/ iso}-\text{PrOH}]+\mathrm{k}_2[\mathrm{CV}]} \quad (7)$$

Substituting the values of k_1 as 8×10^9 $M^{-1}s^{-1}$ [16], k_2 as 5.5×10^8 $M^{-1}s^{-1}$ (using *tert*-BUOH as scavenger) or 6.3×10^8 $M^{-1}s^{-1}$ (using *iso*-PrOH as scavenger) [17] and concentration of CV dye as 3.5×10^{-5} M. The concentration of added *tert*-BUOH or *iso*-PrOH was found to be 10^{-2} M that scavenges nearly 90 % of $^{\bullet}$OH from CV dye containing aqueous solution.

3. RESULTS AND DISCUSSION

During water radiolysis following type of major reactive species, shown in equation (8) are produced. These species then attack the target pollutant and causes its degradation [18].

γ-ray
H_2O.... ^....^...>e^{-}_{aq}(2.6), $^{\bullet}$H (0.55), $^{\bullet}$OH(2.7), H_2(0.45), H_2O_2(0.71), H_3O^+(2.6)
(8)

The number in parenthesis indicates the G-values in molecules / 100 eV corresponding to each species. Among these species the main radicals are e_{aq}^{-}, $^{\bullet}$OH and $^{\bullet}$H. The most interesting advantage of the gamma irradiation process is that it simultaneously generates oxidizing specie such as $^{\bullet}$OH radical and reducing specie such as e_{aq}^{-} in a same system. In a pH range of 3~11, radiolysis of air-free water leads to the formation of a suite of radical species. Hydroxyl radicals preferentially attack the aromatic ring because of their electrophilicity to form hydroxyl-adducted products or ring-opened products. On the other hand, hydrated electrons and hydrogen atoms have less reactivity to the aromatic ring but demonstrate particularly sensitive to well halogenated organic compounds and heavy metals in wastewater [19].

3.1 Reaction of CV dye with $^{\bullet}$OH radicals

In a typical experiment, 3.5×10^{-4} M CV solution was saturated with N_2O gas prior to irradiation procedures and then gamma irradiated with absorbed doses up to 400 Gy The samples were then analyzed by UV-Visible spectrophotometer immediately after gamma -irradiation.

Under this condition all the e_{aq}^{-} are converted into $^{\bullet}$OH radical and thus the concentration of $^{\bullet}$OH radical become higher in the gamma irradiated CV solution as shown by equation (9) [20].

$$N_2O + e_{aq}^{-} \rightarrow {}^{\bullet}OH + {}^{-}OH + N_2 \qquad k = 9.1\times10^9\ M^{-1}s^{-1} \quad (9)$$

The degradation course of CV in dependence of the absorbed dose is shown in Figure 2. It can be seen that in the presence of excess amount of $^{\bullet}$OH radicals nearly 56 % of CV dye was degraded at absorbed dose of 400 Gy.

$D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ for degradation of CV when the sample solution contains high amount of $^{\bullet}$OH radicals are tabulated in table 1. Which shows that 50 %, 90 % and 99 % of CV dye degradation can be achieved at absorbed doses of 315 Gy, 1046 Gy and 2093 Gy, respectively.

Table 2 shows the variation of G values of CV at different absorbed doses. A continuous decreasing trend in G-values was observed from 0.53 - 0.36 molecules/100 eV at absorbed doses from 100 - 400 Gy. This decreasing trend in G-values might be due to the fact that as the absorbed dose increases the concentration of target pollutant (CV) decreases and the concentration of by-products increases which then competes with the CV molecule for reactive radical [21].

