

Degradation Study of Reactive Violet 1 by Gamma Radiation

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Summary: The radiolytic degradation of reactive violet 1 dye in aqueous media as a model system was carried out. The dye solutions (10 to 50 mg/L) were irradiated to the absorbed doses of 2, 5, 10 and 15 kGy using Co-60 gamma radiation source. The change in absorbance, decrease in chemical oxygen demand (COD) and degree of decolouration were investigated in presence of oxygen and hydrogen peroxide. The degraded end products in treated samples were identified using Fourier transform infrared (FTIR) and Gas chromatography- mass spectrometry (GC-MS). Complete decolouration and 80 % COD reduction achieved when dye solutions were exposed to the radiation absorbed dose of 15 kGy. Evaluation of radiolytic end products revealed that dye molecules were completely breakdown into fragments of lower molecular masses.

Key words: Dyes, irradiation, degradation, fragmentation, decolouration, reactive violet.

Introduction

Dyes are the complex organic molecules, cause water pollution due to their fair solubility and visibility even at very low concentration in industrial waste [1]. Over one hundred thousand dyes are commercially available and their presence to a level of 1 ppm is highly visible in water. It is necessary to eliminate dyes from wastewater before being discharged into water bodies as most of the dyes are toxic and carcinogenic [2-3]. Amongst the many techniques employed in the AOP approach are the UV photolytic technique, Fenton process, photo-Fenton process, ozonation process, sonolysis, photocatalytic approach, biodegradation and the radiation induced degradation of dyes. Furthermore, many workers have coupled the various AOP techniques to obtain significant improvement in their results. The present paper is a review of published studies on high energy radiation (α , β and γ) induced degradation/decoloration of dye solutions reported during the period of 2000–2008 [4]. A large number of dyes that are being used in the textile industry are non biodegradable and conventional treatment methods such as chlorination, adsorption, coagulation, filtration, sedimentation, ultra filtration, reverse osmosis, electro coagulation [5-9] etc. are inadequate, since these methods require further treatments [10-12]. There is a need for an effective and innovative process for the treatment of such pollutants in water. Ionizing radiations are proficient to degrade dyes in effluents by primary products formed during radiolysis of water [13]. The radiation dose required for complete degradation of synthetic dyes depends on their structures and reactivity towards primary products produced. Furthermore,

presence of oxygen, oxidizing agents, pH of the medium and concentration of dye also influence the degradation process. The effectiveness of ionizing radiation for elimination of pollutants from wastewater has been established [14-18].

The objective of this study was to evaluate the gamma radiation treatment of reactive violet 1 dye, which is abundantly used in textiles, in the absence and in the presence of H₂O₂ as well as their degradation using UV/Visible spectrophotometer, FTIR and GC-MS.

Results and Discussion

Absorbance Change

The absorption spectrum of untreated reactive violet 1 dye aqueous solution was recorded that showed maximum absorption (λ_{max}) in the visible region at the wavelength of 545 nm, while other peaks appeared at 329, 285 and 219 nm as shown in Fig. 1. The characteristic peaks of dyes decreased with increase in radiation absorbed dose and finally disappeared even at 5 kGy radiation absorbed dose. The disappearance of colour intensity at λ_{max} 545 nm is attributed to radiation induced degradation of characteristic chromophoric group followed by fragmentation of the complex molecule into simpler compounds. The results indicate that the decolouration of dye solution depends on the structural changes in the chromophoric groups of dyes. Complete decolouration was achieved at an absorbed dose of 5 kGy, as Fig. 2 and 3 illustrate that

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the presence of H₂O₂ has positive influence on the degree of decolouration. It is found that when dilute aqueous solution is subjected to gamma irradiation the radicals such as OH[•], H[•] and e⁻_{aq} generated [23]. When molecular oxygen introduced in reaction media, it reacts with H[•] and e⁻_{aq} to form superoxide radical anion, O₂^{•-} and hydroperoxy radical HO₂[•]. Addition of H₂O₂ not only scavenges the reducing species (H[•] and e⁻_{aq}) but also facilitate the oxidation process [24].

