INFLUENCE OF OPERATING PARAMETERS ON DECOLORATION OF INDIGO CARMINE SOLUTIONS USING GAMMA RADIATIONS

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Abstract

It has been observed that the process parameters influence the extent of decoloration of synthetic dyes during gamma radiolysis in aqueous solutions. The influence of some factors viz. concentration of dye, dye solution pH, addition of H_2O_2 on the colour bleaching of Indigo Carmine dye in aqueous medium was studied using ^{60}Co gamma radiation source (dose rate was 0.386 kGy/hr). The dose required for the thorough decoloration was observed to be the direct function of the dye concentration in the solution. Further, when pH of solution was increased, the extent of decoloration reduced, for all the concentrations. H_2O_2 addition had the accelerating effect on the overall decoloration. The addition of H_2O_2 was governed by the critical value which corresponds to optimum dose of H_2O_2 that is required for maximum decoloration.

Keywords -Decoloration, radiolysis, GC-900, H2O2.

1. INTRODUCTION

The large quantities of water are used as a solvent either during the production or during the subsequent applications of the synthetic dyes and pigments. The organic based dyes are used extensively to colour the various substrates in the tremendously large amounts in diverse activities. The wastes that are produced either during the manufacturing of these dyes or by these industries are usually rich in residual dyes as well as their breakdown products which are very highly poisonous, oncogenic, mutagenic and are difficult to reduce. These discharges are found to possess varying pH, strong color, high values of COD, and many more. [1]. The conventional procedures such as physical, chemical and biological methods [2-4] are inadequate and ineffective. But, they fail to serve the purpose since they lead to tributary pollution as they just convert the compounds from one phase to another [5-6]. The discharges from dye using industries are often released into the waterways or to municipal sewage treatment plants directly [7-9]. Thus, it is necessary to destroy them completely before they are released to the regular water bodies. High energy gamma radiations is a best alternative colour bleaching of dye effluents as per the recent reports which have reported the bleaching or decoloration on exposure to the ionizing radiations like gamma rays [10]. This radiolytic approach supports to overcome ecological issues more proficiently predominantly to the waste waters that are obtained from dyeing and associated industries [11]. It also noteworthy that in aqueous solutions, the radiation effect gets strengthened wherein the dye molecules are destroyed more commendably by the products produced due to water radiolysis. The effectiveness of radiolytic degradation of dye containing discharges is influenced by various features like the dose rate of gamma source, absorbed dose, concentration, the pH etc. [12].

The colour removal of many organic artificial dyes using energetic radiations in numerous aqueous as well as non-aqueous systems is documented by many researchers [13-20].

The gamma radiolysis of water yields the species like $H^\bullet$, $^\bullet OH$, hydrated electron (e_{aq}^-), H_2O_2, H_2 and H^+ as per equation (1) in spur and out of these the most active are hydroxyl radical, hydrated electron and hydrogen atom. They attack the pollutants present in the solution thereby degrading them into simpler molecules.

$$H_2O \longrightarrow {}^\bullet OH,\ e_{aq}^-,\ H^\bullet,\ H_2,\ H_2O_2,\ \text{and } H^+ \quad (1)$$

Wastewaters contain some oxygen in dissolved state and hence $H^\bullet$ and e_{aq}^- can react with this O_2 and forms per hydroxyl radical $(HO_2)^\bullet$ which acts as an additional oxidizer.

The present study reports the influence of operational parameters viz. initial concentration of dye solutions, gamma radiation dose exposed as well as the role of pH of dye solution on decoloration of Indigo Carmine solutions in water using gamma radiations**.**

Indigo carmine is a pH indicator and acts as redox indicator also. It finds applications in the capsules manufacturing. Indigo carmine is also used to spot the leaks of amniotic fluid in obstetrics. This dye is used Intravenously in surgery to focus the urinary tract. This dye may lead to severe owing to its toxic nature. It is injurious to the respiratory region if gasped and is an irritant to the eyes as well as to skin.

2. EXPERIMENTAL

2.1 Materials and Methodology

Analytical Reagent grade chemicals were employed during the study. The dye Indigo Carmine was purchased from Hi-Media and was used as received from the manufacturer. The working systems were prepared from the stock solutions afresh before every study and were diluted to desired strengths using distilled water.

