GAMMA RADIATION INDUCED DECOLORIZATION OF INDIGO CARMINE DYE SOLUTIONS

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A B S T R A C T

The use of high energy radiations such as Gamma radiations has been reported to degrade and hence decolorize the synthetic dyes effluents very effectively without affecting the environment. In the present study, the decolorization of aqueous solutions of Indigo Carmine dye which is primarily used as pH indicator and also in the manufacturing of capsules, in surgery used to highlight the urinary tract, was investigated using ^{60}Co as gamma radiation source at a dose rate of 0.386 kGy/hr. The effect of some operational parameters such as initial concentration of dye solution, gamma radiation dose and pH of dye solution on the rate and degree of decolorization was also investigated. It was observed that these parameters influence the rate and degree of decolorization significantly. The dose of gamma radiations required to achieve the complete decolorization was found to depend directly on the concentration of dye solution. It was also observed that, as the pH of dye solution was increased, the rate and extent of decolorization was found to decrease irrespective of the concentration of dye solutions.

Keywords: Decolorization, dose rate, GC-900, water radiolysis.

1. Introduction

Synthetic dyes are used as coloring matter in diverse industries such as textile industry, paper industry, food, plastics, leather, cosmetics, medicines and many more. These results in generating large quantities of effluent by these industries containing the products that are extremely toxic, carcinogenic and difficult to degrade. These effluents are characterized by strong color, high COD and wide range of pH [1].Various conventional procedures that are being used to degrade and hence decolorize the dye effluents include physical, chemical and biological methods, such as adsorption, coagulation, membrane process and oxidation-ozonation [2-4].These conventional processes are ineffective to treat dye waste waters ,as they simply transfer the compounds from aqueous to another phase, there by leading to secondary pollution problems [5-6].As the waste waters from dyeing industries is directly discharged to waterways or to municipal sewage treatment plants[7-9] most of the times, it becomes customary to degrade them without hampering the environment before they enter into main stream water sources.

The gamma radiations can be considered as an alternative method to decolorize the dye effluents as the recent studies revealed that, most colored material undergo bleaching or decoloration when exposed to high energy ionizing radiations [10]. The radiation induced degradation technique helps to solve environmental problems more efficiently specially to waste waters effluents from dye as well as colorant industries [11].The effect of radiations can be intensified in aqueous solutions in which the dye molecules are degraded effectively by the primary products formed from the radiolysis of water. The efficiency of radiation induced degradation of dye colored waste water is affected by factors such as dose rate, radiation dose, substrate concentration and pH etc. [12].

Various researchers have reported the color bleaching of organic dyes by gamma radiations in many aqueous and non aqueous solutions of dyes [13-20].

Interaction of Gamma rays with water brings about the radiolysis of water resulting into generation of species like hydrogen atom ($H^{\bullet}$), hydroxyl radical ($^{\bullet}OH$), hydrated electron (e_{aq}^{-}), hydrogen peroxide (H_2O_2), H_2 and hydrogen ion (H^+). In the spur as per the equation 1.

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

Amongst these, the most reactive are hydroxyl radical, hydrated electron and hydrogen atom. These species react with pollutant in a solution and degrade them to simpler molecules.

Generally, wastewaters contain dissolved oxygen, hence $H^{\bullet}$ and e_{aq}^{-} can react with O_2 to form an additional oxidizing species, per hydroxyl radical $(HO_2)^{\bullet}$ as per the following reactions.

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \text{---------} (2)$$
$$e_{aq}^{-} + O_2 \longrightarrow O_2^{-} \text{-----------} (3)$$
$$O_2^{-} + H^{+} \longrightarrow HO_2^{\bullet} \text{---------} (4)$$
$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 \text{---------} (5)$$

The present communication investigates the effect of various operational parameters such as initial dye concentration, dose of gamma radiations exposed and effect of initial pH of dye solution on radiolytic decolorization of aqueous solutions of Indigo Carmine dye using gamma radiation source ^{60}Co. **S**ome important properties of dye are given in Table 1 while the structure of Indigo Carmine dye is shown below.