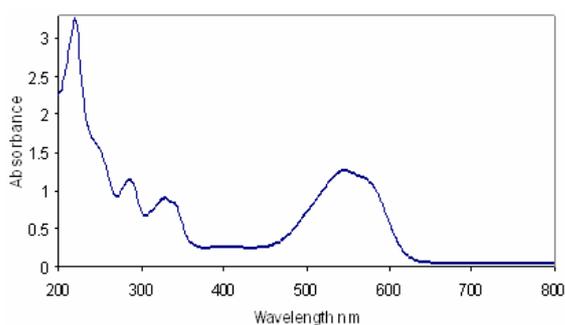


Fig. 1: UV/Vis spectrogram of RV1 dye.

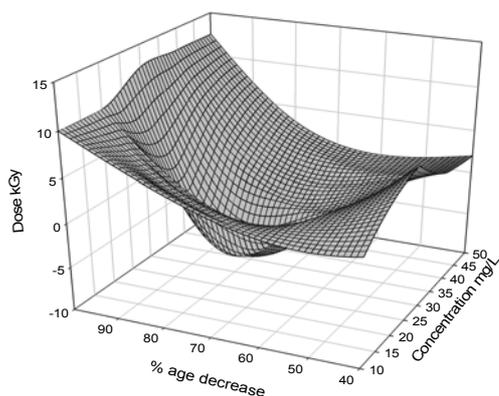


Fig. 2: Effect of gamma radiation on colour intensity of RV1 dye.

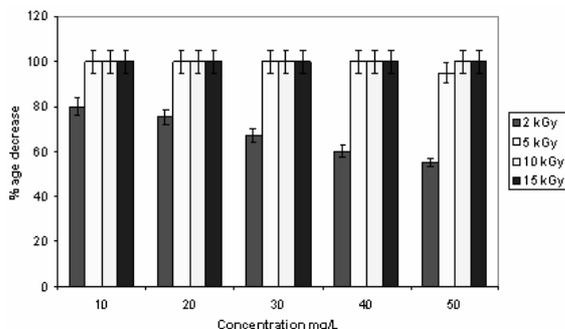


Fig. 3: Effect of gamma radiation in presence of H₂O₂ on colour intensity of RV1 dye

COD Reduction

Chemical oxygen demand (COD) is the most important parameter, as its value reflects the extent of pollution load in the wastewater. The decrease in COD values after treatment of dyes solutions are shown in the Fig. 4AB. It is found that COD reduction depends on the radiation absorbed dose and also influenced by addition of H₂O₂. The decrease in COD was up to 80 % in presence of H₂O₂ while in the absence of H₂O₂ the removal efficiency was 55 %. It is evident that hydrogen peroxide augmented the degradation of dye at the same radiation absorbed dose which caused reduction in COD since hydrogen peroxide interact with e⁻_{aq} and hydrogen radical (H[•]) and may scavenge these species. In fact the oxidative degradation of dyes occurs by hydroxyl radicals (OH[•]) generated during radiolysis and is facilitated in the presence of hydrogen peroxide [24].

The results also indicate that decolouration is easily achieved as compared to the COD reduction since decolouration is attributed to the removal of chromophoric groups where as reduction of COD probably occurs when organic molecules break down into low molecular mass aldehyde and carboxylic acids and ultimately into carbon dioxide and water. The reaction of hydrated electron with the azo group is a fast reaction and the radical anion quickly protonates forming a hydrazyl radical as follows: (-N=N- + e⁻_{aq} → -N=N^{-•} → (+H₂O) → -N[•]-NH- + OH⁻) [23].

Change of pH

When gamma radiation interacts with the complex dye molecules, degradation occur and the possible products may be low molecular mass carboxylic acids [24-25]. However, the change in pH justifies the rationale behind the radiation treatment of dyes samples which is an important water quality parameter. The pH value decreased after the radiation treatment as shown in representative profile (Fig 5) but after a certain dose the pH value stabilized since further treatment may result into the formation of CO₂ and H₂O by the interaction of hydroxyl radicals with the organic molecules and finally equilibrium may be established between these species. These finding are in accordance with Dogbe *et al.* [25] that the aqueous solutions of cibaceon yellow and basilen blue subjected to gamma irradiation to 1 kGy significantly decreased.