Spectronic D-20 which is an UV-VIS spectrophotometer was calibrated appropriately every time. Further we used the model at room temperature to record the absorption spectra of sample solutions pre and post irradiation. The decrease in colour intensity was calculated using the drop in absorbance. The pH of all systems was recorded using pH meter (Elico make) prior and after every irradiation. The systems prepared were taken in Borosil tubes having standard B-24 joints .The sample solutions were then exposed to variable doses of gamma rays by placing them in the radiation source (^{60}Co) GC-900 having 0.1 to 0.5 kGy range . The dose rate was 0.38 kGy/h throughout the entire experimentation. The consequences of variation in pH on the decoloration were investigated at three different pH viz. 3, 6.47(which was the pH of parent dye solution) and 10. These values of pH were retained by adding appropriate quantities of 0.1 N HCl and 0.1 N NaOH. The variations in pH and conductanceof system solution after the irradiation were also measured.

2.2 Irradiation facility

GC-900 which is a **^{60}Co** gamma radiation source was used to irradiate solutions and is present in the Chemistry Department of R.T.M. Nagpur University, Nagpur, India. During the entire course of study, the rate of dose was 0.386 kGy / hr.

Table 1.
Important properties of Indigo Carmine dye

S.N.	Properties	Description
1.	Molecular formula	$C_{16}H_8N_2Na_2O_8S_2$
2.	Molar mass	466.3 g/mol
3.	C.I.Number	73015
4.	Absorption maximum (water)	608 - 612 nm
5.	CAS number	860-22-0
6.	Bulk density	700 - 900 kg/m3

3.0 RESULTS AND DISCUSSION

3.1 Calibration plot

Fig. 2 below shows the calibration plot of the dye which helps to determine the concentration of dye left post irradiation as variation of absorbance with concentration is linear.

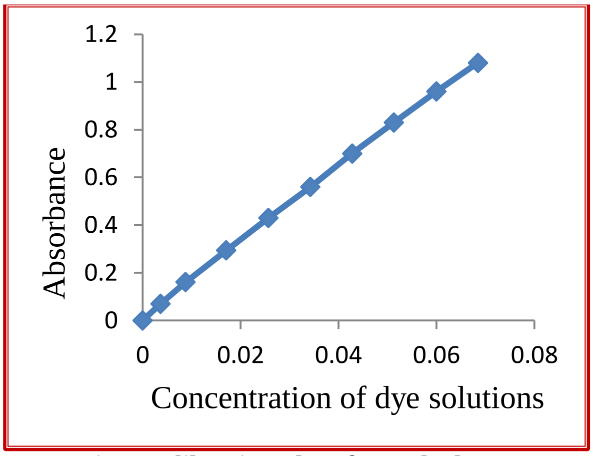


Fig.1 Calibration plot of sample dye

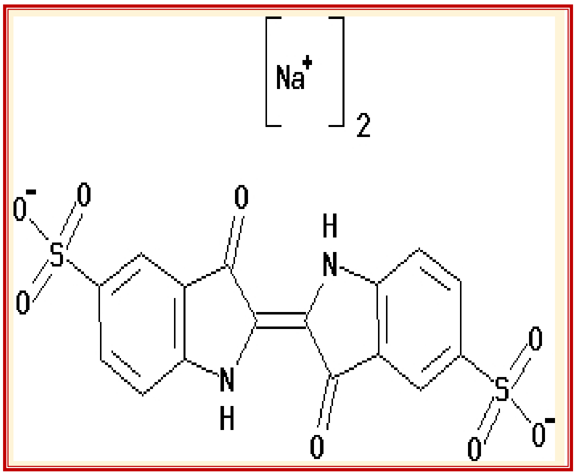


Fig. 2 Structure of Indigo Carmine Dye

3.2 Influence of dye concentration

The degree of decoloration of sample dye solutions as a function of gamma radiation dose is plotted in Fig.3& Fig.4 for all the selected concentrations. For each concentration, the decoloration is found to direct function of gamma dose. As can be seen from graphs that, the decoloration rate is quite high at the onset, goes on increasing gradually but beyond a certain dose, remains almost flat. The gamma radiations dose that is required to achieve the same amount of decoloration increases as the concentration of dye increases.