3.2 Reaction of CV with $^{\bullet}$H radicals

To investigate the involvement of $^{\bullet}$H radicals in the degradation of CV dye. The dye sample solution was bubbled with N_2O gas and spiked with 10^{-2} M of *tert*-BUOH. Under this condition e_{aq}^{-} and $^{\bullet}$OH radicals are scavenged by N_2O gas and *tert*-BUOH according to equations (9) and (10), respectively [20]. SO, only $^{\bullet}$H radicals are available for reaction with CV dye as it has very slow reaction with *tert* - BUOH indicated by equation (11) [17].

tert-BUOH + $^{\bullet}$OH → $^{\bullet}CH_2C(CH_3)_2OH + H_2O$ $k = 5.5\times10^8\ M^{-1}\ s^{-1}$ (10)
tert-BUOH + $^{\bullet}$H → $^{\bullet}CH_2C(CH_3)_2OH + H_2$ $k = 9\times10^4\ M^{-1}\ s^{-1}$ (11)

The radicals formed as a byproducts of *tert*-BuOH reaction with $^{\bullet}$OH and $^{\bullet}$H radicals are assumed to be inert [22].

The % degradation plot of CV when aqueous system contains only $^{\bullet}$H radicals is shown in Fig. 3. The figures shows that nearly 3 % of CV molecules was degraded at absorbed dose 400 Gy. Which also indicates very less involvement of $^{\bullet}$H radicals in the degradation of CV dye. The $D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ values for the degradation of CV dye by $^{\bullet}$H radicals were found to be 1386 Gy, 4605 Gy and 9210 Gy, respectively as given in table 1. Which are higher than the values when the aqueous system contains excessive amount of $^{\bullet}$OH radicals. The G-values for the aqueous system containing $^{\bullet}$H radicals (*tert*-BUOH/ N_2O) are given in table 2 with absorbed doses from 100 to 400 Gy. The G-values were found to be in the range of 0.07 - 0.13 molecules/100 eV at absorbed doses from 100 - 400 Gy. Which are lower as compared to the case when CV dye was degraded in oxidative environment probably due to lower reactivity of $^{\bullet}$H-radicals towards CV dye molecule.

3.3 Reaction of CV with $^{\bullet}$H radicals and e^{-}_{aq}

In this experiment, nitrogen saturated CV solution (3.5×10^{-5} M) containing *tert*-BuOH (1×10^{-2} M) as $^{\bullet}$OH radical scavenger was gamma irradiated at different absorbed doses (100 - 400 Gy). In N_2-saturated solution all the three reactive species i.e. $^{\bullet}$OH radicals, e_{aq}– and $^{\bullet}$H radicals have equal chances of reaction with CV dye molecule [17]. However, *tert*-BUOH scavenges $^{\bullet}$OH radical as shown by equation (10) and thus mainly 83 % e_{aq}^{-} (G = 2.6) and 18 % $^{\bullet}$H atoms (G = 0.5) are involved in the degradation process.

Fig. 4 shows % degradation of CV dye versus absorbed dose. The results shows that 14.37 % of CV dye was degraded at absorbed dose of 400 Gy. The doses required for 50 % , 90 % and 99 % removal of CV dye from aqueous solution containing $^{\bullet}$H radical and e_{aq}^{-} were calculated to be 990 Gy, 3289 Gy and 6578 Gy respectively and are given in table 1. The removal efficiency presented in terms of G-values are given in table 2 which shows a decreasing trend from 0.07 - 0.13 molecules / 100 eV with the increase in the absorbed dose from 100 - 400 Gy.

3.4 Reaction of CV with $^{\bullet}$OH radicals and $O_2^{\bullet-}$

A sample solution containing 3.5×10^{-5} M of CV dye was gamma irradiated in the presence of air, ($O_2 = 1.25\times10^{-3}$ mol dm^{-3}) with absorbed doses up to 400 Gy and then analyzed by UV - Visible spectrophotometer to measure the changes in the absorption spectra of CV dye.