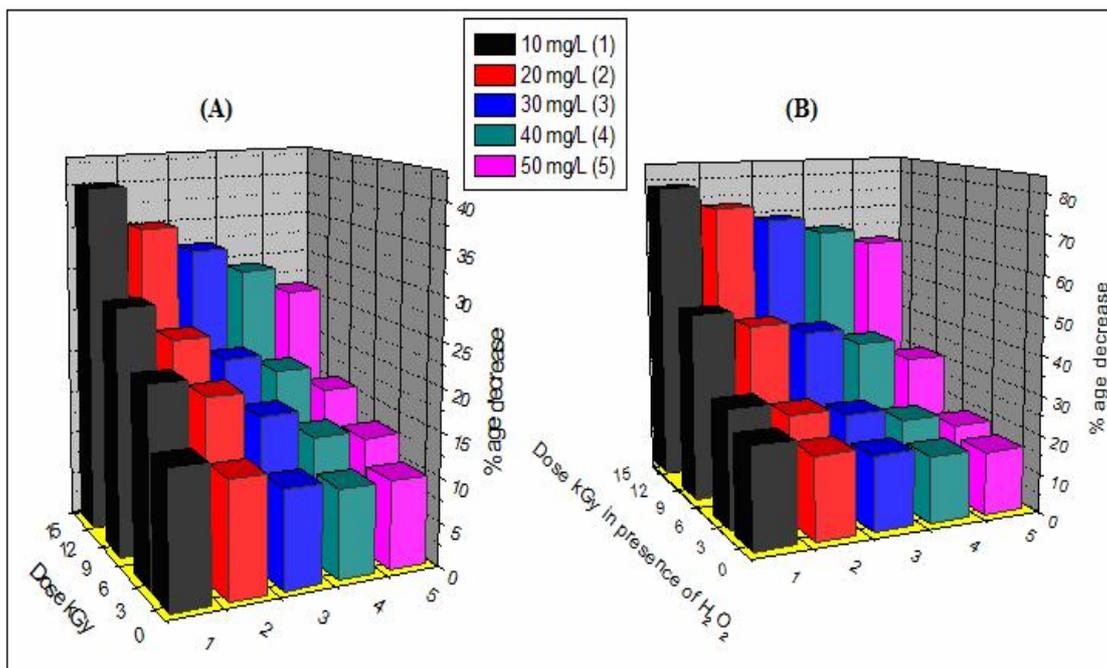


Fig. 4: Effect of gamma radiation on COD reduction (A) and gamma radiation in presence of H_2O_2 (B) of RV1 dye.

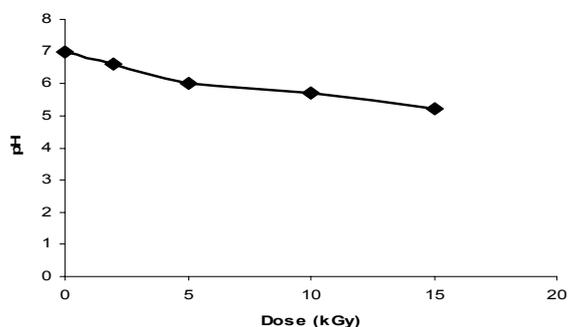


Fig. 5: Effect of radiation absorbed doses on pH of RV1 dye (50 mg/L)

Fourier Transform Infra Red spectrometric (FTIR) Studies

Profile of FTIR for RV1 dye before treatment shows specific vibration peaks, at 3480 cm^{-1} due to NH stretching, 3430 cm^{-1} for OH stretching, 3030 cm^{-1} for aromatic $=C-H$ stretching, 2366 cm^{-1} for NH_2 stretching, 1642 cm^{-1} for NH bending, 1575 cm^{-1} for $N=N$ stretching, 1545 cm^{-1} for $C=C$ stretching, 1403 cm^{-1} for asymmetric CH bending, 1198 cm^{-1} for CO stretching and 1047 cm^{-1} for Ar-Cl respectively. FTIR spectrum of irradiated dye solution at 15 kGy radiation absorbed dose has

significant variations as compared to un-irradiated dye (Fig. 6A). The complete destruction of aromatic rings occur after radiation treatment but some minor peak appeared at 3019 cm^{-1} may be attributed to CH stretching and at 1214 cm^{-1} a peak correspond to CO stretching while other peaks disappeared due to elimination of characteristics vibration. FTIR profile of treated samples, clearly indicate that dye molecules have been degraded which support the assumption that OH^\bullet bring about the chain oxidation reaction to break down complex dye molecule via destruction of aromatic rings into simpler compounds. The results are comparable with previous studies which showed that the oxidative degradation of azo dyes occurred through breakdown of N-N bond, followed by the addition of OH to chromophoric group and finally into CO_2 and water [21].

