Synergistic Effect of H$_2$O$_2$ Addition on Gamma Radiolytic Decoloration of Some commercial Dye Solutions

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Abstract. Gamma radiations have emerged as a potential tool to degrade and decolorize the industrial effluents containing synthetic dyes in eco friendly and efficient manner. The dose and exposure time required to achieve the efficient decolration are quite high using gamma radiations alone during gamma radiolysis of synthetic dyes. Studies have revealed that, it can be brought down significantly on addition of H$_2$O$_2$ as it enhances the degree of decoloration. This happens due to the formation of highly oxidizing $\cdot$OH radicals that are formed due to rapid reaction of H$_2$O$_2$ with hydrated electrons formed during radiolysis of water. Further as the dose of H$_2$O$_2$ increases, extent and rate of decoloration also increases up to a certain value referred to as critical dose. But further increase in dose of H$_2$O$_2$ beyond this critical value affects the extent of decoloration adversely. In present communication, the gamma radiation induced decoloration of Methylene Blue, Malachite Green and Indigo Carmine dyes was achieved using various doses of H$_2$O$_2$. It was observed that, the value of H$_2$O$_2$ Critical dose required for efficient decoloration varies from dye to dye indicating its dependence on structure and concentration of dye solutions.

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

1. Introduction

Various synthetic dyes are employed in vast quantities in varied industries including textile, paper, food, plastics, leather, cosmetics, medicines and so on [1]. The effluents so generated by these industries are loaded with not only the residual dyes but also the products which are very toxic, carcinogenic and resistant to degrade. The dye effluents are rich in colour, variable pH, high amount suspended solids, COD, BOD, metals, temperature [2-4] and salts. The colored effluents which are
discharged into water is a major source of environmental pollution and have harmful effects on aquatic life [5]. Hence, it becomes customary to degrade them effectively prior to release in main stream water sources. The conventional methods like chemical-coagulation, ozonation, activated carbon adsorption, biological treatment and catalytic reduction are generally in use to check this. [6-8]. But these processes are ineffective to achieve the target as they merely transform the contaminants from one form to another and thus cause secondary pollution [9-10].

The gamma radiations can serve as a very promising alternative to treat the dye effluents, as per the recent studies reporting, bleaching or decoloration of most of the colored material on exposure to high energy ionizing radiations [11]. These radiolytic degradation techniques serve the purpose of solving environmental problems more effectively with reference to effluents from dye and colorant industries [12]. The effect of radiations is reported to be intensified in aqueous solutions due to the primary products that are formed due to interaction of gamma radiations with water. Here the dye molecules are degraded more effectively. The dose rate, radiation dose, concentration and pH etc. are some of the operating parameters which govern the effectiveness of radiolytic degradation of dye colored waste water [13]. The decoloration of synthetic dyes by high energy radiations in aqueous and non aqueous solutions of many dyes has been reported by various researchers [14-17].

Gamma rays interact with water resulting into the radiolysis of water which in turn generates species like hydroxyl radical (‘OH), hydrogen atom (H'), hydrogen ion (H”), hydrated electron (e_{aq}^-), hydrogen peroxide (H_{2}O_{2})and H_{2} in the spur as per the equation 1.

H_{2}O  \ H^{'}, ‘OH, e_{aq}^−, H_{2}O_{2}, H_{2} and H^+ ---- (1).

Amongst these, hydroxyl radical, hydrated electron and hydrogen atom are most reactive which react with pollutants in a solution degrading them to simpler molecules. H' and e_{aq}^- may react with O_{2} which is commonly present in waste waters and form per hydroxyl radical (HO_{2})’, another oxidizing species, as per below given reactions.

$$\text{H}^* + \text{O}_2 \rightarrow \text{HO}_2^* \quad \text{(2)}$$
$$\text{e}_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2 \quad \text{(3)}$$
$$\text{O}^2^- + \text{H}^* \rightarrow \text{HO}_2^* \quad \text{(4)}$$
$$\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 \quad \text{(5)}$$

High gamma dose (or exposure time) is required when ionizing radiations are used to degrade the complex organic compounds [18-20]. These demands for an effective and nonhazardous method that could combine with the ionizing radiation process to have the synergistic effect. Hydrogen peroxide (H_{2}O_{2}) can be the answer as some reports shows that addition of small amounts of hydrogen peroxide helps to improve the irradiation capacity by increasing the formation of OH radicals [21-22] via below given reactions.

$$\text{e}_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^- \quad \text{(6)}$$
$$\text{H}_2 + \text{H}_2\text{O}_2 \rightarrow \text{.OH} + \text{H}_2\text{O} \quad \text{(7)}$$

Yulin et al. [23] had also demonstrated that the gamma radiation/H_{2}O_{2} process was more cost-effective than sole H_{2}O_{2} or irradiation.

Hydrogen peroxide is a stable chemical and as such no special equipment is required since it is can be stored easily, is non-corroding versatile chemical. It is mixes freely with water and have no limitations
of solubility and hence it becomes more beneficial in the oxidation procedure than other reagents like NaOCl and O₃, that are to be used carefully during application.

The present communication investigates the effect of addition of H₂O₂ on gamma radiolytic decoloration of Indigo Carmine, Methylene Blue and Malachite Green dyes aqueous solutions, particularly with respect to the optimum dose of H₂O₂, also referred to as Critical dose, which should be added for efficient decoloration. The structures of dyes are given in Figure 1 while their properties are given in Table 1.