The pH and conductance of all the sample solutions was observed to alter after the irradiation for all the concentrations which may be due to the degradation of dye to simpler molecule.

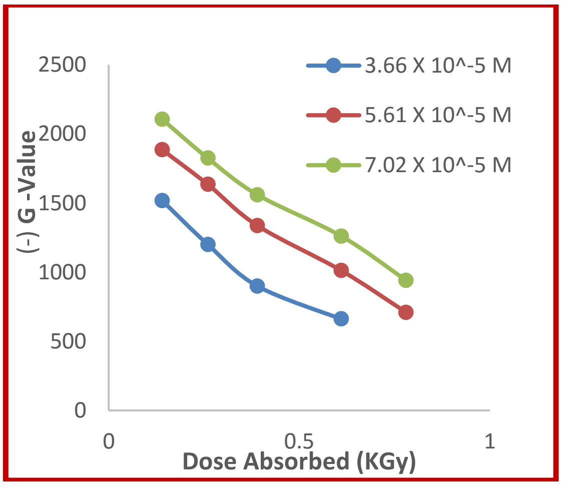


Fig.3 Dye decoloration with Gamma ray dose exposed (G-Value).

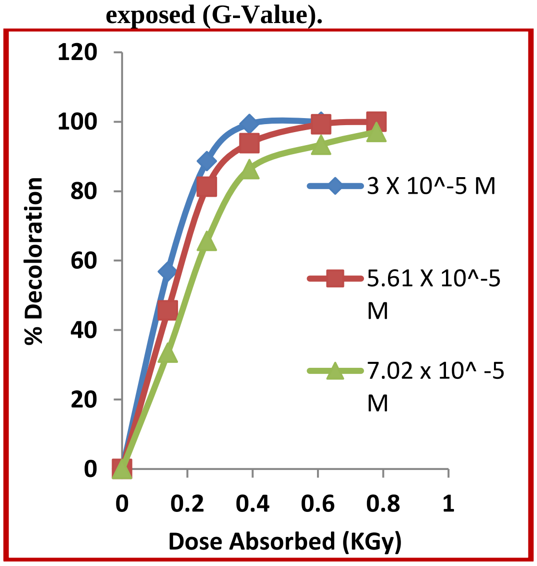


Fig.4 Dye decoloration (%) with gamma dose

Table 2.

Variation of decoloration with gamma dose

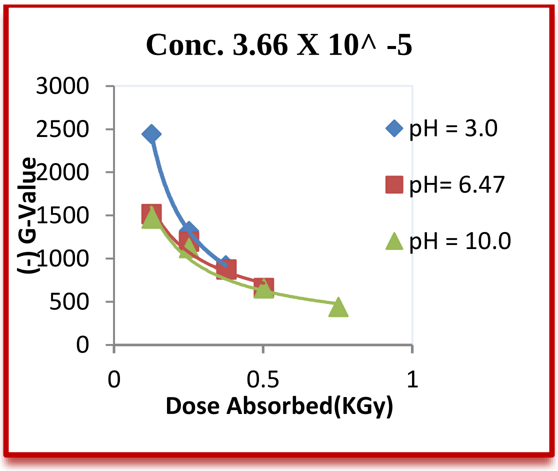
Dose absorbed (kGy)	Concentration of dye (M)					
	3.66×10^{-5}		5.61×10^{-5}		7.02×10^{-5}	
	% Decol.	G-Value	% Decol.	G-Value	% Decol.	G-Value
0.14	56.84	1518	45.63	1887	33.52	2107
0.26	88.66	1201	81.22	1635	65.66	1825
0.39	99.32	900.21	93.81	1337	86.36	1560
0.61	100	662.3	99.27	1012.01	93.36	1261
0.78			100	710.36	97.02	942

It is assumed that carboxylic acid molecules are generated in systems which get degraded further and yield CO2 and H2O. The significant decoloration obtained using gamma radiations may be the outcome of various ionization products such as hydroxyl and hydrogen ions that are formed in spur on water radiolysis which attacks the colour bearing chromophore groups in the dye molecules. The direct destruction by high energy gamma radiations is also possible.