Basically Indigo carmine is used as a pH indicator. It is also a redox indicator. It is also used as a dye in the manufacturing of capsules, and in obstetrics, Indigo carmine-based dye is used to detect amniotic fluid leaks. In surgery, intravenous indigo carmine is used to highlight the urinary tract. Indigo carmine is harmful to the respiratory tract if inhaled and can cause a potentially dangerous increase in blood pressure in some cases. It is also an irritant to the skin and eyes.

2. Experimental

1.1. Materials

All chemicals used were of AR grade. The Indigo Carmine dye was procured from Hi Media and was used as received without any further purification. All the solutions were prepared afresh using double distilled water prior to experimentation.

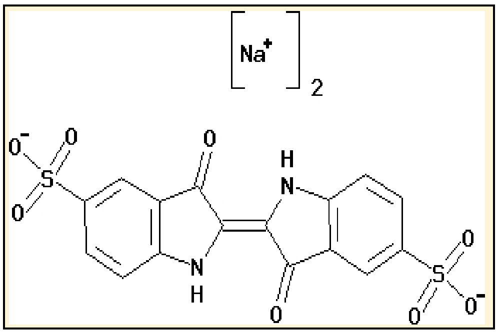
1.2. Radiation source

In order to carry out irradiation of samples, ^{60}Co gamma source GC-900 housed in Post Graduate Teaching Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India, having dose rate of 0.386 kGy per hour was used as shown in fig.2.

Table 1. Properties of Indigo Carmine dye

	Properties	Description
1.	Molecular formula	$C_{16}H_8N_2Na_2O_8S_2$
2.	Molar mass	466.36 g/mol
3.	C.I.Number	C.I. 73015
4.	Absorption maximum (water)	608 - 612 nm
5.	CAS number	860-22-0
6.	Bulk density	700 - 900 kg/m3

Fig.1. Structure of Indigo Carmine Dye



2.3 Methodology

The systems containing different concentrations of Indigo Carmine dye were prepared from stock solution by appropriate dilution with doubly deionized water. The stock solution was prepared afresh prior to every study. Spectronic D-20 model UV-VIS spectrophotometer was used at ambient temperature to measure absorption spectra of the irradiated and unirradiated sample solutions. The degree of decoloration was estimated from the reduction in absorbance. Before and after irradiation, pH of the solutions was measured by Elico model pH meter.The systems were exposed to different doses of gamma radiations in ^{60}Co gamma radiation source GC-900 in the range 0.1 to 0.5 kGy, using Borosil tubes fitted with standard B-24 joints in air at a dose rate of 0.38 kGy/h. In order to study the effect of pH on the degree of decoloration, three pH viz. 3, the original pH of dye solution and 10 were selected. The pH value was maintained at the required value by using 0.1 N HCl and NaOH solutions. The change in process parameters such as pH and conductance was also recorded.

3. Results and Discussion

3.1 Calibration plot

In order to determine the concentration of dye left in the solution after irradiation, the calibration curve for Indigo Carmine dye (Fig.3.) is prepared by plotting absorbance values against concentration of dye solutions. The change in absorbance with dye concentrations is found to be linear.

