

Effect of gamma-irradiation on aqueous solutions of Apollofix dyes

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Abstract. Radiation processing has been considered as a promising process for the treatment of textile industry waste effluents. In this study, the possibility of using gamma-rays to degrade and decolorize Apollofix dyes in water has been investigated. Two different Apollofix dyes, Apollofix Red (AR) and Apollofix Yellow (AY) in aqueous solutions were irradiated in air with doses from 1.0 kGy to 8.0 kGy at a 0.14 kGy/h of dose rate. The change in absorption spectra, pH, chemical oxygen demand (COD), biological oxygen demand (BOD) and the degree of decoloration (percent reduction in optical density) were examined in the presence and absence of H₂O₂. The absorption bands at 534 nm and 420 nm for AR and AY were observed to decrease rapidly with increasing irradiation dose. The degree of decoloration of each dye solution with irradiation dose was estimated as 100 percent for the lower concentration (50 ppm) dye solutions. The complete decoloration was observed after 2.0 kGy and 1.0 kGy doses for AR and AY dyes. The COD and BOD reduction and the change of pH for all dye solutions on irradiation showed similar behavior.

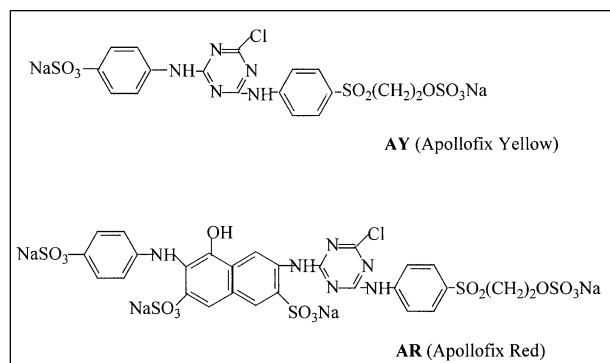
Key words: gamma irradiation • Apollofix dyes • decoloration • organic pollutants degradation • wastewater treatment

Introduction

Textile dyeing wastewater is one of the major environmental problems in Turkey and is a common problem faced by many countries. These types of wastewaters are generally high in biological oxygen demand (BOD), chemical oxygen demand (COD), total solids, and strongly colored. Neither simple chemical nor biological treatment has proved to be adequate in removing the color and organic matter. It is well known that dyes are not readily biodegradable [3]. The toxicity and mass production of dyes lead to the necessity of developing new techniques. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes [13]. Physical processes, such as coagulation and adsorption, merely transfer the pollutants from wastewater to other media and cause secondary pollution. Ionizing radiation proved to be more effective for the treatment of this type of wastewaters than conventional methods. The effect of radiation can be intensified in aqueous solution in which the dye molecules are degraded effectively by primary products formed from the radiolysis of water. It was found that the decomposition of nondegradable organic compounds can be enhanced by addition of H₂O₂ or ozone when reactions are carried out under condition

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Scheme 1. Chemical structure of the dyes.

of simultaneous application with radiation [4–6, 11, 15, 19, 20]. Apollofix dyes are one of the most important class of synthetic organic dyes in the textile industry, hence among common industrial pollutants in Turkey. Our present study provides results describing the decoloration and degradation of Apollofix Red and Apollofix Yellow, commercial reactive dyes used in textile dyeing, γ -irradiated in the presence and absence of H_2O_2 up to 8 kGy dose.

Experimental

Chemicals

Apollofix Red (AR) and Apollofix Yellow (AY) dyes used in this study are of commercial grades used directly in the textile industry in Turkey. The chemical structure of the two dyes is presented in Scheme 1.

Deionized water was used in all preparations. All other reagents used in COD and BOD measurements were of analytical grade.

Apparatus and methods

Deionized water was used to prepare (0.050–0.200 g/L) concentration range of the two reactive dyes. A Philips 8510 model UV-vis spectrophotometer at ambient temperature was used to measure absorption spectra of the irradiated and unirradiated dye solutions. The degree of decoloration was estimated from the reduction in absorbance. Before and after irradiation, pH of the solutions was measured by a JENWAY 3010 model pH meter. Irradiations were carried out with gamma-rays in the dose range of 1.0–8.0 kGy in a ^{60}Co gamma chamber using pyrex tubes in air at a dose rate of 0.14 kGy/h. Hydrogen peroxide as an oxidizing agent was added to dye solutions to obtain a synergistic effect on the degradation of the two reactive dyes. COD was determined by using the chromic method [9]. BOD_5 was measured by an Oxitop100 model BOD device [2, 10].

Results and discussions

It was found that the two dyes have absorption bands in the visible region and some absorption bands in the

UV region of the spectrum, which are attributed to the skeleton of the dye molecule. The peaks at about 220 nm wavelength are attributable to substituted aromatic rings and those in the visible region of the spectrum are attributed to the chromophore group and its auxochromic substituents [7]. The absorption spectra were recorded for the irradiated Apollofix Red (AR) and Apollofix Yellow (AY) at different concentrations. The absorbance at 534 nm and 420 nm decreased with increasing dose and decreasing concentration for AR and AY, respectively.