In aerated media all the e_{aq}^{-} and $^{\bullet}$H are converted to peroxyl radicals and superoxide radicals as shown by equations (12) and (13)), respectively [19].

$$^{\bullet}H + O_2 \rightarrow HO_2^{\bullet} \qquad k = 2.1\times10^{10}\ M^{-1}s^{-1} \quad (12)$$

$$e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet-} \qquad k = 1.9\times10^{10}\ M^{-1}s^{-1} \quad (13)$$

$$HO_2 \approx H^{+} + O_2^{\bullet-} \qquad pK = 4.8 \quad (14)$$

The plot showing % degradation of CV dye at various absorbed doses is presented in Fig. 5. At absorbed dose of 400 Gy nearly 47 % of CV dye was degraded. $D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ values for air - saturated aqueous solution of CV dye were calculated as 495 Gy, 1644 Gy and 3289 Gy , respectively and are given in table 1. Under this conditions the G-values were in the range of 0.35 - 0.31 molecules / 100 eV at absorb doses from 100 - 400 Gy as shown in table 2.

3.5 Reaction of CV with $^{\bullet}$OH radicals, e_{aq}^- and $^{\bullet}$H radicals

Aqueous solution of CV dye (3.5×10^{-5} M) was bubbled with N_2-gas for 20 minutes and then was gamma irradiated for different absorbed doses. In N_2 saturated solution, all the three primary reactive species i.e. $^{\bullet}$OH radicals, $^{\bullet}$H radicals and e_{aq}^- are playing their role in the degradation of CV dye [23]. At absorbed dose of 400 Gy, 36 % degradation of CV dye was observed as shown in Fig. 6. Under these conditions 46 % $^{\bullet}$OH (G = 2.7), 44 % e_{aq}^- (G = 2.6) and 8 % $^{\bullet}$H (G = 0.5) are operative for degradation of CV dye. By using equation (2), (3) and (4) $D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ values for the removal of N_2 saturated aqueous CV dye solution were calculated as 462 Gy, 1535 Gy and 3070 Gy, respectively as given in table 1. The G-values for the removal of CV dye from aqueous solution was calculated in the range of 0.17 - 0.22 molecules / 100 eV with absorbed doses from 100 - 400 Gy. The removal efficiency (G-value) was decreased from 0.17 to 0.14 molecules / 100 eV when the absorbed dose was increased from 100 to 400 Gy. Which is in accordance with previous reported results for destruction of methyl *tert*-butyl ether in water in presence of chloroform [21].

3.6 Reaction of CV with e_{aq}^-

The role of e_{aq}^- in the degradation of CV dye was examined by purging the sample solution with N_2 gas for 20 minutes. In this experiment the N_2 - saturated CV dye solution was spiked with 10^{-2} M *iso*-propanol solution. iso-propanol scavenges $^{\bullet}$OH radicals and $^{\bullet}$H atoms by a very fast reaction as shown in the equation (15) and (16), respectively [17]. So, under these conditions mainly e_{aq}^- are involved in the degradation of CV dye.

$$^{\bullet}OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2C^{\bullet}OH \quad k = 6.3\times10^{8}\ M^{-1}\ s^{-1} \qquad (15)$$

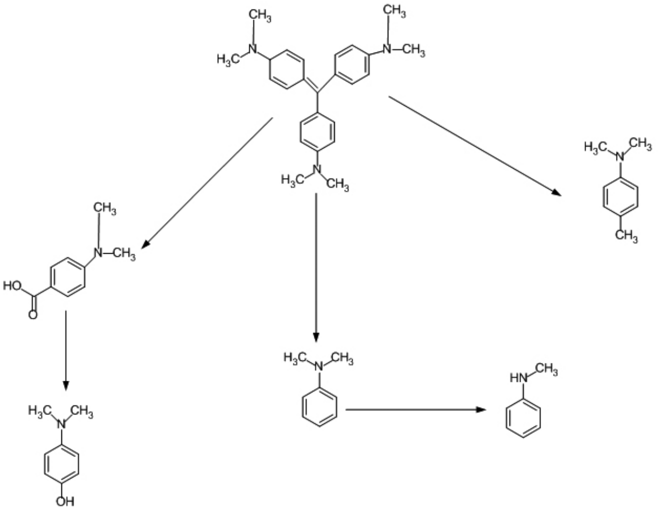
$$^{\bullet}H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2C^{\bullet}OH \quad k = 1.6\times10^{9}\ M^{-1}\ s^{-1} \qquad (16)$$