Fig2. Radiation Source GC-900

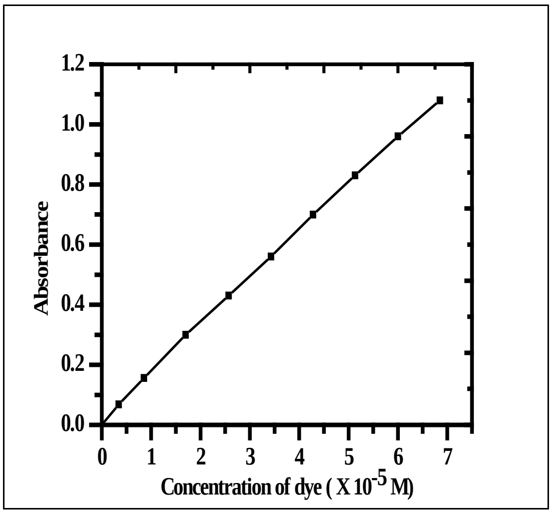


Fig.3. Calibration plot of Indigo Carmine dye

3.2 Effect of initial dye concentration

Fig. 4 and5 shows the percent decolorization of Indigo Carmine dye with dose of gamma radiations exposed for different dye concentrations. From the fig. it is observed that, for a particular dye concentration, the rate of decolorization increases with increase of dose. The rate of decolorization is high initially, but as the dose of gamma radiations increases, the rate of decolorization increases gradually and beyond a particular dose, it remains almost flat. It can be also inferred that as the concentration of dye increases, the dose of gamma radiations required for achieving the same extent of decolorization also increases.

Fig.4. Extent of dye decolorization with Gamma ray dose exposed in terms Of G-Value.

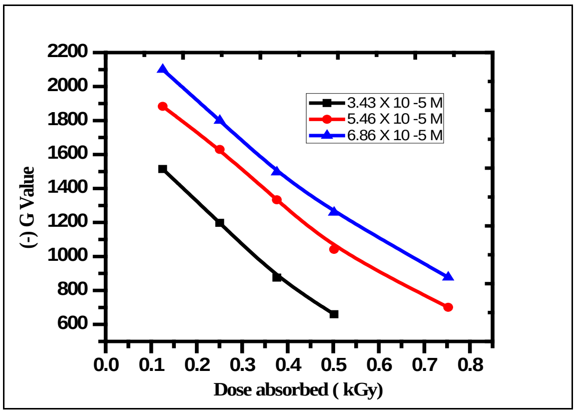


Fig.5.Extent of dye decolorization (%) with gamma ray dose exposed.

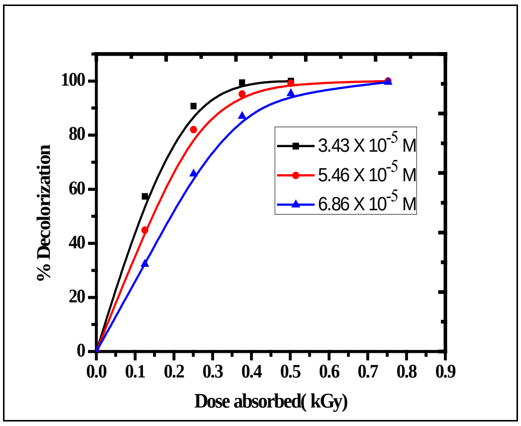


Table 2. Extent of decolration with dose of gamma radiations exposed

Dose absorbed (kGy)	Concentration of dye					
	3.43×10^{-5} M		5.46×10^{-5} M		6.86×10^{-5} M	
	% Decolorization	G-Value	% Decolorization	G-Value	% Decolorization	G-Value
0.13	57.36	1514.44	44.83	1883.57	32.33	2100
0.25	90.73	1197.82	82.01	1630	65.70	1800
0.38	99.44	875.24	95.20	1333.43	87.02	1496
0.5	100	660.10	99.16	1041.65	95.36	1259.01
0.75	-	-	100	700.31	99.63	876.87

The dose of gamma radiations required for the complete decolorization is found to depend directly on the concentration of dye solution. It was also observed that there was alteration in pH as well as conductance of irradiated samples for all dye concentrations. This variation may be attributed to the fact that, dye molecules are degraded to simpler molecule like carboxylic acids upon irradiation, which further gets degraded to CO_2 and H_2O. The high degree of decolorization achieved by gamma radiations may be attributed to the ionization products of water radiolysis such as hydroxyl ion and hydrogen ion which attacks the colour bearing chromophoric group of the dye molecules and as well as to the direct destruction of dye molecules by high energy gamma radiations.

3.3 Effect of pH

It can be seen from the graph that, as the pH of dye solution is increased, the rate and extent of decolorization decreases irrespective of the concentration of dye. It is further observed that, for a particular pH, as the dose of gamma radiations increases, the rate and extent of decolorization also increases, the rate being high initially.

