Pak. j. sci. ind. res. Ser. A: phys. sci. 2022 **65A**(2) 122-127

Radiolysis Induced Degradation of a Synthetic Dye and its Possible Use for Radiation

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(received February 20, 2019; revised March 17, 2021; accepted April 12, 2021)

Abstract. The aim of this work is to investigate the radiolysis induced degradation and possibility of reactive black B (BB) dye to be used as passive dosimeter. For this purpose, the aqueous solutions of BB dye were irradiated under g-rays by utilizing Cs137 gamma radiation source within 0.1-0.9 kilo-Gray (kGy) dose range. Sample solutions were analyzed spectrophotometrically by using UV-visible spectrophotometer within 300-800 nm range. The absorbance (A) of sample solutions decreases with absorbed dose (D). Post-irradiation stability, physical response, % decolouration (% D), change in absorbance (DA) and change in pH (DpH) of BB dye upon irradiation are discussed. The BB dye follows Beer's law acceptably. The response curves of different parameters show linearity within the selected dose interval with correlation coefficients of 0.9127 and 0.9053. The reported results show the effective degradation of BB dye and encourage its possibility to be used as a dosimeter within selected dose range.

Keywords: reactive black B, dye, radiolysis, gamma dosimetry, spectrophotometer, degradation

Introduction

Reactive azo dyes are the extensively used synthetic materials in textile industry. Dyes are also being used in radiation measurements, an intensive research has been conducted to check their applicability in radiation dosimetry either in the form of films or aqueous solutions. Polyvinyl-chloride (PVC) films containing malachitegreen (MG) were studied spectrophotometrically for high dose radiation dosimetry. The response of PVC-MG films was stable for more than two months in darkness. Nevertheless, the response was strongly affected by day light. The response was unaffected by the dose rate and irradiation temperature (Kattan *et al*., 2007). The relevance of PVA films having tetrazolium violet (TZV) was explored and found convenient for dosimetric calculations in kGy range. The quantifiable dose range can be expanded by further addition of TZV. The reaction of TZV-PVA films was influenced by irradiation temperature. Furthermore, the reaction of TZV-PVA film was steady which gave another favourable position for its application in radiation handling (Emi-Reynolds *et al*., 2007). The absorbance of acidic and alkaline aqueous solutions of methyl red (MR) was decreased with respect to absorbed dose. The suitable dose range for alkaline solutions was between 50 and 6000Gy. For acidic solutions this range can be increased up to 1250 Gy by the addition of ethanol (Ajji, 2006). Aqueous solutions of reactive yellow 145A dye were found to be useful for the dosimetric calculations in the range 0.1-1 kGy. The response of the selected dye was almost same although the irradiation source was replaced from Co^{60} to Cs^{137} (Hussain *et al*., 2012). Because of their high uses, dyes are generally discharged into the climate without proper treatment. Most of reactive dyes are toxic and affect the environment perilously. For the reason of the high stability and toxic effects of textile reactive dyes, these are defiant to the physical treatment methods. These methods can only turn the industrial discharge into another form of toxin. To overcome this issue, gamma radiations were used and affectively remove the dyes content from the subjected solutions. Radiolysis of several dyes have been reported. Gamma irradiation causes the decolouration of Rhodamine B (RB) and Sandocryl blue B-3G (SCBG). Furthermore, RB was found useful for dose determination up to 20 kGy dose ranges and SCBG was useful up to 15 kGy dose range (Barakat *et al*., 2011). The solutions of Janus Green B (JGB), Reactive Black 5 (RB5) and Apollofix Red (AR) dyes were irradiated with gamma radiation by using Co^{60} gamma source with dose rate 2 kGy/h. Experimental results showed that JGB, RB5 and AR were effectively decolourized by treatment with gamma radiation. The initial G values of decolourization were around 1 particle/100 eV for RB5 and AR and ~0.3 for JGB. The G value was sturdily decreased with the decreasing dose that may be

