Decolorization and Degradation of Textile Wastewater by Gamma Irradiation in Presence of H_2O_2

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Abstract: Gamma irradiation is a contemporary idea of textile wastewater treatment. The irradiation can decolorize and decompose the waste content satisfactorily. However the process efficiency can improve significantly by using hydrogen peroxide with wastewater during irradiation. The wastewater was collected from a knit dyeing industry, irradiated at 10kGy radiation dose with a dose rate 13 kGy/h in presence of different concentrations of hydrogen peroxide. Then the change in pH and decoloration percentage, reduction of total suspended solids (TSS), five-day biological oxygen demand (BOD_5) and variation of chemical oxygen demand (COD) were investigated. It was found that colored wastewater become almost colorless due to the destruction of the chromophore group of the dye molecules by radiation. Smaller acidic organic compounds formed due to the fragmentation of larger dye molecules, resulting on the reduction of pH of irradiated water. Total suspended solids (TSS) were also reduced because of the degradation of the solid particles. The COD and BOD_5 values of irradiated wastewater also decreased significantly. However the COD values were found to increase in presence of H_2O_2 by dichromate method as it behaves as a reductant and oxidized by potassium dichromate resulting significant increment in COD reading.
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1. Introduction

Textile industries are the major source of water pollution releasing highly colored waste stream in the surface water bodies. The wastewater generated in textile processing plants is contaminated with toxic synthetic colorants and various perilous chemicals. The nature of the wastewater depends on the types of fibers and the chemicals used, the type of textile facility, and the processes and technologies being operated. The processing of textile materials is carried out through aqueous medium and generates large volume of wastewater [1]. Nearly 70 to 150L water is required for the processing of 1 kg cotton fabric [2]. The dyeing of cotton fibers which accounts for almost 48% [3, 4] of the total fiber consumed by the textile industry all over the globe are mainly performed with reactive dyes [5]. These dyes are water soluble anionic dyes exhibit one or more functional group capable of forming covalent bond with cellulose and are not suitable for recycling [6]. A considerable amount (10-40%) of unfixed hydrolyzed dyes remains in textile wastewater causing highly colored effluent discharge [7]. Color present in the water absorbs sunlight which reduces the availability of sunlight for the plants and phytoplanktons. As a result the self-purification capacity of natural water bodies decreases significantly [8]. The removal of color from dyehouse wastewaters is currently a major environmental issue in textile sector.

The color of textile wastewater cannot be removed efficiently by ordinary treatment technologies. Typical techniques for treatment of wastewater include the classical methods such as adsorption [9, 10, 11], coagulation [12, 13], filtration [14] and sedimentation [15]. All these techniques have some degree of effectiveness but all of them generate secondary waste which needs to be tackled further [16]. On the contrary, biological treatment based on activated sludge can efficiently reduce the COD but complete color removal is not possible with this technique [17]. Moreover, huge space is required to set up a biological plant. In addition, applications of membrane technologies in textile industries are not yet very common [17]. Again the ultra-filtration techniques prove its success mainly for the recovery of size materials from desizing effluent and indigo dye particles from the discharged dye liquor.

In this regard ionization radiation technology is the promising technique to decolorize and decompose the textile wastewater [18]. The radiation technology methods normally utilize a strong oxidizing species such as $^{\bullet}OH$ radicals which have high electrochemical oxidation potential and cause a sequence of reactions thereafter to breakdown the macromolecules of dye into smaller substances [19]. High energy radiation produces instantaneous radiolytic transformation through energy transfer from high energy accelerated electrons to the orbital electrons of water molecules. Absorbed energy disturbs the electron system of the molecule resulting in the breakage of interatomic bonds and ionizing the water molecules forming H_2O^+. Various active species are produced due to the radiation interaction between gamma rays with water as shown in the equations given below.

$$H_2O^{+} + e^{-} \longrightarrow {}^{\bullet}OH + {}^{\bullet}H$$
$$H^{+} + H_2O + e^{-} \longrightarrow H_3O^{+} + e^{-} \longrightarrow 2H^{\bullet} + {}^{\bullet}OH$$
$$OH^{+} + H_2O + e^{-} \longrightarrow {}^{\bullet}H + 2\,{}^{\bullet}OH$$