Fig. 6 (a)

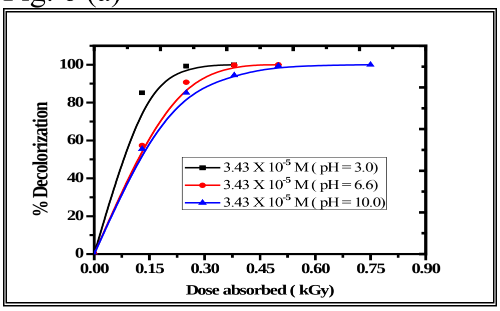


Fig. 6 (b)

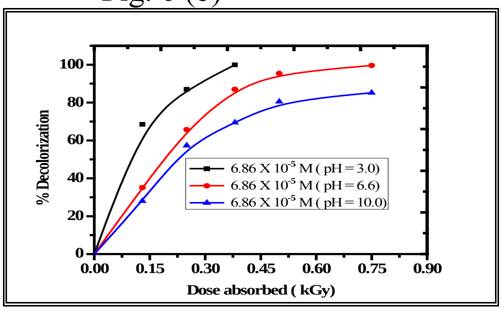


Fig. 6 (c)

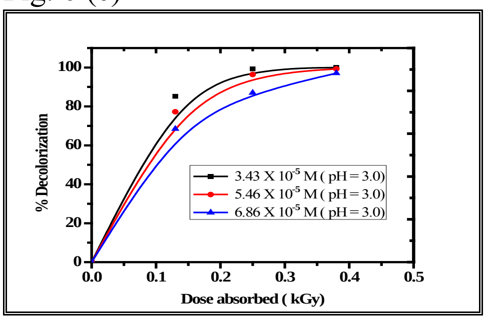


Fig. 6 (d)

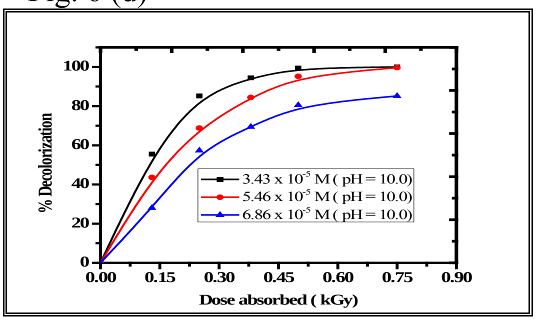


Fig. 6 (e)

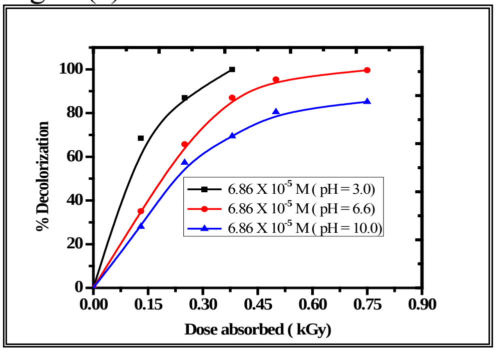
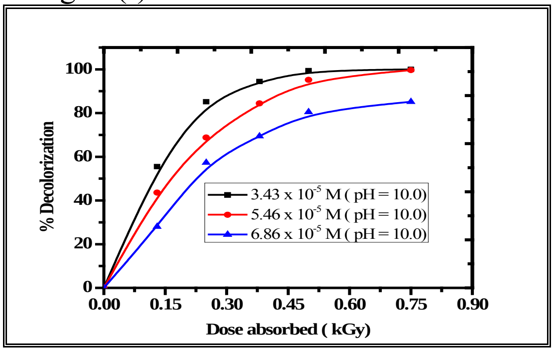


Fig. 6 (f)