Fig. 7 shows % degradation of CV dye solution at different absorbed doses. From this Fig. it can be seen that 10.76 % degradation of CV dye can be achieved at absorbed dose of 400 Gy. Under these conditions the doses required for 50 % ($D_{0.5}$), 90 % ($D_{0.9}$) and 99 % ($D_{0.99}$) degradation of CV dye are 231 Gy, 767 Gy and 1535 Gy, respectively as given in table 1. Table 2 shows variations in G-values for the removal of N_2-saturated CV dye from aqueous solution spiked with 10^{-2} M *iso*-propanol. The G-values obtained under reductive environment (e_{aq}^- reactions) were lower than the oxidative environment ($^{\bullet}$OH radical reactions) which shows that removal efficiency of e_{aq}^- for removing CV dye from aqueous solution is not as effective as $^{\bullet}$OH radical.

Fig. 8 shows comparative removal of CV dye from aqueous solution under different reaction conditions. The decay constant ($k_{obs.}$) for the removal of CV dye from aqueous solution was found in the order of N_2O > Air > N_2 > *iso* - PrOH/N_2 > *tert* - BUOH/N_2 > *tert* - BUOH / N_2O. The highest % degradation of CV dye in N_2O saturated media is due to high concentration of $^{\bullet}$OH radicals availability for reaction with CV dye.

Degradation pathway of CV dye

Identification of main byproducts of CV dye was done by using HPLC-Ms analytical tool. 10 mg L^{-1} of CV dye at natural pH (pH = 6.4) was introduced into HPLC-MS. Five degradation byproducts were originated; N-methyl aniline, N,N-dimethyl aniline, 4-methyl-N,N-dimethylaniline, 4-dimethylamino phenol, and 4-dimethylamino benzoic acid. Fan and co-workers [24] also investigated similar byproducts during degradation of CV dye by Fenton processes. The formation of these by-products suggests that during degradation of CV dye, the main specie involve in the degradation process is $^{\bullet}$OH radical. The evaluated degradation products are arranged to establish a degradation pathway (as given in scheme 1).



Scheme 1: Proposed degradation pathway of CV by gamma irradiation.

CONCLUSIONS

The removal of CV dye from aqueous solution as a function of absorbed dose has been investigated under various experimental conditions. The highest removal efficiency was observed when the CV dye solution is saturated with N_2O gas and then gamma-irradiated. All the three main reactive species i.e. $^{\bullet}$OH radicals, e_{aq}^- and $^{\bullet}$H radicals are playing their role in the degradation of CV dye. However, $^{\bullet}$OH radicals were observed to be the dominant species in the removal of CV dye. The $^{\bullet}$OH-radical scavengers like *tert*-BUOH and *iso*-PrOH restrained the degradation process of CV dye.

ACKNOWLEDGEMENTS

Authors are highly thankful to Higher Education Commission (HEC) of Pakistan and Director NCE Physical Chemistry, University of Peshawar ,Pakistan for providing research facilities.