In the presence of dissolved air or oxygen, a radical known as perhydroxyl radical i.e. ${}^{\bullet}HO_2$ is also formed:

$${}^{\bullet}H + O_2 \longrightarrow {}^{\bullet}HO_2$$

Generally these species are hydroxyl radical (${}^{\bullet}OH$), hydrogen radical ($H^{\bullet}$), hydrated electron (e^{-}_{aq}), and so on [18]. From these products, the most reactive species are hydroxyl radical, hydrated electron. Hydroxyl radical attacks the conjugated double bond of the dye particle and breaks it [20]. Thus the colored dye molecules are converted into colorless smaller molecules which results in decoloration of the effluent.

The efficiency of the gamma radiation induced decolorization of textile wastewater can be enhanced by the application of hydrogen peroxide. Hydrogen peroxide is a potent source of free radicals and a powerful oxidizing agent, which leads the various applications of this chemical [21]. It is a non-corrosive and versatile liquid [22]. Furthermore, it is totally miscible with water as it has no solubility limitations. This makes it more advantageous in the oxidative process than chemicals such as sodium hypochlorite and ozone [22], which require more care in application. The ${}^{\bullet}OH$ radicals are formed from hydrogen peroxide by rapid reaction with hydrated electron of the radiolysis water.

$$H_2O_2 + e^{-}_{aq} \longrightarrow {}^{\bullet}OH + {}^{-}OH$$

The application of gamma irradiation in the presence of hydrogen peroxide is a rapid and effective way of treating textile wastewater. Again hydrogen peroxide is a low cost additive which is beneficial for cost effective treatment. The addition of H_2O_2 in irradiative decolorization process enhances the color removal efficiency of gamma radiation. The aim of this study is to investigate the effect of hydrogen peroxide addition in the conventional gamma irradiative decolorization and degradation of textile wastewater.

2. Materials and methods

2.1 Sample collection and irradiation

Textile wastewater was collected directly from the equalization basin of Effluent Treatment Plant (ETP) of Divine Textiles Mills Ltd, Gazipur, Bangladesh. Then different type of wastewater samples were prepared in transparent 500 ml plastic bottles as shown in Table-1 and irradiated at 10 kGy radiation dose of dose rate 13 kGy/h without any further treatment or dilution. Hydrogen peroxide (H_2O_2) used to prepare solution was analytical grade of 30% strength and collected from MERCK, India.

Table 1. Test sample coding

Test sample types	Code
Raw wastewater	RW
Irradiated at 10 kGy without H_2O_2	IW
Irradiated at 10 kGy with 0.5% H_2O_2 solution	R1
Irradiated at 10 kGy with 1.0% H_2O_2 solution	R2
Irradiated at 10 kGy with 2.0% H_2O_2 solution	R3
Irradiated at 10 kGy with 3.0% H_2O_2 solution	R4

The electromagnetic radiation (gamma radiation) from Cobalt-60 source was carried out at Institute of Radiation and Polymer Technology (IRPT), Bangladesh Atomic Energy Commission, Dhaka. Then the presence of color, pH, TSS, COD & BOD_5 values wastewater was measured.

2.2 Laboratory analysis and calculation

The pH of the raw wastewater and irradiated samples was measured directly by digital pH meter (Ecoscen, model no-1161795) from Eutech Instruments, Singapore. The color absorbance of raw and irradiated wastewater was measured by UV-Vis spectrophotometer (T60, PG Instrument UK). The degree of decolorization was then calculated from the decrease of absorbance at maximum absorption wavelength after irradiation as follows [16].

$$Decoloration\ (\%) = \frac{A_0 - A_1}{A_0} \times 100 \quad (1)$$

Where, A_0 and A_1 are the maximum absorbance in visible area of the textile wastewater before and after irradiation.

The test of Total Suspended Solids (TSS) was performed by filtering the wastewater through a fiber pad filter and then measuring the dry weight (obtained by drying the filter and its content at 103-105ºC) of the material.