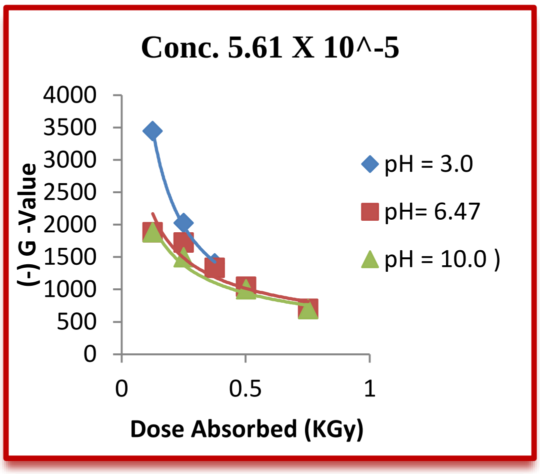
3.3 Effect of pH

The effluent dye and its by-product containing waste waters mostly released have variable pH depending on the applications. The change in decoloration trend with initial pH is presented in Fig.5 (a,b,c) below.

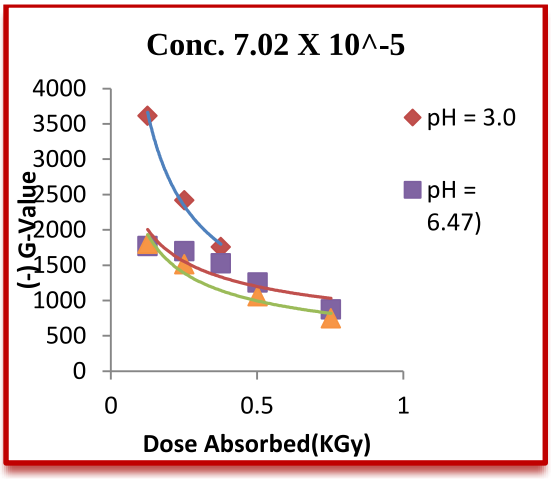
The graphs clearly show that, the decoloration is inversely proportional to the pH of dye solution and is independent of dye concentration. Further, it is seen that, for certain value of pH, the rate as well as amount of decoloration also increases with the gamma, the rate being high initially.



(a)



(b)



(c)

Fig.5 (a,b,c) Effect of initial pH on extent of decoloration

In the acidic conditions (lower pH values) the decoloration is generally high, but decreases gradually with increase in the pH. Although the influence of pH on the degradation of dyes is not reported extensively, it can be explained on account of OH radical's acid-base properties.

The OH radicals get dissociated to feebly active $\cdot O^-$ radicals in the heavy basic conditions (i.e. pH greater than 10) as per following equation.

$$\cdot OH \longrightarrow H^+ + \cdot O^-$$

Whereas in the acidic conditions, we have:

$$e^-_{aq} + {}^+H \longrightarrow H\cdot$$

Here, the O_2 scavenges the reducing hydrogen atoms and forms $HO_2\cdot$ which gets involved in process of dye molecule degradation. Since, $\cdot O^-$ and $\cdot O_2^-$ formed at higher pH values are chemically inactive towards dye molecules thereby results in retardation in the amount of degradation at higher pH values (pH>10).

4.0 Conclusions

The gamma radiolysis can be used effectively for removal of color bleaching of the effluents containing synthetic dyes and their by-products. In this case, the colour bleaching of Indigo Carmine dye solutions was realized successfully. Being a clean and eco-friendly process is the stand out characteristic of this process. Moreover, this technique does not generate any precipitate and also does not add to the dissolved solid contents in solutions which rules out the chances of secondary pollution which occurs due to the use of conventional procedures. The results reveals that, the Indigo Carmine dye solutions are bleached and degraded at lower pH (acidic conditions) with ease and effectively than higher pH conditions (pH>9.0).The alteration in various process factors such as pH and conductance occurs during the course of gamma radiolysis, which can be attributed to breaking down of dye molecules into lower and simpler molecules.

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