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interpreted in terms of reactions of the intermediates of the water radiolysis not only with the dye molecules but also with the decolorized products (Solpan *et al*., 2003). The absorbance of irradiated solutions of Congo Red (CR) dye was decreased. Sample solutions were subjected to different irradiation doses. However, the complete decolouration of sample solutions was observed at 5 kGy. The decolouration efficiency of dye solution owes to the breakdown of chromophoric group(s) present in dye molecule (Muneer *et al*., 2019). The aim of this work is to check the radiolysis induced degradation of Reactive Black B (BB) dye and its possible use in gamma dosimetry within selected dose range.

Materials and Methods

Sample preparation. Reactive black B (BB) MW: 991.82 amu; molecular formula: ($C_{26}H_{21}N_5Na_4O_{19}S_6$) was collected from Kamal Industries Pvt. Ltd., Pakistan (Fig. 1). Further experimental scheme was same as pursued by Hayat *et al*. (2017). 0.125 g of the selected dye was dissolved in one liter of deionized water (purchased from Pakistan Scientific Traders, Jinnah colony, Faisalabad, Pakistan). One molar solution of HCl and NaOH were used to maintain the pH of the sample solutions. Sample solutions having pH 7 were prepared and stored in dark. A double beam UV-visible spectrophotometer (CECIL 7200) was used for spectrophotometric analysis of the sample solutions. For the representation of physical response of BB, Samsung J7 prime mobile phone with 13MP rear camera was utilized. To minimize the external light effect, snaps of sample solutions were taken in semi shaded area.

Sample irradiation. Cs^{137} gamma ray source (dose rate 660 Gy/h) available at Nuclear Institute of Agriculture and Biology was utilized to irradiate the sample solutions. The sample solutions were exposed to different gamma doses i.e., 0.1, 0.3, 0.5, 0.7 and 0.9 kGy individually and stored in dark for further investigation.

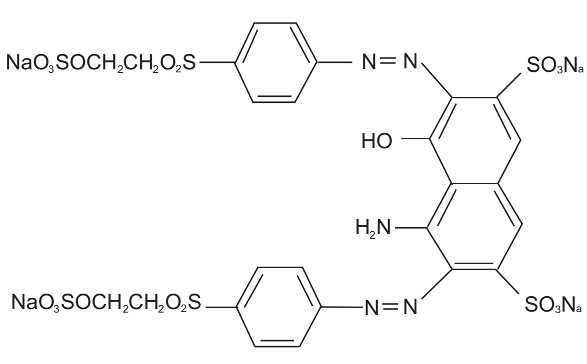

Fig. 1. Molecular structure of BB.

Results and Discussion

The sample solutions of BB dye were scanned within 300-800 nm wavelength range and showed two absorption bands in near-UV region at 315 and 396 nm, while one absorption band in visible region at 596 nm. Dyes molecules containing aromatic rings have strong absorbance (A) around 300 nm. The absorbance (A) of sample solutions is decreased due to devastation of aromatic conjugation (AC) in this region. Furthermore, in visible region, absorbance (A) is decreased due to the devastation of extensive conjugation (EC) present in dye molecule. Figure 2 gives the response curve for the absorbance (A) of BB dye with respect to wavelength (nm). The absorption peak at 596 nm is attributed to chromophoric group of BB dye (Nagai and Suzuki, 1976).

The absorbance (A) of the sample solutions of BB dye is increased with concentration (C) and hence follows Beer's law acceptably. Fig. 3 demonstrates the response of BB dye with respect to concentration (C).