GC-MS Study

Gas chromatographic-mass spectrometric study was performed in order to study the degradation of the RV1 dye and to identify the degraded end products in extracted samples. The results clearly indicate that after treatment with 15 kGy radiation absorbed dose (Fig. 6B) no characteristics peak was appeared, which shows that complete degradation as well as mineralization was achieved at 15 kGy treatments.

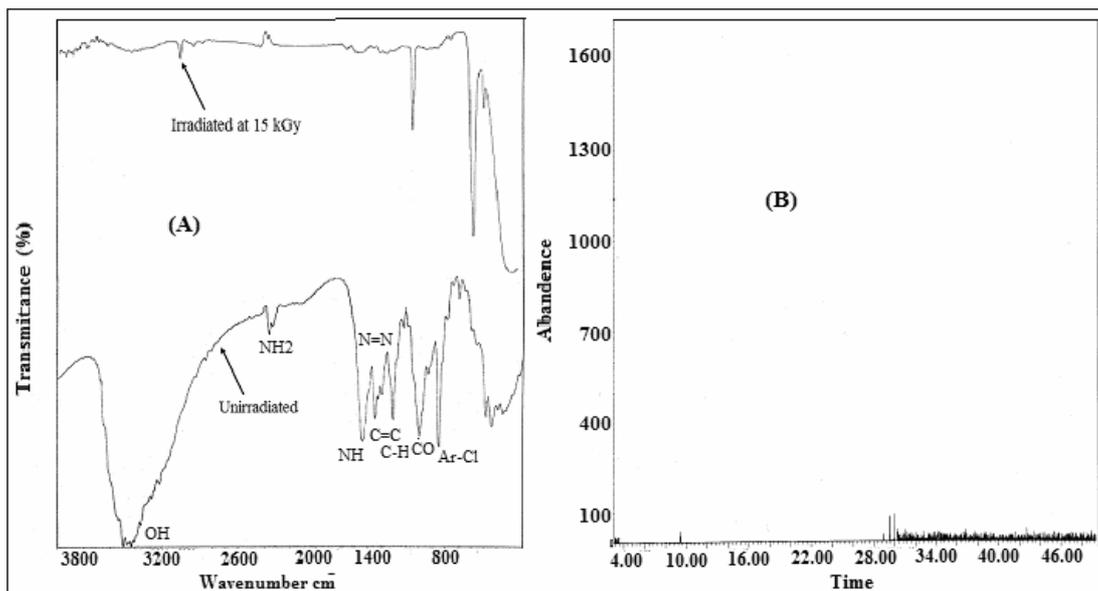
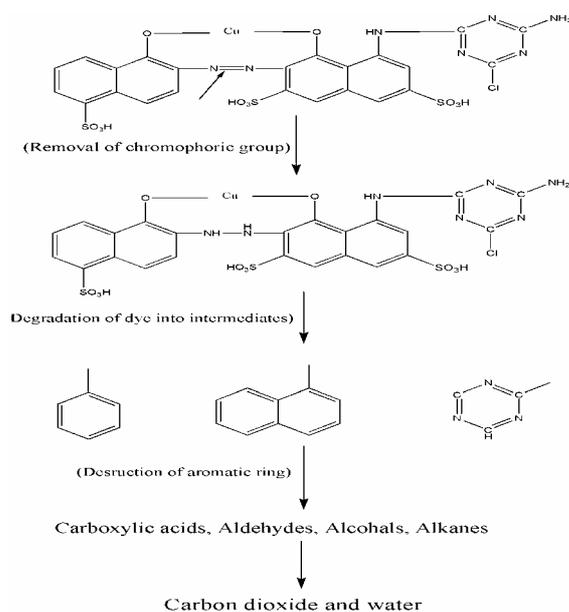


Fig. 6: FTIR profiles of un-irradiated and irradiated (A) and GC-MS profile of irradiated (B) RV1 dye aqueous solution.



