Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1125804

57 (2016) 21545–21551
September

Taylor & Francis
Taylor & Francis Group

Decolorization and decontamination of textile wastewater by gamma irradiation in presence of H_2O_2

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Received 10 August 2015; Accepted 19 November 2015

ABSTRACT

Gamma irradiation is a contemporary concept for the treatment of textile wastewater. The organic pollutants and coloring materials of wastewater can be decomposed acceptably by gamma irradiation. However, the process efficiency can be improved significantly by integrating H_2O_2 as an additive with wastewater during irradiation. The treatment of combined textile wastewater collected from a knit dyeing industry was carried out using a Cobalt-60 gamma radiation source at 10 kGy irradiation dose with a dose rate of 13 kGy/h in presence of 0.5, 1.0, 2.0, and 3.0% concentrations of H_2O_2. Then the change in pH and decoloration percentage, reduction in total suspended solids (TSS), five-day biological oxygen demand (BOD_5), and variation of chemical oxygen demand (COD) were extensively investigated. It was observed that colored wastewater become almost colorless due to destruction of the chromophore group of the dye molecules by irradiation. Moreover, the alkaline pH of wastewater is also reduced to neutral condition by fragmentation of larger dye macromolecules resulting in the formation of smaller acidic organic compounds. The degradation of the solid particles and refractory organic matters leads to a considerable reduction in TSS and BOD_5 values and consequently the COD of wastewater after irradiation. 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 in a significant increment in COD reading. So it can be summarized that the application of gamma irradiation with the incorporation of H_2O_2 is a promising tool for the treatment of textile wastewater by decontaminating its organic pollutants effectively. This effectual degradation of organic matter can eliminate environmental hazard significantly after discharging a large volume of irradiated wastewater to the environment with the minimum concentration of perilous organic matters and coloring substances.

Keywords: Decolorization; Decontamination; Gamma irradiation; Textile wastewater; H_2O_2

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1. Introduction

Textile industries are the major sources of water pollution by 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 as well as the processes and technologies being operated. The processing of textile materials is carried out in aqueous medium and thus generates a large volume of wastewater [1]. Nearly 70–150 L water is required for the processing of 1 kg of 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 a 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 wastewater 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 [9–11], 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. 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 ultrafiltration 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 hydroxyl radicals (·OH) which have high electrochemical oxidation potential and trigger a sequence of reactions resulting in the breakdown of the dye macromolecules 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 generated as a result of interaction between gamma rays and water such as hydroxyl radical (·OH), hydrogen radical (H·), hydrated electron (e^-_{aq}), and so on [20]. Hydroxyl radical attacks the conjugated double bond of the dye particle and breaks it [21]. 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 to the various applications of this chemical [22]. It is a non-corrosive and versatile liquid and 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 [23], which require more care in application. The ·OH radicals are formed from hydrogen peroxide by rapid reaction with hydrated electron of the radiolysis water:

$$H_2O_2 + e^-_{aq} \rightarrow {}^{\cdot}OH + {}^{-}OH$$

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 in integration with gamma irradiation for decolorization and degradation of combined textile wastewater.

2. Experimental program

2.1. Materials

The wastewater samples of this study were collected directly from the equalization tank of Effluent Treatment Plant (ETP) of Divine Textiles Mills Ltd, Gazipur, Bangladesh. Wastewater samples were collected and irradiated in 500-ml plastic bottle. Hydrogen peroxide (H_2O_2) used to prepare solution was analytical grade of 30% strength and collected from MERCK, India. The test of chemical oxygen

demand (COD) of wastewater was performed using higher range COD (HR COD) vials having range 0–1,500 mg/L that was supplied by HACH, USA.

2.2. Methods

2.2.1. Sample collection and irradiation

The wastewater samples in this study were obtained directly from the equalization tank of ETP of a knit dyeing industry. Samples were collected in 500-ml plastic bottles, packed in polyethylene bags, and sealed for the safety prior to being subjected to gamma irradiation. H_2O_2 was added with the textile wastewater to prepare solution of 0.5, 1.0, 2.0, and 3.0% concentrations. For the ease of identification, all the test samples were coded as shown in Table 1.