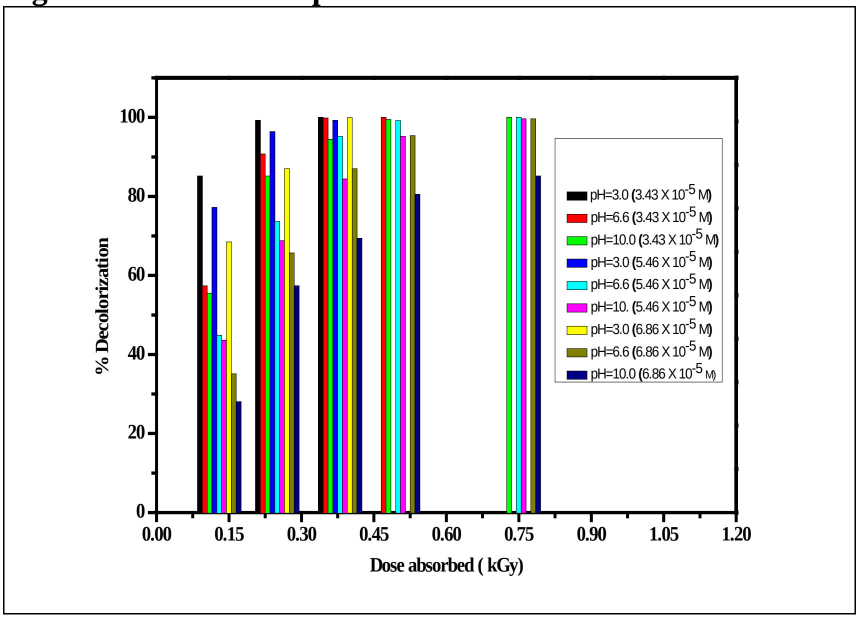


Figs. 6(a), 6(b) and 6(c) represent the effect of pH (for a particular dye concentration) on degree of decoloration.

Figs. 6(d), 6(e) and 6(f) represent the effect of dye concentration (for a constant pH) on degree of decoloration.

During the decolorization study, the effect of initial pH of dye solution on rate and extent of decolorization was also investigated, as the effluent containing synthetic dyes are discharged at variable pH depending on the purpose for which the dyes are used. The effect of initial pH of dye solution on decolration is depicted in fig.6.

Fig.7 Effect of initial pH on extent of Decolorization



At the lower value of pH (acidic condition) the degree of decolorization is high, but as the pH increases, it gradually decreases. Though the degradation behavior of dyes at different pH values is not documented much, a possible explanation could be based on the acid-base properties of OH radicals.

In the strong basic solution (pH>10), the OH radicals dissociates as per following reaction to yield less reactive $^{\cdot}O^{-}$radical

$$^{\cdot}OH \longrightarrow H^{+} + {}^{\cdot}O^{-} \text{------------------------- (6)}$$

While in the acidic solutions:

$$e^{-}_{aq} + {}^{+}H \longrightarrow H^{\cdot} \text{ ------------------ (7)}$$

The reducing hydrogen atoms are scavenged by oxygen resulting into formation of $HO_2^{\cdot}$which may be involved in the degradation of dye molecules. The $^{\cdot}O_2^{-}$ are not very reactive and thus the decrease in the degradation at higher pH values (pH>9) may be due to lower reactivity of $^{\cdot}O^{-}$ and $^{\cdot}O_2^{-}$ species towards the dye molecules.

4. Conclusions

The decoloration of Indigo Carmine dye was achieved successfully using the gamma radiations. The results, obtained in the present study strongly supported the fact that, gamma radiations can be considered as a powerful and promising tool to effectively degrade and hence decolorize the dye effluents. The significant advantage of gamma radiolysis is that it is a environment friendly clean process as it does not involve formation of any precipitate as well as does not increase the dissolved solids in systems, thereby eliminating the chances of secondary pollution that may arise due to use of conventional techniques. It was also observed that, the Indigo Carmine can be degraded more effectively at lower pH (acidic conditions) value than at high pH(pH>9.0).The process parameters like pH and conductance were found to be altered during the course of decolorization due to breakdown of dye molecules into simpler molecules.

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