The test of Chemical Oxygen Demand (COD) was carried out by dichromate method, adding 2 ml of wastewater sample to a solution of a strong oxidizing agent (potassium dichromate) in a strongly acidic medium (H_2SO_4) containing a silver sulfate catalyst. The sample was refluxed at 150ºC for 2-3 hours and COD values were measured by HACH spectrophotometer (Model no-DR 2800, USA).

Biological Oxygen Demand (BOD_5) was measured by dilution method. The method consists of filling with sample to an airtight bottle of 300 ml size and incubating it 20°C for 5 days. Dissolved oxygen (DO) was measured by DO meter (HQ40d portable DO meter, HACH, USA) initially and after incubation, and the BOD_5 is computed from the difference between initial and final DO. BOD_5 is calculated as follows:

$$\text{Seeded BOD}_5 = \frac{(D_0 - D_5) - (B_0 - B_5)f}{P} \quad (2)$$

Where, D_0 is the dissolved oxygen (DO) of the diluted solution after preparation (mg/l), D_5 is the DO of the diluted solution after 5 day incubation (mg/l), P is the decimal dilution factor, B_0 is the DO of diluted seed sample after preparation (mg/l), B_5 is the DO of diluted seed sample after 5 day incubation (mg/l) and f is the ratio of seed volume in dilution solution to seed volume in BOD test on seed.

3. Results and discussions

3.1 Reduction of pH

The actual pH of the reactive dyebath normally lies between 10 to 11. However, as wastewaters from dyebath mixed with other different types of wastewater discharged at various other stages of processing, final pH of the wastewater in mixing tank was found around 8 to 9. After irradiation the pH values of the wastewater decreased from 9 to nearly neutral value (7-7.5) due to the formation of organic acids (such as dicarboxylic acids or monocarboxylic acids like acetic acid, and other acidic aromatic compounds or carbonic acid) due to the breakdown of aromatic rings[20, 23].

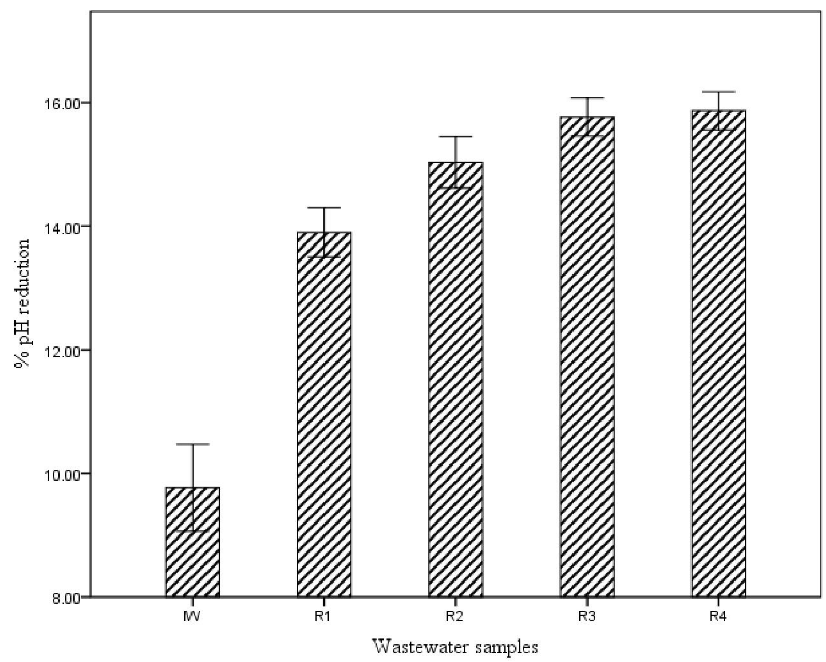

Figure 1. Reduction of pH of textile wastewater after gamma irradiation in presence of H_2O_2

Though the pH of the final wastewater of a textile industry may vary depending on the nature of processing but the radiation is capable of lowering the pH in all cases as shown in Figure-1. However, the pH of irradiated wastewater is reduced considerably for the addition of H_2O_2 up to a maximum limit of 2%. Beyond this limit, the change of pH is not significant as the organic acid resulted from the breakdown of benzene ring, is converted to further smaller components.