The absorbance (A) of BB is decreased as a function of absorbed dose (D), which is the evidence of radiation induced degradation of dye. Linearity in response of BB upon irradiation is observed. Fig. 4 gives the response and regression model along with R^2 value and shows strong relationship between the radiation dose and degradation of BB. System loses linearity at 0.7 kGy

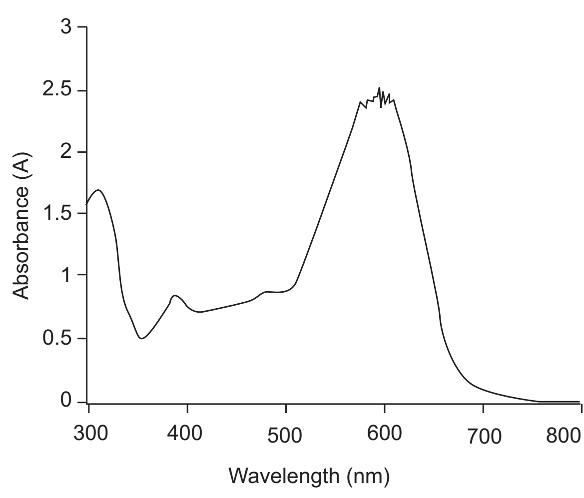

Fig. 2. Scan curve for the absorbance (A) of BB with respect to wavelength (nm).

dose, which is possibly due to physico-chemical processes occurring during the irradiation of the sample solution. The results are in consistence with the previous work of Batool *et al*. (2012), as the sample solutions of direct yellow 12 dye having pH 7 also lose linearity at some doses.

Figure 5 demonstrates the response of BB with respect to storage time. The response of BB is almost stable up to 8 days and system loses its linearity in 9 and 10 days for the sample solutions irradiated at 0.1 kGy dose i.e., absorbance increases. The 0.1 kGy is the least irradiation dose and most of the solute is present in solution. Possible cause of this increase is the formation of species in the solution which are more absorbent as compare to initial compound. The increase in absorbance may also be contributed to the regeneration of the dye molecule by spontaneous oxidation (Batool *et al.,* 2012).

Molecular structure of BB contains two N=N groups and most presumably the first action of radiation is the decimation of this double bond. Hence, decrease in colour intensity is observed upon irradiation. The transient species (*i.e*., $\dot{O}H$, $\dot{H}$, e_{aq}^{-} and so forth) also respond to dye molecule and partake in degradation of dye (Sharma *et al*., 2003). The $\dot{O}H$ radicals also contribute in decoloration (Đ) of water-soluble dyes; addition of $\dot{O}H$ to N=N causes the formation of transient with maximum wavelength in visible range (Wojnárovits *et al*., 2008). Figure 6 shows the physical response of BB at different irradiation doses.

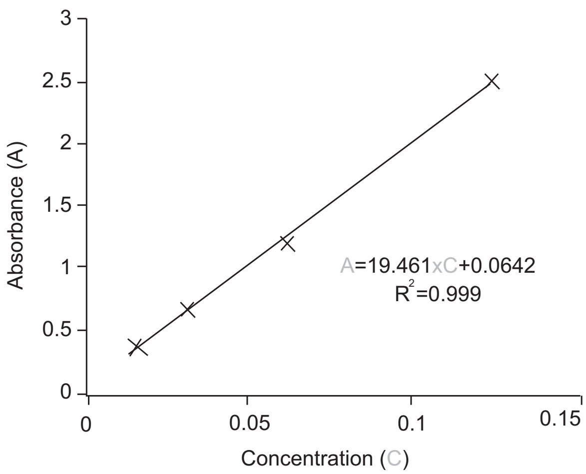

Fig. 3. Response of BB with respect to concentration.

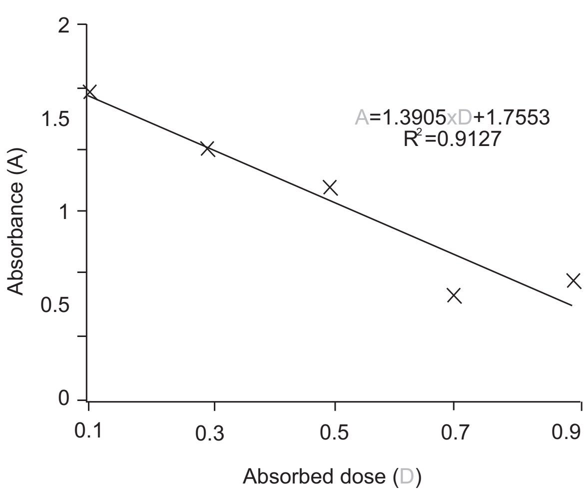

Fig. 4. Response of BB at different irradiation doses.

