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Gamma Radiolysis Studies of Aqueous Solution of Brilliant Green Dye

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Abstract: The effect of γ–radiation on colour intensity of aqueous solution of Brilliant Green has been investigated at two different concentrations. The degradation of Brilliant Green (BG) has also been investigated in presence of suspended ZnO, by adding different amounts of ZnO. Simultaneously the conductance and pH of each solution system were measured before and after γ-irradiation. All the γ–irradiations were performed at a dose rate of 0.60 $kGyhr^{-1}$ in GC-900. The maximum dose required for the complete degradation of the dye was found to be 0.39 kGy. G(-dye) values were found to decrease with increase in gamma dose and were in the range 4.26 - 12.81. The conductance (7.6 - 25.3 μS) and pH values increased marginally with dose for both the concentrations. The rate of decolouration was found to be high at lower doses and the efficiency of dye removal was higher at low concentration of the dye. This may be attributed to the presence of reaction by-products from the destruction of parent compound build up and compete for reaction intermediate species. The rate of reaction and rate constants were calculated and it was found that the degradation reaction follows first order kinetics. It was found that the decolouration percentage was more in dye systems in absence of ZnO.

Keywords: Radiolysis, G-value, Kinetics, Brilliant Green, Zinc oxide

Introduction

Dyes are the compounds that have been used extensively in various industries and particularly in textile industries. Water plays important role in dyeing process and therefore waste water has intense colours. The ordinary treatment processes do not degrade the majority of dyes present in waste water from the textile industries. In such a case ionizing radiations seems to be a promising method. This is because the use of γ–radiation can be intensified in aqueous solution of dyes[1-3]. Other technique comprises the use of advanced oxidation process for the decolouration of textile waste water taken from different textile plants. The advanced oxidation processes making use of ozone, γ–radiation, hydrogen peroxide and UV-radiation have given good decolouration results[4].

The effect of γ–radiation on colour intensity of aerated, oxygenated, N_2, N_2O saturated aqueous solution of dyes have also been reported[5,6]. Mansoori *et al.*[7] have studied the photographic bleaching of Rhodamine-B (Rh-B) over the zinc powder in presence of light. Sharma *et al.*[8] investigated the photocatalytic bleaching of Orange-G dye in aqueous ZnO solutions. Magesh *et al.* [9] have reported the photocatalytic behaviour of CeO_2-TiO_2 system for the degradation of Methylene blue. Panwar *et al.*[10] investigated the use of zirconium phosphate as a photocatalyst in a photobleacing of Eriochrme Black-T, Methylene Blue and Malchite Green. In the present work we are reporting degradation or decolouration of Brilliant Green dye in its aqueous solutions in presence and absence of ZnO at different concentrations.

Experimental

The dose rate of GC-900 was determined using Fricke dosimeter[11]. Brilliant Green[12] (abbreviated as BG) (C.I. 42020), molecular weight 385.55 g/mole ($C_{27}H_{33}N_2$), obtained from B.D.H. was used without further purification. Other reagents used were of analytical grade and all the solutions were prepared in double distilled water in all glass apparatus. Absorbances were measured on Spectronic 20 D+/ GCB Cintra 2e spectrophotometer.

The λ_{max} of BG was obtained by preparing stock solution of. 5.23×10^{-4} M which was diluted to give 0.53×10^{-5}M, 1.55×10^{-5}M and 2.6×10^{-5}M solutions. For the preparation of calibration plot, the solutions of concentration range 5.2×10^{-6} M to 12.5×10^{-6} M were prepared and absorbance of each solution systems was measured at λ_{max}= 630 nm. The stability of dye was checked by measuring the absorbance of the solution after every half an hour. This was continued till there was a change in absorbance of about 10%.

For the present work, BG dye was studied in high as well as low concentrations 1.84×10^{-5} M and 0.92×10^{-5} M (*i.e* 0.018 and 0.0092 mM). The dye solution (10 mL) was taken in a glass tube with B-24 standard joints and irradiated at different doses. The irradiations were carried out in ^{60}Co Gamma Chamber-900 (GC-900) housed in Department of Chemistry, RTM Nagpur University, India. The dose rate during the study was 0.60 $kGyhr^{-1}$. The irradiations were carried out at room temperature (around 3 ±1 ^{0}C). The conductance and pH of the solutions were measured before and after irradiation on ELICO CM-180 conductometer and ELICO LI-63 pH meter respectively. The systems mentioned above have also been irradiated by adding 0.1 g, 0.2 g and 0.4 g of ZnO. The solutions were centrifuged for 10 min after irradiation to settle the suspended particles of ZnO and the absorbance, conductance and pH values were measured.

