# Radiation induced degradation of Congo red dye: a mechanistic study

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**Abstract.** Synthetic dyes are persistent pollutants with poor biodegradability. The present study is about the degradation of direct Congo red dye in aqueous media using the Co-60 gamma radiation source. The experimental conditions such as gamma-ray absorbed doses, amount of oxidant ($H_2O_2$) and pH conditions were evaluated. The $\lambda_{max}$ of dye solution was noted as 498 nm, and then, decrease in absorbance and reduction in chemical oxygen demand (COD) were examined. The complete colour removal of dye was observed at 5 kGy, while a significant COD removal was observed at 15 kGy gamma-ray absorbed dose in conjunction with oxidant for 50 mg/L concentration. It was found that pH has no influence on degradation efficiency. A possible degradation pathway was proposed. The radiolytic end products were monitored by Fourier transform infrared (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS) to explore the degradation mechanism. It was imperative to study the oxidative degradation pathway to provide directions for potential applicability of advanced oxidation process (AOP) in industrial wastewater treatment.

**Keywords:** Congo red • radiolytic product • irradiation • advanced oxidation process

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## Introduction

The synthetic dyes have been utilized extensively in various industries such as dyes, paper, textile, plastics, leather, food and cosmetic. The application of dyes in industries imposed a threat to surface as well as ground water [1–3]. The azo dyes are toxic, non-biodegradable and have been frequently utilized in the textile sector due to their characteristics such as resistance toward light, temperature, washing and better colour fastness ability [4, 5]. The wastewater expelled may contain toxic by-products of textile auxiliaries due to low fixation on fabrics and get mixed in water bodies [6, 7].

Access to pure water is the primary need for human beings. The environment faces threat as a result of rapid industrial growth. The industrial effluents are resistant toward usual treatments options and have disadvantages of ineffective treatment, sludge formation, non-destructive method and phase change [8, 9]. There is a need of some effective treatment technologies for degradation of pollutants to resolve the issues associated with conventional methods. The advanced oxidation processes (AOPs) are characterized due to generation of hydroxyl radicals (•OH). These methods have gained attention and are thought to be effective for degradation/mineralization of complex organic compounds or industrial effluents [10–12].

**Fig. 1.** Effect of gamma radiation on absorbance of direct Congo red dye.



**Fig. 2.** Effect of gamma radiation in the presence of $H_2O_2$ on absorbance of direct Congo red dye solutions.

AOPs are promising for the degradation of pollutants such as pesticides, antibiotics, dyes and pharmaceutical wastes. The hydroxyl radicals generated by gamma radiation in the presence of hydrogen peroxide are currently utilized for radiolytic degradation of pollutants and industrial/domestic effluents [13, 14].

Very little literature is available regarding the current study. This work aimed to treat Congo red dye solutions by gamma radiation in the presence of oxidants. The study of radiolytic degradation was performed by UV/Vis, spectroscopy, Fourier transform infrared (FTIR) and gas chromatography--mass spectrometry (GC-MS) analyses along with determination of chemical oxygen demand (COD).

## Results and discussion

### Effect of gamma-ray absorbed dose on colour intensity

The Congo red dye exhibits $\lambda_{max}$ at 498 nm. The decrease in absorbance after gamma-ray treatment was evaluated. The dye solution having a concentration of 10–50 mg/L was subjected to gamma-ray treatment alone and then treatment in the presence of oxidant. The complete colour removal was observed at 5 kGy as shown in Figs. 1 and 2. The colour removal efficiency of dye solution owe to breakdown of chromophoric group(s), while mineralization occurred due to breakdown of complex structure into simpler fragments [15, 16]. The 5 kGy gamma-ray absorbed dose is ineffective to destruct the molecule, and this assumption was also proven by analysis of COD: reduction was only 37% at this absorbed dose even in the presence of oxidant.