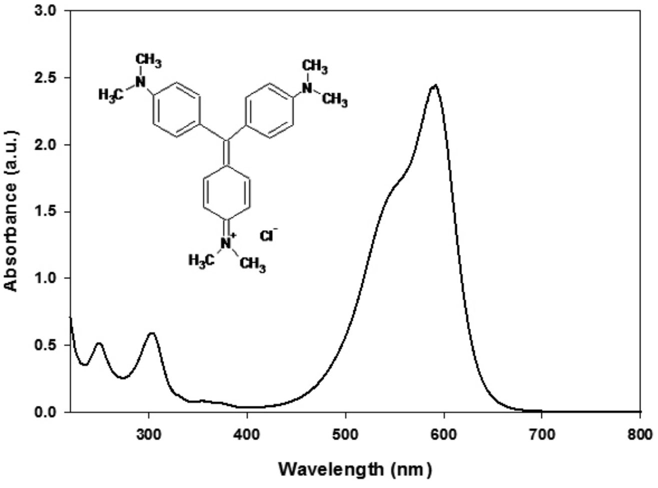


Fig.1 UV absorption spectra of CV dye aqueous solution, inset shows molecular structure of CV dye.

Table. 1 $D_{0.5}$, $D_{0.9}$ and $D_{0.99}$ values for the removal of CV dye from aqueous solution under different experimental conditions.

Absorbed dose (Gy)		**Air - saturated**	**N_2 - saturated**	**N_2O - saturated**	***iso*-PrOH / N_2**	***tert* -BUOH / N_2**	***tert*-BUOH / N_2O**
0 - 400	**$D_{0.5}$ (Gy)**	495	462	315	231	990	1386
	$D_{0.9}$ (Gy)	1644	1535	1046	767	3289	4605
	$D_{0.99}$ (Gy)	3289	3070	2093	1535	6578	9210

Table. 2 G-values for the removal of CV dye from aqueous solution under different experimental conditions.

Absorbed dose (Gy)	**G -Value (molecules/ 100 eV)**					
	Air - saturated	**N_2 -saturated**	**N_2O -saturated**	***iso*-PrOH/ N_2**	***tert*-BuOH/ N_2**	***tert*-BuOH/ N_2O**
0	-	-	-	-	-	-
100	0.35	0.17	0.53	0.09	0.07	0.07
200	0.39	0.15	0.44	0.12	0.11	0.11
400	0.31	0.14	0.36	0.08	0.13	0.13

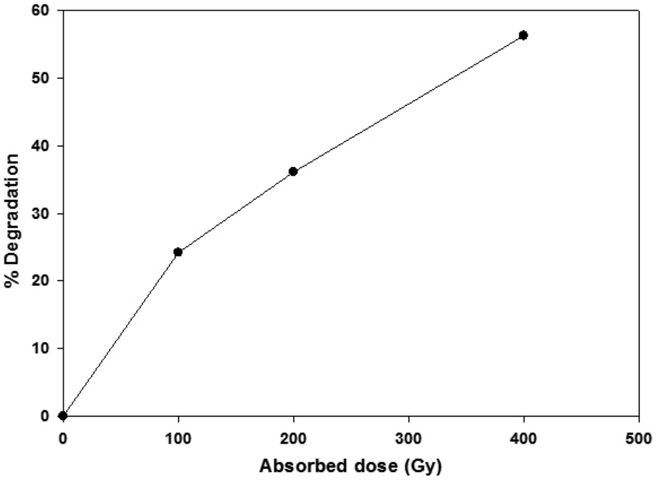


Fig. 2 Degradation of N_2O saturated aqueous solution of CV dye.