Results and Discussion

The λ_{max} of BG dye was found to be at 630 nm. The experimental and calculated parameters are given in Tables 1 to 4 for different concentrations. The radiation chemical yield of BG dye, G (-BG) decreased with increase in dose for both the concentrations and were in the range of 4.26-12.81. The rate of decolouration was found to be higher at lower doses (in both the cases *i.e.* the systems with and without ZnO). The maximum degradation was found in case of 0.2 g of ZnO for the systems with ZnO. The aqueous systems required dose 0.39 kGy for 1.84×10^{-5} M and 0.17 kGy for 0.92×10^{-5} M BG solution while the systems with 0.2 g 0f ZnO require 0.34 kGy for 1.84×10^{-5} M and 0.14 kGy for 0.92×10^{-5} M BG solution. This shows that the required gamma dose for the system with ZnO was less. The efficiency of dye removal is higher at low concentrations. The explanation for this is probably that the presence of reactions by-products from the destruction of parent compound build up and compete for reaction intermediates species, acting as scavengers of the reactive species[13].

Table 1. Experimental and calculated values for (1.84×10^{-5} M) Brilliant green dye

Dose (kGy)	Concentration 10^{-5}, M	Conductance, 200 μs	pH	G, BG	Rate of reaction 10^{-5}, moles $dm^3 h^{-1}$	Reaction constant, kGy^{-1}
Unirradiated	1.84	19.0	6.5	0	0	0
0.0563	1.25	10.5	6.4	10.15	7.11	6.87
0.1126	0.75	14.0	6.4	9.38	6.57	7.97
0.1689	0.475	16.5	6.4	7.80	5.46	8.01
0.2252	0.25	20.1	6.4	6.88	4.82	8.86
0.2816	0.20	25.2	6.4	5.58	3.90	7.88
0.3379	0.125	29.3	6.2	4.90	3.43	7.95
0.3942	0.10	30.1	5.9	4.26	2.98	7.39

Table 2. Experimental and calculated values for (0.92×10^{-5} M) Brilliant green dye

Dose, kGy	Concentration 10^{-5} M	Conductance, 200 μs	pH	G, BG	Rate of reaction 10^{-5}, moles $dm^3 h^{-1}$	Reaction constant kGy^{-1}
Unirradiated	0.92	7.6	6.2	0	0	0
0.0563	0.375	7.8	6.2	9.38	6.56	15.94
0.1126	0.175	9.2	6.4	6.41	4. 49	14.73
0.1689	0.075	11.3	6.4	4.83	3.38	14.84

Table 3. Experimental and calculated values for (1.84×10^{-5} M) Brilliant green dye with 0.2 g ZnO

Dose, kGy	Concentration 10^{-5} M	Conductance, 200 μs	pH	G, BG	Rate of reaction 10^{-5} moles $dm^3 h^{-1}$	Reaction constant, kGy^{-1}
Unirradiated	1.84	24.0	7.1	0	0	0
0.1126	0.35	42.3	7.0	12.81	8.98	14.74
0.2252	0.30	35.2	7.0	6.66	4.67	8.05
0.3379	0.20	33.0	7.0	4.68	3.28	6.57

Table 4. Experimental and calculated values for (0.92×10^{-5} M) Brilliant green dye with 0.2 g ZnO

Dose, kGy	Concentration 10^{-5} M	Conductance, 200 μs	pH	G, BG	Rate of reaction 10^{-5} moles $dm^3 h^{-1}$	Reaction constant, kGy^{-1}
Unirradiated	0.92	19.8	7.0	0	0	0
0.0446	0.375	21.6	7.2	11.79	8.25	20.12
0.0898	0.175	24.9	7.2	7.99	5.60	18.48
0.1351	0.125	25.3	7.2	5.67	3.98	14.77

Figure 1 and 2 show variation in G-value for aqueous systems. Similarly Figure 3 and 4 show variation in G-value for systems with ZnO. The addition of ZnO in aqueous dye solutions shows odd behavior in decrease in G-values and absorbance.