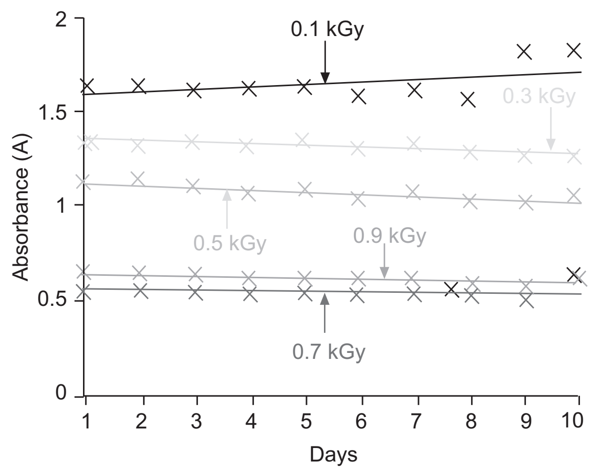

Fig. 5. Response of BB with respect to storage time.

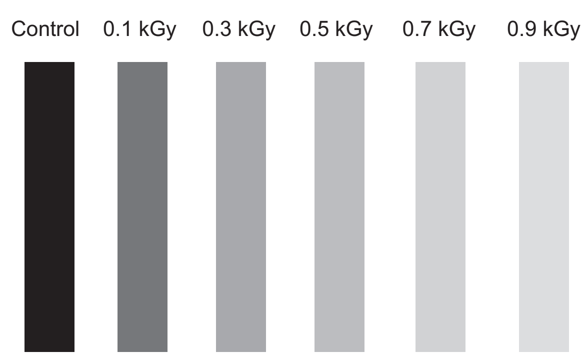

Fig. 6. Physical response of BB within 0.1-0.9 kGy dose range.

The % decolouration (% D) is calculated in terms of absorbance of the sample solutions at pre and post irradiation stages (Hayat *et al*., 2016). Figure 7 demonstrates % D as a function of absorbed dose (D) and regression model along with R^2 value for the linear response of % D with respect to absorbed dose (D). The % D is increased with absorbed dose (D) and nearly 78% decolouration is achieved within the selected radiation dose range.

The ΔA is the measure of difference between the absorbance value of control and irradiated sample solutions. The absorbance (A) of irradiated sample solutions is less than control sample solution; hence, the value of ΔA increases as dose increases from 0.1 to 0.9 kGy. Fig. 8 represent the increase in ΔA with respect to radiation dose.

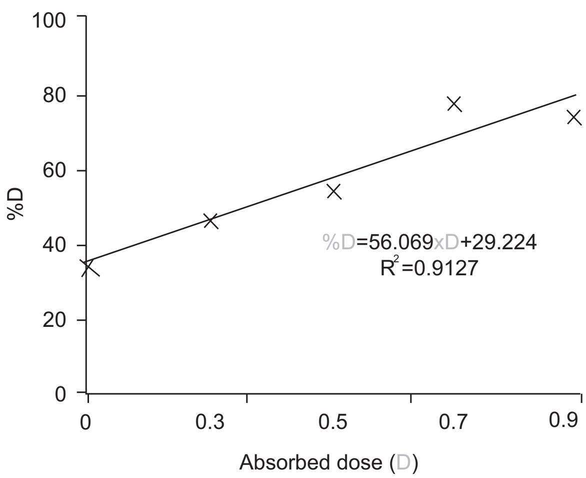

Fig. 7. Response of % D with respect to absorbed dose (D).