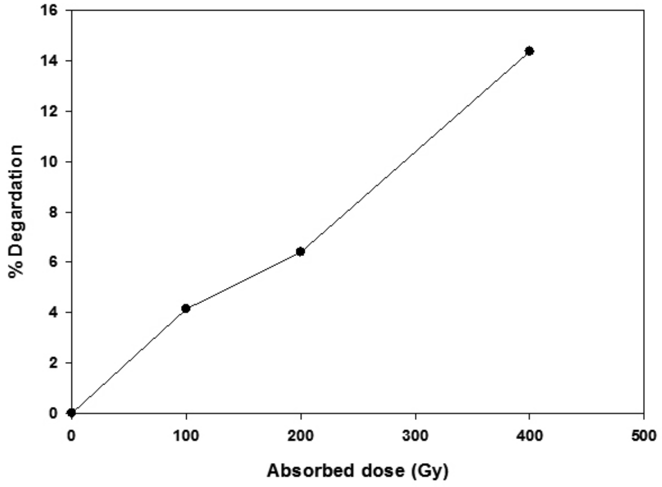


Fig. 4 Degradation of N_2 saturated CV dye containing 10^{-2} M *tert*-BUOH

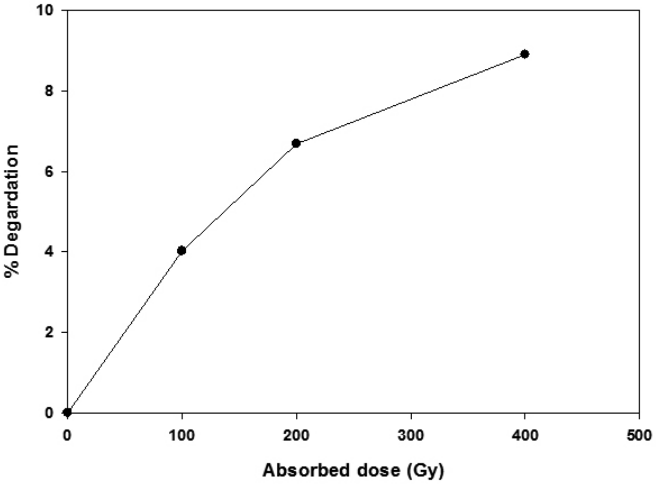


Fig.3 Degradation of N_2O saturated CV dye containing 10^{-2} M *tert*-BUOH.