When gamma radiation interacts with dilute dye aqueous solution, radicals such as $OH^\bullet$, $H^\bullet$ and $e^-_{aq}$ are generated with minor species. The presence of oxygen resulted in the formation of $^\bullet O_2^-$ and hydro-
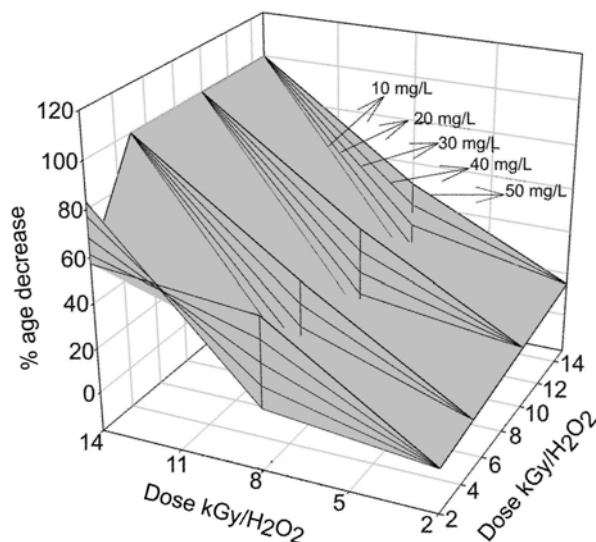
peroxy radical $^\bullet HO_2$. The presence of oxidant ($H_2O_2$) promotes the dye bleaching efficiency, scavenges the reducing species ($H^\bullet$ and $e^-_{aq}$) and promotes the oxidation process [17].

### Effect of gamma-ray treatment on chemical oxygen demand

As a result of treatment of dye solution, the reduction in COD was due to fragmentation of complex molecule into end product [18]. The noted COD removal was up to 20, 24, 30 and 47% when the dye solutions were treated with 2, 5, 10 and 15 kGy gamma-ray absorbed doses, while the decrease in COD was 29, 37, 45 and 80% when the treatment was carried out by gamma ray in the presence of 0.5 mL of oxidant $H_2O_2$ in 100 mL of solution as shown in Figs. 3 and 4. The addition of oxidant significantly improved the treatment efficiency and not only scavenged the reducing species but also enhanced $OH^\bullet$ radicals [19]. The attributed fact behind this notion is that decolouration of dye is just destruction of chromophore(s), while COD reduction indicated splitting of dye molecules into lower mass aldehyde, carboxylic acids, $CO_2$ and $H_2O$ [20].

### FTIR studies

The FTIR profile of untreated Congo red dye (Fig. 5) shows various functional groups: 3480 cm⁻¹ peak refers to NH stretching of amine, 2370 cm⁻¹ to $NH_2$ stretching vibration, 1633 cm⁻¹ to NH bending, 1560 cm⁻¹ to N=N stretching, 1510 cm⁻¹ may be to aromatic C=C stretching, 1400 cm⁻¹ to asymmetric CH bending, 1356 cm⁻¹ to CN bending and 1200 cm⁻¹ may be to CO stretching. The FTIR spectrum of treated dye (Fig. 6) indicates complete degradation of aromatic rings after treatment, but some minor peaks appeared such as 3020 cm⁻¹ attributed
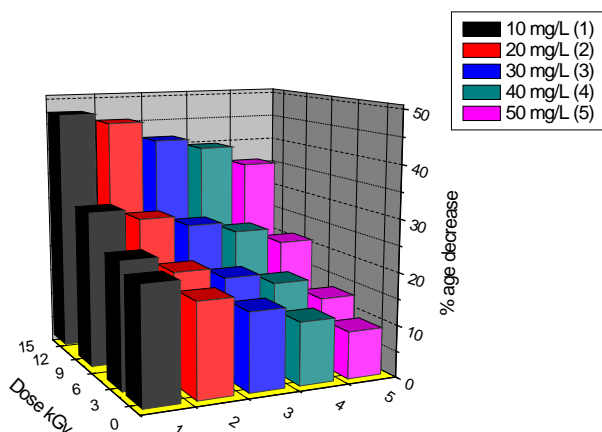
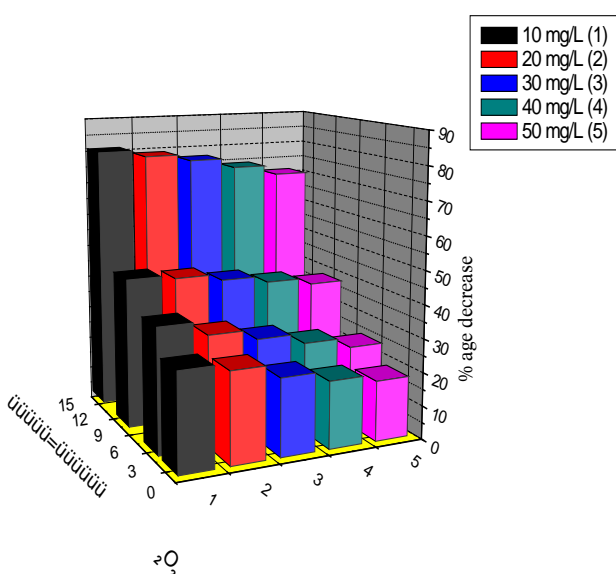**Fig. 3.** Effect of gamma radiation on COD reduction of direct Congo red dye.