3.2 Measurement of color removal efficiency

Color removal efficiency was analyzed by measuring the presence of color in irradiated and unirradiated wastewater through UV-Vis spectrophotometer. However, the color of the textile wastewater differs significantly according to the type of processing, use of chemicals and selection of dyes. The color reduction is influenced by the amount of color present in wastewater and the structure of dye [19]. In this study textile wastewater was irradiated at 10 kGy radiation dose and then color reduction percentages were calculated.

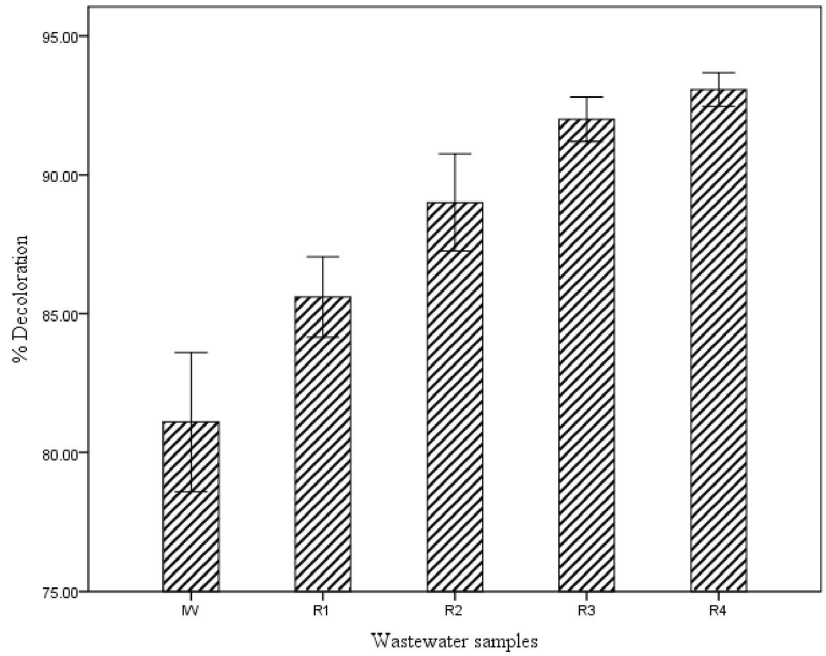

Figure 2. Color reduction (%) of wastewater in presence of H_2O_2 after gamma irradiation

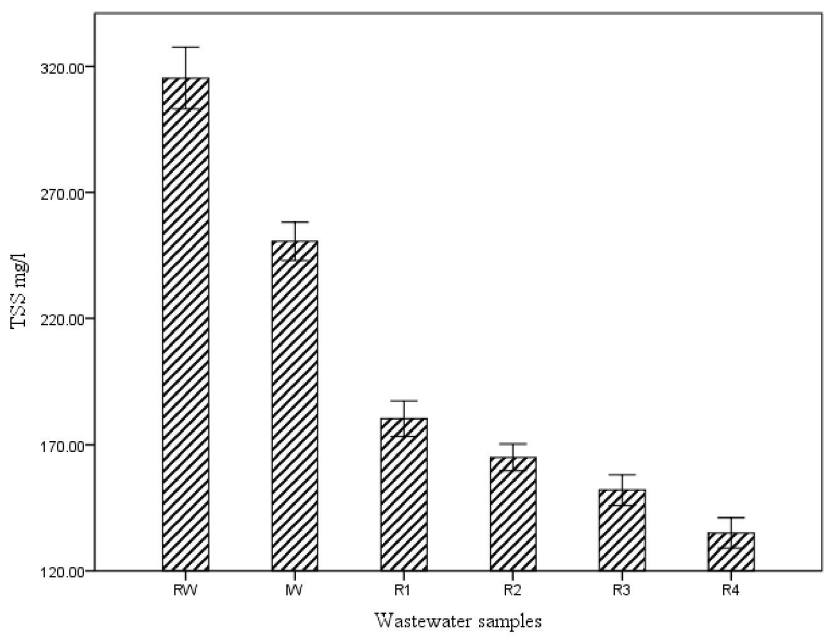

Figure 3. Reduction of total suspended solids of textile wastewater by gamma irradiation