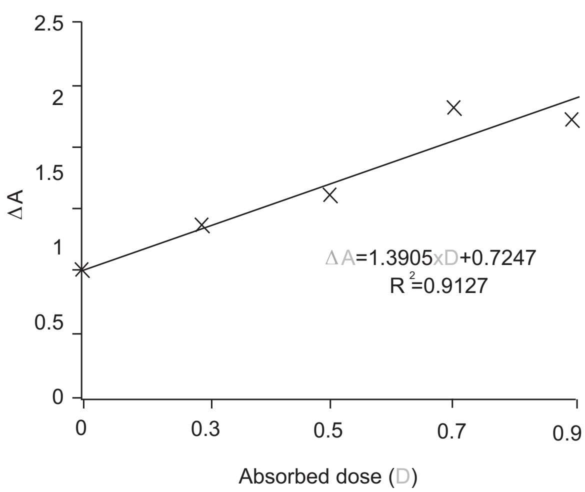

Fig. 8. Change in absorbance (ΔA) with respect to absorbed dose (D).

Effect of dose on the pH of irradiated samples. The interaction of gamma radiation with dye solution is responsible for producing more acidic solution. The change in pH of sample solutions depends upon the structure of dye molecule (Wojnárovits *et al*., 2005), with the increase of radiation dose pH of sample solutions gradually decreases from 7 to 4.14; which is the evidence of formation of more acidic solution (Jun *et al*., 2008; Zhang *et al*., 2005) i.e., the amount of +H ions in solution increases, which consequently increases the acidity of the sample solutions. The pH of the sample solutions of BB dye is decreased with respect to absorbed dose (D). The ΔpH of the sample solutions of BB dye is graphically represented in Fig. 9.

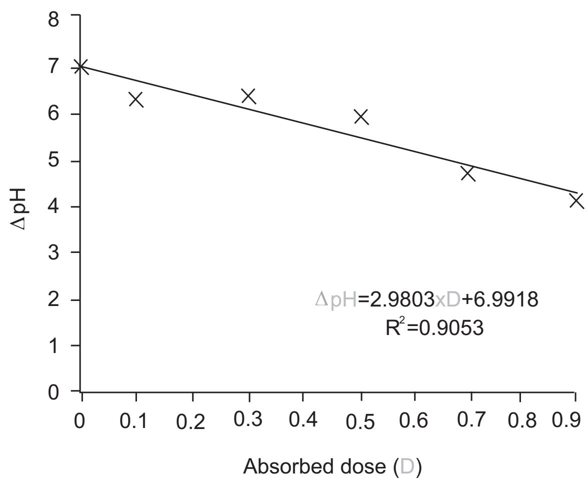

Fig. 9. Change in pH with respect absorbed dose (D).

Conclusion

Possibility of Reactive Black B (BB) dye to be used as radiation dosimeter was checked by considering the absorbance (A) versus concentration (C), absorbance (A), change in absorbance (ΔA), storage time and physical response of BB dye at different irradiation doses. While, physical response, % decolouration (% D) and change in absorbance (ΔA) were considered for degradation of BB dye. BB dye followed Beer's law acceptably. The absorbance (A) of the sample solution was decreased as a function of absorbed dose (D).

Except sample solution irradiated at 0.1 kGy, the response of BB was stable up till the study period of ten days. BB showed a good physical response upon irradiation. The decolouration (% D) and acidity of BB were increased with absorbed dose (D). The BB dye responded linearly within selected gamma dose range. The aqueous solutions of BB have showed a satisfactory response and can be used as passive dosimeter within less sensitive gamma dose ranges. The results of physical response, % D and ΔA of BB dye have shown that most of the dye has been degraded. However, additional studies are still required to increase the degradation of BB dye and its applicability as a radiation dosimeter within more sensitive dose ranges.

Conflict of Interest. The authors declare no conflict of interest.

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