**Fig. 4.** Effect of gamma radiation in the presence of $H_2O_2$ on COD reduction of direct Congo red dye.

to CH stretching and 1215 cm$^{-1}$ corresponding to CO stretching; the remaining group disappeared in the treated dye sample. It is assumed that dye molecules have been broken through chain oxidation initiated by OH$^{\cdot}$ radical via destruction of aromatic rings into simpler compounds. The same observations of oxidative degradation of dyes initiated by destruction of N-N bond and then mineralization have also been reported previously [21].
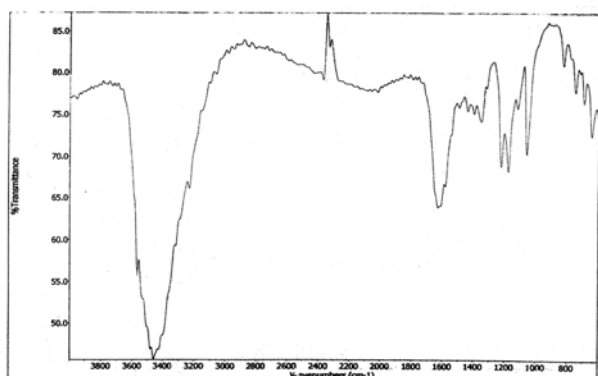


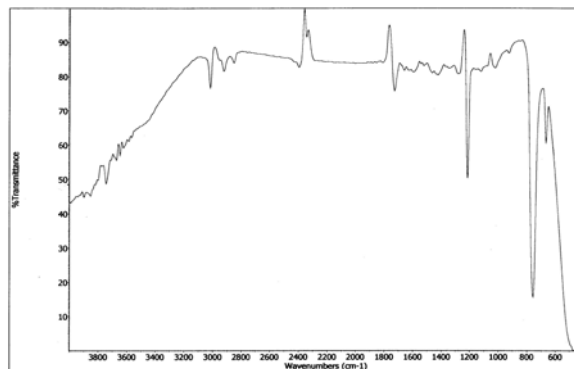**Fig. 5.** FTIR profile of unirradiated direct Congo red dye.



**Fig. 6.** FTIR profile of treated direct Congo red dye at 15 kGy in the presence of $H_2O_2$.

## GC-MS studies

The GC-MS analyses were performed in order to ensure the degradation in treated samples of Congo red dye. No characteristic peak was recorded in GC-MS spectra except some minor peaks after 15 kGy radiation treatment. On the base of mass spectral fragments in Table 1, a proposed mechanism (Scheme 1) commenced from the removal of azo linkage and breakdown of complex molecule. The further reaction further degraded intermediates into low--molecular weight fragments and then converted them into $CO_2$ and water, and results have harmony with the work of degradation of C.I. Reactive Red 2 [19].
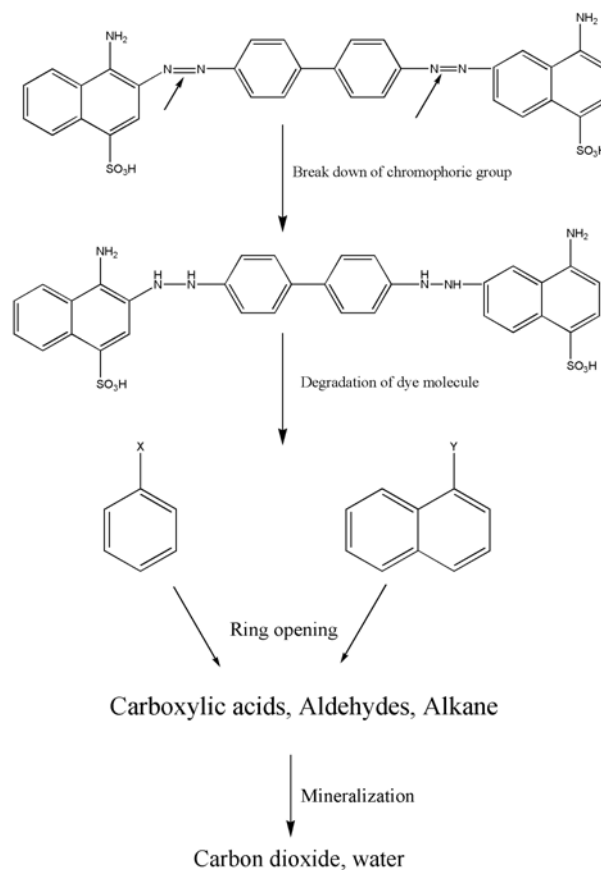