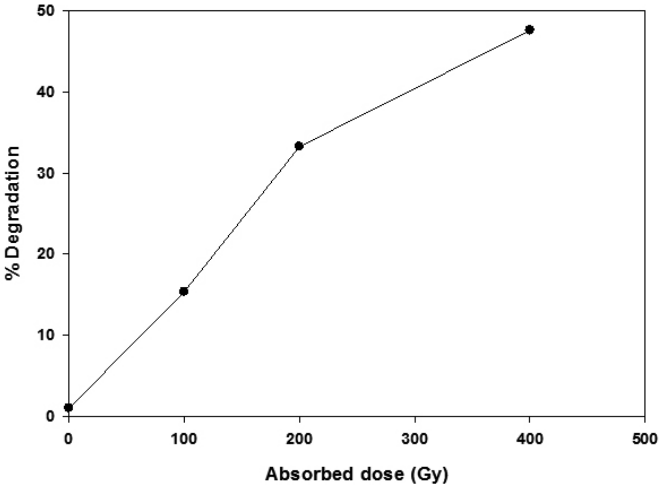


Fig. 5 Degradation of air- saturated CV dye solution

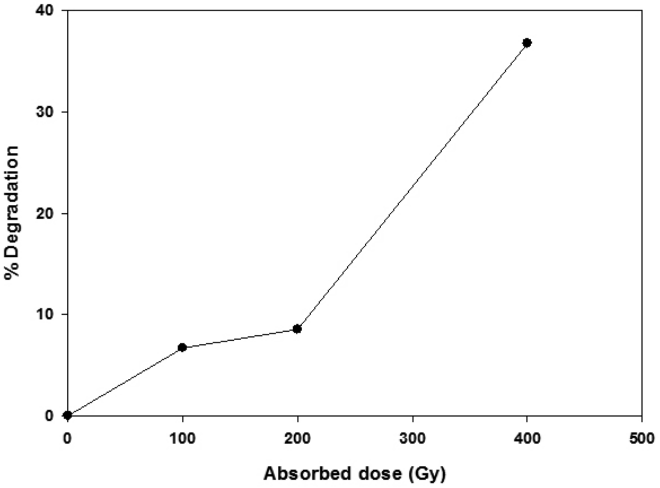


Fig. 6 Degradation of N_2- saturated CV dye solution

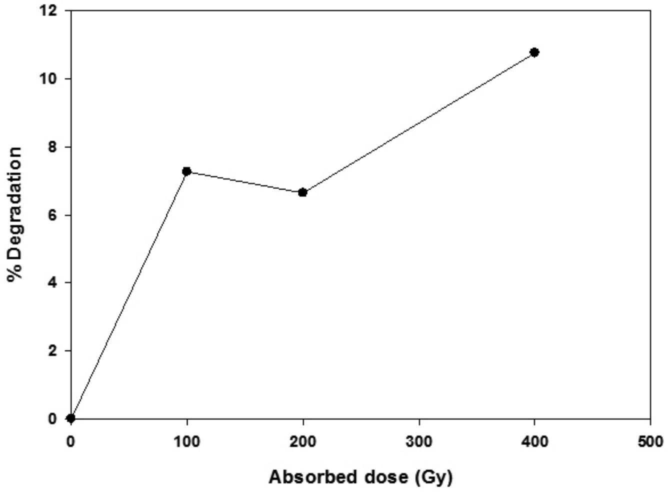


Fig. 7 Degradation of N_2- saturated CV dye solution spiked with 10^{-2} M iso-PrOH

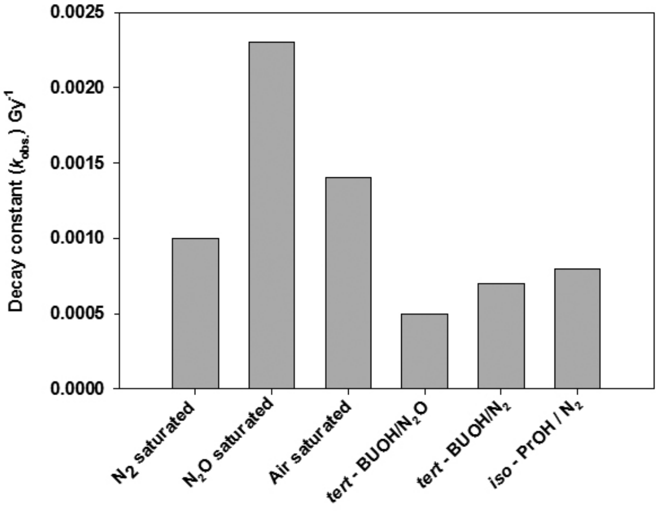


Fig. 8 Comparative removal of CV dye from aqueous solution under various experimental conditions