![Malachite Green](image1.png) ![Indigo Carmine](image2.png) ![Methylene Blue](image3.png)

**Figure 1.** Structure of dyes

**Table 1.** Properties of Dyes.

| Dye               | Mol. weight | λₘₐₓ in aq. Solution (nm) | Color Index No. |
|-------------------|-------------|--------------------------|-----------------|
| Erythrosine-B     | 879.87      | 526                      | 45430           |
| Indigo Carmine    | 466.36      | 612                      | 73015           |
| Malachite Green   | 364.9       | 619                      | 42000           |
| Methylene Blue    | 284.4       | 665                      | 52015           |
| Sunset Yellow FCF | 452.37      | 452.37                   | 15985           |
2. EXPERIMENTAL

2.1 MATERIALS

The chemicals used during investigation were of Analytical Reagent grade. All the dyes were purchased and were used as obtained. All the solutions including stock solutions were prepared freshly every time using double distilled water before experimentation every time.

2.2 RADIATION SOURCE

All the working samples were irradiated using GC-900; $^{60}\text{Co}$ gamma source available at Nuclear Chemistry Laboratory of P.G.T. D. of Chemistry, R. T. M. Nagpur University, Nagpur, India, with a dose rate of 0.386 kGy per hour during the present study. (Figure.2).

2.3 METHODOLOGY

The stock solutions of every dye were prepared afresh before experimentation. The stock solutions of all the dyes were prepared and verified for the wavelength corresponding to maximum absorbance i.e. $\lambda_{\text{max}}$ and were found to be in good agreement with the theoretical values. Then various systems having different concentrations of Methylene Blue, Malachite Green and Indigo Carmine dye were prepared from respective stock solution by dilutions using double distilled water. Spectronic D-20
spectrophotometer was employed to record absorption spectra of all the samples before and after irradiation. The extent of decolorization was calculated from the decrease in absorbance. The samples were irradiated using different doses of gamma radiations in $^{60}$Co gamma radiation source having the range 0.1 - 0.5 kGy. The sample solutions were taken in Borosil tubes having standard B-24 joints. While investigation, the dose rate was 0.38 kGy/h.

The synergistic effect of $H_2O_2$ addition on gamma radiolysis was studied first by adding different quantities of $H_2O_2$ to the systems so as to arrive at the optimum quantity by trial and error method for each dye. Then a appropriate concentration of each dye was chosen in order to study the effect of $H_2O_2$. All the measurements were carried out at ambient temperatures in open air.

3. RESULTS AND DISCUSSION

The synergistic effect of $H_2O_2$ addition on gamma radiolysis was studied by performing a sequence of experiments with varying doses of $H_2O_2$. The corresponding change in extent of decoloration as a function of $H_2O_2$ dose for all the dyes are depicted in Figure 3(a-c). The results noticeably reveal that the extent of decoloration is accelerated on addition of hydrogen peroxide. Hydrogen peroxide reacts quickly with hydrated electrons which are formed as a consequence of radiolysis of water leading to the formation of •OH radicals as per the equation (6) stated above. This increase in the extent of decoloration could be attributed directly to the increase in •OH radicals which are formed via above reaction. This finding supports the fact that •OH radical are able to destroy the color bearing chromospheres more proficiently than does the hydrated electron. The graphs also reveal that for all the dyes, the rate of decoloration accelerates with increase in hydrogen peroxide dose, till it reaches a particular dose which corresponds to the maximum decolorization. This dose corresponding to maximum decoloration under the given conditions is referred to as `critical dose` and it varies from dye to dye as evident from the results.

![Methylene Blue](image1.png) ![Indigo Carmine](image2.png)

**Figure 3(a).** Effect of $H_2O_2$ on Gamma Radiolysis of Methylene Blue

**Figure 3(b).** Effect of $H_2O_2$ on Gamma Radiolysis of Indigo Carmine

However, the graphs also points at the fact that, as the quantity of $H_2O_2$ added is increased beyond the so called critical dose, decline in the extent of decoloration is observed[24]. This decrease in extent of decoloration could be justified on the basis that, when the hydrogen peroxide concentration increases beyond a critical value, a part of the •OH radicals gets scavenged [25-26] by the excess hydrogen peroxide as per equations (9-11).
H$_2$O$_2$ + •OH → HO$_2$ + H$_2$O

H$_2$O$_2$ + HO$_2$ → •OH + H$_2$O + O$_2$

HO$_2$ (or •OH) + HO$_2$ → H$_2$O$_2$ (or H$_2$O) + O$_2$—

4. CONCLUSIONS

The gamma radiations or H$_2$O$_2$ alone are not efficient in bringing the effective decoloration of synthetic dye effluents. The addition of H$_2$O$_2$ has the synergistic effect on gamma radiolytic decoloration of the dyes studied in present work.

The addition of H$_2$O$_2$ enhances the degree of decoloration thereby decreasing the dose and exposure time significantly. As the dose of H$_2$O$_2$ increases, degree and rate of decoloration increases but beyond the Critical dose, the rate and extent of decoloration start decreasing. The value of H$_2$O$_2$ Critical dose varies from dye to dye indicating that it depends on structure and concentration of dye solutions.

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