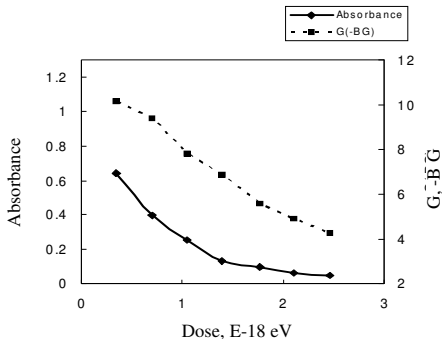

Figure 1. Variation in G-value and absorbance with dose for ($1.84x10^{-5}$ M) Brilliant Green

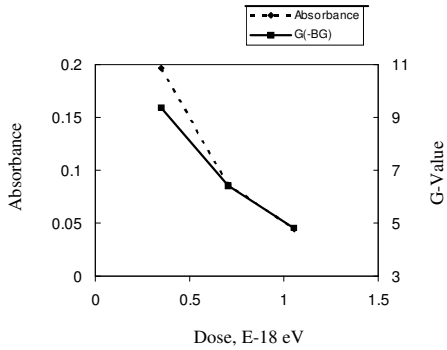

Figure 2. Variation in G-value and absorbance with dose for ($0.92x10^{-5}$ M) Brilliant Green

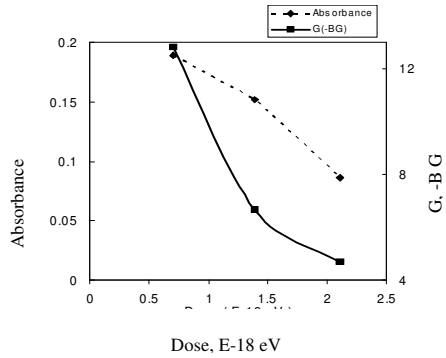

Figure 3. Variation in G-value and G-value and absorbance for ($1.84x10^{-5}$ M) Brilliant Green with 0.2 g ZnO

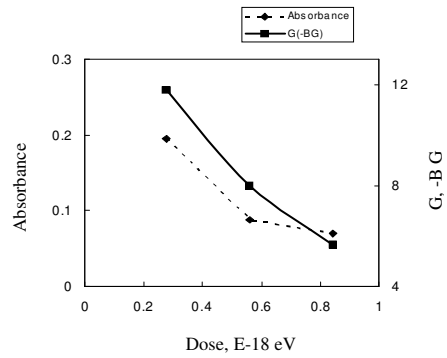

Figure 4. Variation in absorbance for ($0.92x10^{-5}$ M) Brilliant Green with 0.2 g ZnO

The conductance was found to be increasing for both aqueous as well as the aqueous systems with ZnO. The conductance of dyes solutions did not change very much after irradiation because dyes do not form ions when dissolved in water. The conductance values were found to be in the range of 7.6 - 42.3 μS. It was observed that the pH of systems did not change significantly. It was slightly decreased for $1.84x10^{-5}$ M while it increased with dose for $0.92X10^{-5}$ M BG solution. The pH values did not change for $1.84x10^{-5}$ M with 0.2 g of ZnO while slightly increased for $0.92x10^{-5}$ M BG with 0.2g ZnO.

It was found that the degradation reactions are of first order reactions. In case of degradation kinetics in the present work, the rate of reaction and reaction constants were calculated[3] using following expressions (for first order reaction).

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration}}{\text{Time}} \quad (1)$$

$$k = \frac{\ln C_0 - \ln C}{D} \quad (2)$$

Where,

k = Reaction constant, C_0 = Initial concentration (before irradiation), C = Residual concentration (after irradiation), D = Absorbed dose (eV), t = Time (hours)

The rate of degradation reaction was found to decrease with increase in gamma dose. It decreased from $7.1x10^{-5}$-$2.98x10^{-5}$ moles dm^3 h^{-1} for $1.84x10^{-5}$ M while $6.56x10^{-5}$-$3.38x10^{-5}$ moles dm^3 h^{-1} for $0.92x10^{-5}$ M aqueous systems. It was found to decrease from $8.98x10^{-5}$ - $3.28x10^{-5}$ moles dm^3 h^{-1} for $1.84x10^{-5}$ M of BG with 0.2 g of ZnO and $8.25x10^{-5}$ – $3.98x10^{-5}$ moles dm^3 h^{-1} for $0.92x10^{-5}$ M of BG with 0.2 g ZnO.

The reaction rate constants[14] were calculated graphically as well as using expression (2). The reaction constants were in the range of 6.87 - 20.04 kGy^{-1} (calculated using expression 2) and the values calculated graphically were in the range 6.00 - 15.09 kGy^{-1}, showing a good correlation.

Conclusion

The G-values decrease regularly as the absorbed dose increases. The decolouration percentage was near about same in dye systems in absence and presence of ZnO. No significant changes in conductance and pH values were observed after γ-irradiation. The degradation of dyes using γ-irradiation can be used for decolouration of wastewater.

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