As discussed earlier, hydrated electron and hydroxyl radical (•OH) that form from radiolysis of water is responsible for decolorization of wastewater. The active hydroxyl radicals attack the chromophore groups of dye molecule and produces colorless smaller organic compounds. Hence the addition of H_2O_2 at radiation stage generates additional hydroxyl radical which promotes the decolorization rate [24]. The bar diagram in Figure-2 shows that color reduction percentage increases from around 82% to 93% for the increment of H_2O_2 concentration from 0% to 3%. Thus it can be concluded that presence of H_2O_2 enhances the decolorization efficiency of gamma irradiation.

3.3 Reduction of total suspended solids

The solid contents in textile wastewater vary considerably, depending on the process involved. Typically, suspended solids carry a major portion of organic material, thus significantly contributing to the organic load of the wastewater. Again, suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases level of dissolved oxygen. Hence, effective solid removal can appreciably contribute to wastewater treatment.

The degradation of total suspended solids (TSS) by gamma radiation is shown in Figure 3. The average TSS value of irradiated water containing 3% H_2O_2 was found 140 mg/l whereas this value was 310 mg/l for raw wastewater (RW) and 260 mg/l in case of irradiation without H_2O_2. The results indicate that TSS can be effectively decomposed by irradiation in presence of H_2O_2. The •OH radicals react with suspended solid materials, precipitates due to the degradation of organic substances and suspended matter in wastewater [25].

3.3 Study on the variation of chemical oxygen demand

The chemical oxygen demand (COD) is one of the most widely used parameters that is indicative of the characteristics of wastewater [21]. The COD is the equivalent amount of oxygen required to chemically oxidize the organic matter contained in a known volume of wastewater using a standard test in which a strong oxidant (potassium dichromate) is used. The test was performed by dichromate method and the sample was refluxed at 150ºC for 2 hours and COD values were measured by a spectrophotometer. The COD values of wastewater and irradiated water are shown in Figure 4.

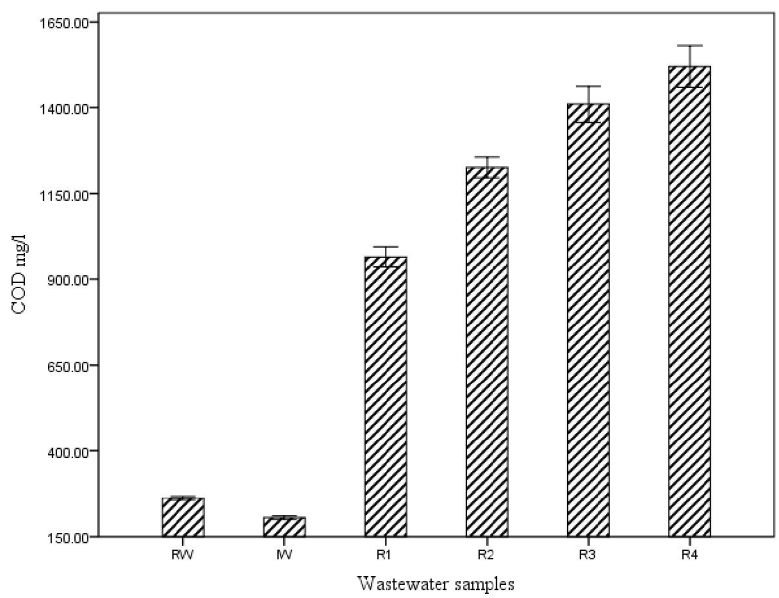

Figure 4. Variation of COD values of gamma irradiated textile wastewater in presence of H_2O_2

From the figure it has been found that, the COD value of wastewater has reduced after irradiation due to the decomposition of organic pollutants in the water. As a consequence, due to the addition of hydrogen peroxide solution, the degradation of organic matter is also enhanced which should give the lower values of COD. But practically, the COD values of the irradiated wastewater rise drastically with the addition of H_2O_2 as observed by the dichromate method. From the experiment it has been found that, when potassium dichromate is added to the hydrogen peroxide solution which is acidified with sulphuric acid, a green color appears. It is mainly due to the Cr^{3+} ions formed by the reduction of potassium dichromate as follows [21].