REFERENCES

1. M Lučić, N Milosavljević, M Radetić, Z Šaponjić, M Radoičić, MK Krušić: The potential application of TiO 2/hydrogel nanocomposite for removal of various textile azo dyes. *Separation and Purification Technology* 2014, 122:206-216.
2. H Olvera-Vargas, N Oturan, C Aravindakumar, MS Paul, VK Sharma, MA Oturan: Electro-oxidation of the dye azure B: kinetics, mechanism, and by-products. *Environmental Science and Pollution Research* 2014, 21:8379-8386.
3. M Tichonovas, E Krugly, V Racys, R Hippler, V Kauneliene, I Stasiulaitiene, D Martuzevicius: Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment. *Chemical Engineering Journal* 2013, 229:9-19.
4. F Zhang, C Feng, W Li, J Cui: Indirect electrochemical oxidation of dye wastewater containing Acid Orange 7 using Ti/RuO2-Pt electrode. *Int. J. Electrochem. Sci.* 2014, 9:943-954.
5. A Azarkohan, F Shemirani, M Alvand: Fast analysis of water samples for trace amount of crystal violet dye based on solid phase extraction using nanoporous SBA-3 prior to determination by fiber optic-linear array detection spectrophotometry. *Journal of Chemistry* 2013, 2013.
6. S Mondal: Methods of dye removal from dye house effluentâ€"an overview. *Environmental Engineering Science* 2008, 25:383-396.
7. F Al-Momani, E Touraud, J Degorce-Dumas, J Roussy, O Thomas: Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis. *Journal of photochemistry and Photobiology A: Chemistry* 2002, 153:191-197.
8. DR Manenti, PA Soares, TnF Silva, AN MÃ³denes, FR Espinoza-QuiÃ±ones, Rn Bergamasco, RA Boaventura, VJ Vilar: Performance evaluation of different solar advanced oxidation processes applied to the treatment of a real textile dyeing wastewater. *Environmental Science and Pollution Research* 2014, 22:833-845.
9. Y-H Huang, Y-F Huang, C-i Huang, C-Y Chen: Efficient decolorization of azo dye Reactive Black B involving aromatic fragment degradation in buffered Co 2+/PMS oxidative processes with a ppb level dosage of Co 2+-catalyst. *Journal of hazardous materials* 2009, 170:1110-1118.
10. L Abdou, O Hakeim, M Mahmoud, A El-Naggar: Comparative study between the efficiency of electron beam and gamma irradiation for treatment of dye solutions. *Chemical Engineering Journal* 2011, 168:752-758.
11. H Fricke, EJ Hart: Chemical dosimetry. *Radiation dosimetry* 1966, 2:167-239.
12. X Jun, W Jianlong: Radiolysis of pentachlorophenol (PCP) in aqueous solution by gamma radiation. *Journal of Environmental Sciences* 2008, 20:1153-1157.
13. M Ismail, HM Khan, M Sayed, WJ Cooper: Advanced oxidation for the treatment of chlorpyrifos in aqueous solution. *Chemosphere* 2013, 93:645-651.
14. W Sun, L Chen, J Tian, J Wang, S He: Degradation of a monoazo dye Alizarin Yellow GG in aqueous solutions by gamma irradiation: decolorization and biodegradability enhancement. *Radiation Physics and Chemistry* 2013, 83:86-89.
15. JWT Spinks, RJ Woods: An introduction to radiation chemistry. 1990.
16. A Bhasikuttan, A Sapre, L Shastri: Oxidation of crystal violet and malachite green in aqueous solutionsâ€"a kinetic spectrophotometric study. *Journal of photochemistry and Photobiology A: Chemistry* 1995, 90:177-182.
17. GV Buxton, CL Greenstock, WP Helman, AB Ross: Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (â‹… OH/â‹… Oâˆ' in aqueous solution. *Journal of physical and chemical reference data* 1988, 17:513-886.
18. Z Guo, F Zhou, Y Zhao, C Zhang, F Liu, C Bao, M Lin: Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms. *Chemical Engineering Journal* 2012, 191:256-262.
19. Y Peng, S He, J Wang, W Gong: Comparison of different chlorophenols degradation in aqueous solutions by gamma irradiation under reducing conditions. *Radiation Physics and Chemistry* 2012, 81:1629-1633.
20. NS Shah, JA Khan, S Nawaz, HM Khan: Role of aqueous electron and hydroxyl radical in the removal of endosulfan from aqueous solution using gamma irradiation. *Journal of hazardous materials* 2014, 278:40-48.
21. AA Basfar, HM Khan, AA Al-Shahrani, WJ Cooper: Radiation induced decomposition of methyl tert-butyl ether in water in presence of chloroform: kinetic modelling. *Water research* 2005, 39:2085-2095.

22. M SÃ¡nchez-Polo, J LÃ³pez-PeÃ±alver, G Prados-Joya, M Ferro-GarcÃa, J Rivera-Utrilla: Gamma irradiation of pharmaceutical compounds, nitroimidazoles, as a new alternative for water treatment. *Water research* 2009, 43:4028-4036.
23. N Getoff: Radiation-induced degradation of water pollutantsâ€”state of the art. *Radiation Physics and Chemistry* 1996, 47:581-593.
24. H-J Fan, S-T Huang, W-H Chung, J-L Jan, W-Y Lin, C-C Chen: Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification. *Journal of hazardous materials* 2009, 171:1032-1044.