The wastewater samples were submitted to Cobalt-60 gamma radiation source provided in the Institute of Radiation and Polymer Technology (IRPT), Atomic Energy Research Establishment, Savar, Dhaka. The irradiation was performed with 10 kGy radiation dose of dose rate 13 kGy/h without any further treatment or dilution. The radiation dose was determined by Amber Perpex dosimeter.

2.2.2. 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 decoloration was then calculated from the decrease in absorbance at maximum absorption wavelength after irradiation using the Eq. (1) [16]:

$$\text{Decoloration}\,(\%) = \frac{A_0 - A_1}{A_0} \times 10 \quad (1)$$

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

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 103–105°C) of the material.

The test of 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 150°C for 2–3 h and COD values were measured by HACH spectrophotometer (Model-DR 2800, USA).

Biological oxygen demand (BOD_5) was measured by dilution method. The method consists of filling sample in an airtight bottle of 300-ml size and incubating it 20°C for 5 d. 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 through Eq. (2):

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

where D_0 is the DO of the diluted solution after preparation (mg/L), D_5 is the DO of the diluted solution after 5 d 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 d incubation (mg/L), and f is the ratio of seed volume in diluted solution to seed volume in BOD test on seed.

3. Results and discussions

3.1. Reduction in pH

The actual pH of the dyebath in case of dyeing of cotton fiber with reactive dye normally lies between 10 and 11 [4]. However, as wastewater from dyebath mixed with other different types of wastewater discharged at various other stages of textile processing, final pH of the effluent in mixing tank was found around 8–9. Again after gamma irradiation the pH values of the treated water was reduced from 9 to nearly neutral value (7–7.5).

Fig. 1 illustrates the reduction in pH of wastewater due to gamma irradiation in presence of H_2O_2. The change in pH is influenced by the structures of dye molecule present in the wastewater and its

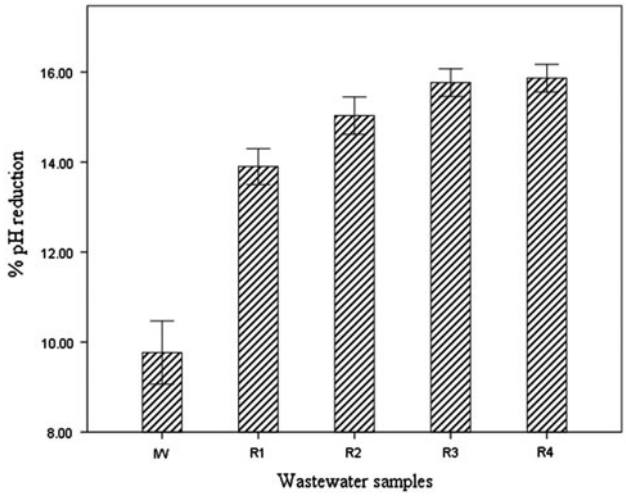

Fig. 1. Reduction in pH of textile wastewater after gamma irradiation in presence of H_2O_2.

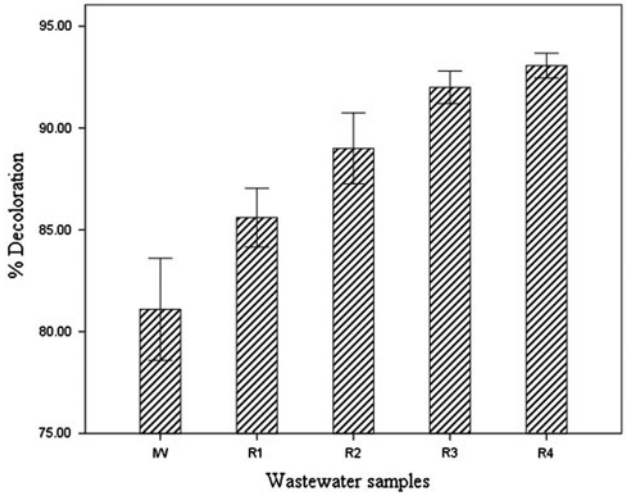

Fig. 2. Color reduction (%) of wastewater after gamma irradiation with the integration of H_2O_2.