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \quad (3)$$

The rate of interference of H_2O_2 on COD with the stoichiometry of the equation shows, each mg/l of H_2O_2 gives rise to a contribution of 0.47 mg/l to the COD reading through its reduction from Cr^{6+} to Cr^{3+}. Equation -3 reflects that although H_2O_2 is normally a powerful oxidant, when it is in the presence of the even more powerful oxidant, the dichromate ion, $Cr_2O_7^{-2}$, H_2O_2 behaves as a reductant and is itself oxidized, thereby contributing positively (and spuriously) to the COD reading.

3.4 Effect of irradiation in removal of BOD_5

The BOD_5 of a wastewater is defined as the amount of oxygen required by aerobic microorganisms to (partially) oxidize the organic matter in a known volume of wastewater according to a standardized test. BOD_5 is typically expressed in mg of oxygen/L of wastewater. The test was carried out of incubating the wastewater (appropriately diluted) samples for five days at 20°C temperature, and measuring the amount of residual oxygen at the end of the test to determine the amount of oxygen consumed.

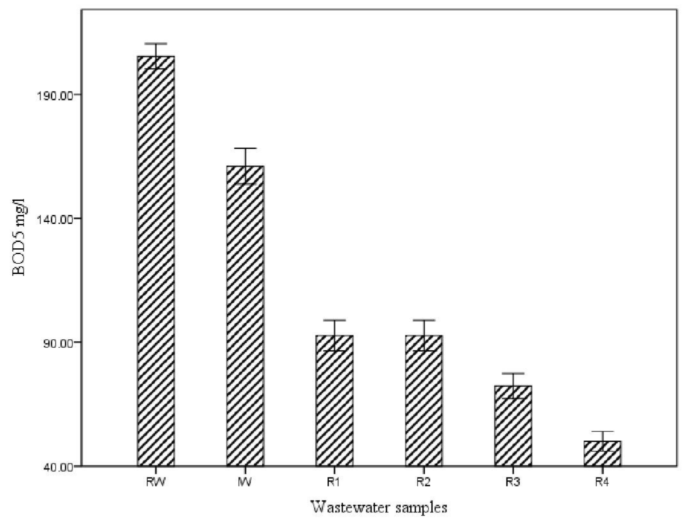

Figure 5. Reduction of BOD_5 of irradiated wastewater in presence of H_2O_2

Gamma irradiation can effectively decompose the organic matter in wastewater. Due to the decomposition of organic pollutants in wastewater, the amount of biodegradable organic matter decreases which results in lower BOD_5 values of the irradiated water. Again, the presence of hydrogen peroxide during irradiation enhances the degradation of organic matter. In Figure-5, it is shown that the BOD_5 value is reduced about 170mg/l from the initial value of about 210 mg/l in raw wastewater. The BOD_5 value further reduced when H_2O_2 is used during irradiation and it continues to lower with the gradual increment of H_2O_2 concentration.

4. Conclusion

The decolorization and degradation of textile wastewater by gamma irradiation in presence of H_2O_2 have been investigated. The detailed study has demonstrated that, the treatment of textile wastewater by gamma radiation with the addition of H_2O_2 can effectively breaks coloring substances resulting in higher color removal efficiency and lowering the pH values. The addition of H_2O_2 can also greatly promote the degradation of organic materials and decrease the BOD_5 values. Although, the COD values of irradiated wastewater have increased due to the interference of H_2O_2 with potassium dichromate in dichromate method but the lower BOD_5 values indicate that the organic components are decomposed in the treated water. The results of pH lowering, decoloration and degradation of organic pollutant in irradiated water recommend an impressive potential of using gamma irradiation in wastewater treatment with the incorporation of H_2O_2.

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