Scheme 1: Proposed pathway for degradation of Reactive Violet 1 dye.

The dye solutions were not only decolorized but dye molecules effectively degraded. The suggested degradation process initiates from the break down of the azo group, which changes into intermediates of some aromatic compounds and further reaction ruptures the aromatic ring to form low molecular mass species such as carboxylic acids,

aldehyde, etc. which ultimately change into simpler compounds such as carbon dioxide and water as described in scheme 1 [22, 26, 27]. The previous are in support to our study such as Solpan *et al.* [28] reported the degradation and decolorization of Apollofix dyes to absorbed doses of 1.0 kGy to 8.0 kGy and found that the change in absorption spectra, pH, COD, BOD and the degree of were examined in the presence and absence of H_2O_2 . The complete dye decoloration was observed after 2.0 kGy and 1.0 kGy doses for AR and AY dyes. Similarly, Paul [29] studied the effect on gamma irradiation on decoloration and degradation of aqueous solution of Reactive Red 120 dye and the decoloration and degradation efficiency were measured in terms of % decoloration and % TOC reduction. Decoloration was observed to be most efficient under reducing condition at a dose of 3 kGy and these studies are in accordance with our study that the degradation was achieved at low absorbed doses.

Experimental

Materials

The reactive violet 1 dye as shown in the Fig. 1 was provided by Haaris dyes and Chemical (PVT) limited, Faisalabad, Pakistan. The commercial dye powder was used without purification while hydrogen peroxide was purchased from Fluka, Germany. The chemicals used in this study such as

ethyl acetate, potassium dichromate, ferrous ammonium sulphate, sodium hydroxide and sulphuric acid were of analytical grade, Merck, Germany. Triply distilled water was used for the preparation of different concentrations of dye (10-50 mg/L) and other solutions used during study.

Treatment of samples

The dyes aqueous solutions filled in Pyrex bottle were subjected to radiation treatment by using Co-60 gamma radiation source at Nuclear Institute for Food and Agriculture (NIFA) Ternab, Peshawar. The dose rate of the gamma irradiator was determined by Fricke dosimetry [19] and irradiation of the samples was performed at ambient temperature to absorbed doses 2, 5, 10 and 15 kGy respectively.

Analysis

The pH of the solutions was measured by using pH meter, Hanna HI 9818. Chemical oxygen demand (COD) was determined following the standard method [20]. The dye solutions were analyzed spectrophotometrically before and after treatment by double beam UV-Visible Spectrophotometer (U-2001 Hitachi, Japan) using triply distilled water as a blank. Gas chromatography-mass spectrometry (GC-MS) and Fourier transform infra red (FTIR) analyses were performed in order to identify the degraded products. Prior to analyses, the irradiated samples were extracted with redistilled ethyl acetate. The organic phases were decanted followed by dehydration with MgSO₄ for 24 hours; the samples were concentrated by rotatory vacuum evaporator and stored for analysis [21]. The GC (Agilent Technologies 6890N) having DB-5 capillary column coupled with MS detector through EI interface using Helium as a carrier gas. The m/e ratios of fragments were determined by Chem. station software and the identified compounds were then compared with software library. For FTIR analysis, the organic extracts were evaporated, ground with KBR powder, pressed to form a uniform disk [22] and then analyze by FTIR (Schimadzu U-2001 Japan) at Pakistan Council for Scientific and Industrial Research (PCSIR) Lahore.

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Conclusion

The decolouration and degradation of dye in aqueous solution by gamma radiation in the presence and absence of H₂O₂ has been investigated. The results shows that colour removal as well as COD reduction mainly depend upon radiation absorbed dose and complete decolouration and 80 % COD reduction was achieved as a result of gamma irradiation treatment. A considerable change in dye solution was observed which decreases from initial pH 7 to less than 6. The addition of H₂O₂ enhances the overall efficiency of treatment by facilitating the oxidation process and scavenging the reducing species. The degraded end products were monitored by FTIR and GC-MS studies that reveal the radiation treatment is innovative, effective, non selective, safe and environmental friendly method which need no further treatment. The FTIR showed the following functional group (NH, OH, =C-H, NH₂, N=N, C=C, asymmetric CH, CO and Ar-Cl) which were disappeared after treatment. The radiation treatment may be extended to treat the wastewater of dye industries.

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