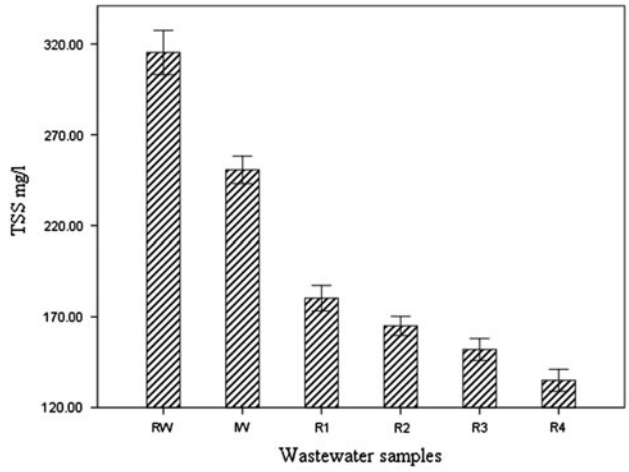

Fig. 3. Reduction in TSS of textile wastewater by gamma irradiation.

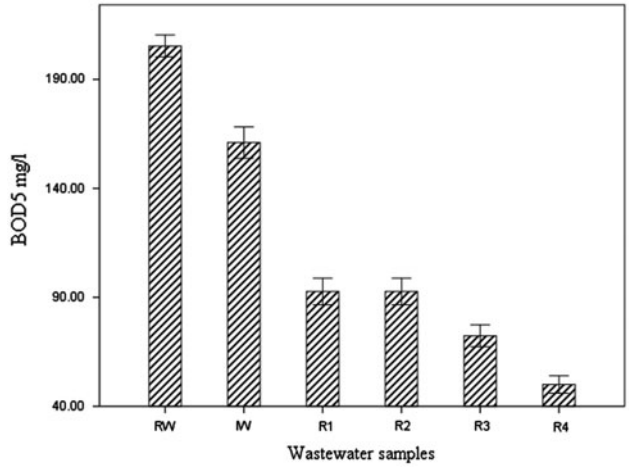

Fig. 4. Reduction in BOD_5 values of textile wastewater after gamma irradiated in presence of H_2O_2.

degradation during irradiation [21]. 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 fragmentation of aromatic rings [24] of dye molecules induced by ionizing irradiation instigate the reduction in pH from alkaline to neutral condition. From the study, it has been observed that though the pH of the final wastewater of a textile industry may vary depending on the nature of processing but 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 in pH is not significant, as the organic acid resulted from the breakdown of benzene ring which is converted to further smaller components [15].

3.2. Measurement of color removal efficiency

Color removal efficiency of gamma irradiation from wastewater was analyzed by measuring the presence of color in irradiated and unirradiated wastewater through UV–vis spectrophotometer. The color of the textile wastewater differs considerably according to the type of processing, use of chemicals, and selection of dyes. On the contrary, the color reduction is influenced by the structure of dye and the amount of color present in wastewater [19]. The percentages of

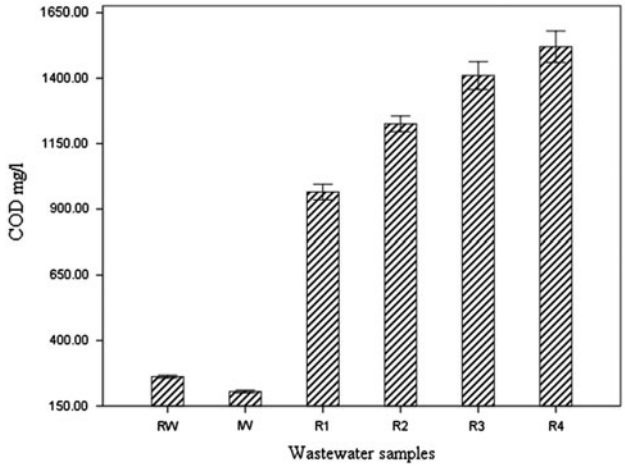

Fig. 5. Variation of COD values of gamma irradiated textile wastewater in presence of H_2O_2.

color reduction of dye wastewater induced by gamma irradiation in the presence of H_2O_2 are shown in Fig. 2.