**Scheme 1.** Proposed mechanism for degradation pathway of direct Congo red dye.

**Table 1.** Mass spectra analysis of intermediate fragments of direct Congo red dye

| No. | Retention time | Compound identified by MS (probable) | Major ions ($m/z$) |
|---|---|---|---|
| 1 | 17.5 | *n*-hexane decanoic acid | 250, 227, 213, 185, 149,129, 115, 97, 83, 73, 60, 55 |
| 2 | 19.3 | octadecanoic acid | 284, 255, 241, 227, 185, 129, 111, 83, 69, 55 |
| 3 | 22.5 | 1,2-benzenedicarboxylic acid | 167, 149, 132, 121, 113, 104, 83, 76, 70, 57 |
| 10 | 24.5 | 2,6-di-*tert*-butyl-4-methyl phenol | 220, 190, 173, 166, 149, 123, 89, 65, 55 |

## Experimental

### Chemicals used

The commercial Congo red dye was procured from the local market. Hydrogen peroxide was purchased from Fluka (Germany). Ethyl acetate, potassium dichromate, ferrous ammonium sulphate, sodium hydroxide and sulphuric acid were provided by Merck (Germany). The solutions and dilution were prepared using triply distilled water.

### Radiation treatment of dyes solution

The irradiation of dye aqueous solutions was performed by Co-60 gamma radiation source available at the Nuclear Institute for Food and Agriculture (NIFA), Tarnab, Peshawar, in Pyrex vials at ambient temperature, while gamma-ray absorbed doses were 2, 5, 10 and 15 kGy alone and then in conjunction with oxidant ($H_2O_2$). The optimum amount 0.5 mL of $H_2O_2$ (37%) was added to 100 mL of dye solution in order to scavenge the reducing species and produce hydroxyl radicals. The dose rate was determined by Fricke dosimetry according to the standard method [22].

### Analysis

#### *Determination of colour intensity*

The $\lambda_{max}$ of dye solutions and then change in absorbance were measured before and after treatment by double beam UV-visible spectrophotometer (Hitachi U-2001, Japan).

#### *pH and COD measurement*

The pH of the solutions was monitored by the pH meter, while COD was analysed by the open reflux method according to the standard method [23].

#### *FTIR and GC-MS analysis*

The FTIR spectroscopy (Shimadzu U-2001, Japan) and GC-MS (Agilent Technologies 6890N) were conducted at the Pakistan Council for Scientific and Industrial Research (PCSIR), Lahore. The GC-MS analyses were performed to be acquainted with radiolytic end products. The GC having DB-5 capillary column coupled with MS detector through electron impact ionization mode (EI) interface using helium as a carrier gas while mass to charge ratios of frag-

ments were determined by ChemStation software and the identified compounds were then compared using software library. Before analyses, the treated samples were extracted, decanted and then dehydrated for further analysis [24, 25].

## Conclusion

The gamma ray-induced degradation of synthetic dyes in the presence of oxidant ($H_2O_2$) is a promising, safe and green method beyond the threat of radioactivity. The method has proven to be a best choice in order to remove the colour intensity along with the pollution load in terms of reduction in COD. Complete colour removal with more than 80% COD reduction has been achieved. The addition of $H_2O_2$ promotes treatment efficiency and not only scavenges the reducing species but also promotes oxidation. The change in pH of media was insignificant, and degradation efficiency was uniform at all pH values. The degraded end products were monitored by FTIR and GC-MS studies that revealed that the radiation treatment has mineralized the targeted compound. Furthermore, the treatment may be extended to treat the wastewater of industrial origin.

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