The bar diagrams in Fig. 2 show the change in color reduction percentages according to the gradual increment in H_2O_2 concentration. The color reduction of wastewater increases 82–93% for the increment in H_2O_2 concentration from 0 to 3%. 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 radicals which promote the decolorization rate [25]. Thus, it can be summarized that presence of H_2O_2 enhances the decolorization of dye wastewater by gamma irradiation.

3.3. Reduction in TSS

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 DO. Hence, effective solid removal can appreciably contribute to wastewater treatment.

The degradation of TSS in wastewater by gamma irradiation is shown in Fig. 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, and 260 mg/L in case of irradiation without H_2O_2. The results indicate that TSS such as cellulose and other organic solid materials of wastewater were effectively decomposed by irradiation in presence of H_2O_2. The action of ionizing radiation on cellulose macromolecule as well as on other polysaccharides is random scission and degradation of the polymeric chain [26]. Hydroxyl radicals (·OH) formed from H_2O_2 by rapid reaction with hydrated electron of the radiolysis water react with suspended solid materials and cotton cellulose leading to the formation of glucose, glyoxal, cellobiose, cellotriose, cellotetraose, cellopentaose, cellohexaose, and other micro molecular products [26]. The higher concentration of H_2O_2 in irradiated wastewater accelerates the decomposition of cellulose and other organic materials resulting in the considerable reduction in TSS in wastewater after gamma irradiation.

3.4. Reduction in BOD_5

The BOD_5 of a wastewater is defined as the amount of oxygen required by aerobic micro-organisms to oxidize the biodegradable organic matter in a known volume of wastewater according to a standardized test condition. The test is carried out in five days known as BOD_5 is typically expressed in mg of oxygen/L of wastewater is consumed by aerobic microorganisms at the end of the test. The reduction in BOD_5 values signifies the decomposition of biodegradable organic pollutant in wastewater.

In Fig. 4, it has been observed that the BOD_5 value was reduced to 170 mg/L after irradiation from the initial value of 210 mg/L in raw wastewater. The BOD_5 value further reduced when H_2O_2 was used during irradiation and it continues to decrease with the gradual increment of H_2O_2 concentration. The trend of reduction in BOD_5 values is shown in Fig. 4 revealed that when the wastewater was exposed to ionizing irradiation, the water molecule undergoes radiolysis process to produce ionized and excited water molecules and reactive species (·OH, e^-_{aq}, and ·H). Perhydroxyl radical i.e. $HO^{\cdot}_2$ was also formed in the presence of dissolved air or oxygen [27]. Reactions between pollutants and primary products of water radiolysis and secondary short-lived species lead to the removal of refractory organic pollutants from the wastewater. Again, hydroxyl radicals (·OH) responsible for radicals–pollutants reactions were also formed from H_2O_2 by rapid reaction with hydrated electron of the radiolysis water. Hydroxyl radical which have high electrochemical oxidation potential causes the breakdown of the chemical bonds and leads to

decomposition of pollutants [21]. Therefore, a higher reduction in BOD_5 value of irradiated water results from a greater decomposition of biodegradable organic pollutants due to the formation of more hydroxyl radical at higher concentration of H_2O_2.

3.5. Variation of COD

The COD is one of the most widely used parameters that is indicative of the characteristics of wastewater [22]. 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 COD values of wastewater and irradiated water are shown in Fig. 5.

The COD value of wastewater has reduced after irradiation due to the decomposition of organic pollutants in the water is shown in Fig. 5. 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 sulfuric acid, a green color appears. It is mainly due to the Cr^{3+} ions formed by the reduction of potassium dichromate as follows [22]:

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

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+}. Eq. (3) reflects that although H_2O_2 is normally a powerful oxidant, but in the presence of an 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.

4. Conclusion

The decolorization and decontamination 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 efficiently break down the 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 refractory organic materials and decrease the TSS and BOD_5 values considerably. Although the COD values of irradiated wastewater have increased due to the interference of H_2O_2 with potassium dichromate in dichromate method, the lower BOD_5 values signify that the organic components are decomposed in the treated water. The effective decolorization and degradation of coloring matter as well as toxic organic pollutants of combined textile wastewater recommend an impressive potential of using gamma irradiation in wastewater treatment with the integration of H_2O_2.

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