The radiation-induced decoloration of dyes

Figures 1 and 2 show the change of spectrum of AR and AY after irradiation at a 0.075 g/L dye concentration. The absorption in the UV and visible regions decreased as the irradiation dose increased. These decreases are obviously due to the destruction of the conjugated systems within the dye molecules. The rate of decrease of the intensity of the absorption band in the visible region (decoloration) is higher than that for the peaks in UV region (degradation). In other words, complete decoloration (indicated by complete disappearance of the absorption band in the visible region) can be attained at doses lower than that needed for complete degradation of the respective dyes. Similar absorption spectrum was recorded for AY dye solution in Fig. 2. The decoloration of water soluble dyes primarily

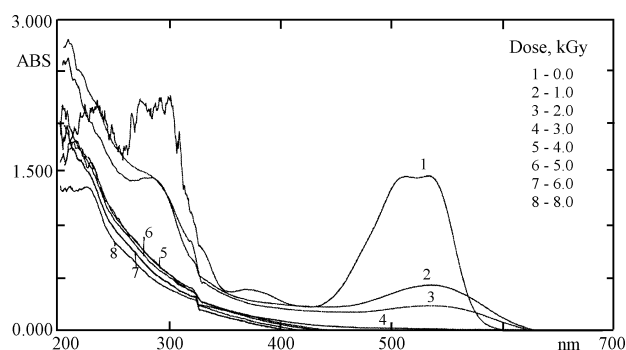


Fig. 1. Absorption spectra of aqueous AR dye solution unirradiated and irradiated to different irradiation doses. [AR] = 0.075 g/L.

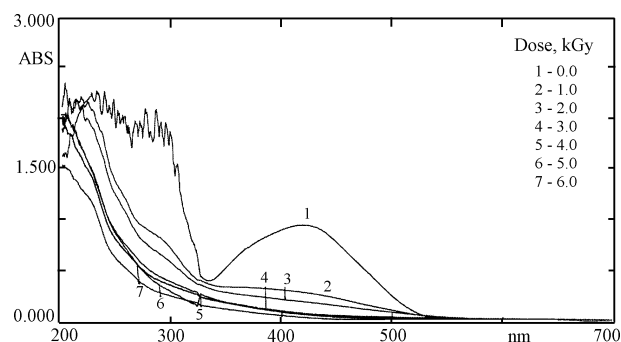


Fig. 2. Absorption spectra of aqueous AY dye solution unirradiated and irradiated to different irradiation doses. [AY] = 0.075 g/L.

resulted from the reactions of textile dyes with the $\cdot\text{OH}$ radicals produced by water radiolysis. The radiolysis yield is the highest for $\cdot\text{OH}$ radicals when the aqueous solution of textile dyes was irradiated by gamma-rays. $\cdot\text{OH}$ radicals are the most important oxidizing and reactive agents. The decoloration primarily resulted from dye reactions with $\cdot\text{OH}$ radicals. In the latter, hydrated electrons reacting with a dye form a semi-reduced species, which, in turn, can partially interact with the products of dye reactions with $\cdot\text{OH}$ radicals to regenerate the initial dye. In aerated solutions, e_{aq}^- reacts with oxygen; the resulting HO_2^\cdot and $\text{O}_2^{\cdot-}$ radicals are characterized by low reactivity (if any) toward dyes [18].

The absorption band at 534 nm decreased with increasing irradiation dose and disappeared almost completely at a 2.0 kGy irradiation dose for 0.05 g/L AR solution. However, the required irradiation dose for the absorption band at 420 nm to disappear completely was 1.0 kGy. The degree of decoloration was determined by measuring the absorptivities in the visible region (534 and 420 nm) as shown in Figs. 3 and 4 for AR and AY dyes, respectively. The maximum decoloration of AR and AY dyes (100%) were achieved at a dose of 2.0 kGy and 1.0 kGy respectively for a 0.05 g/L dye concentration.

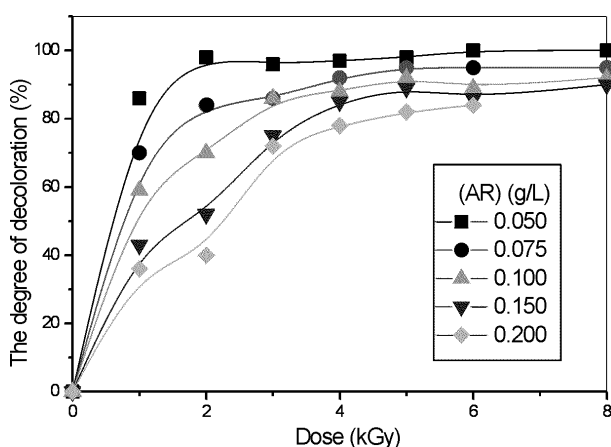


Fig. 3. Variation of the degree of decoloration of AR dye solutions as a function of irradiation dose at 534 nm.

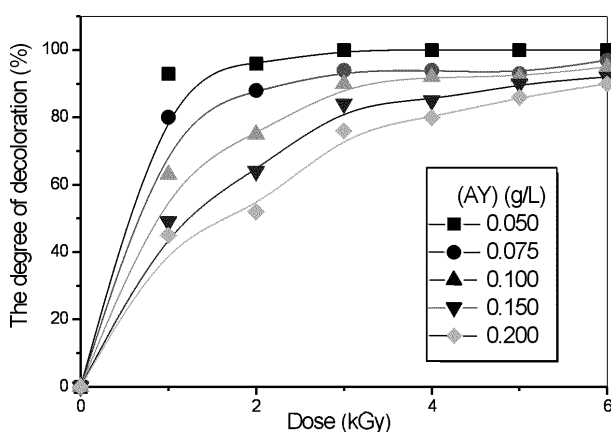


Fig. 4. Variation of the degree of decoloration of AY dye solutions as a function of irradiation dose at 420 nm.

Table 1. The change of pH as a function of irradiation dose (kGy) at various concentrations of Apollofix Red (AR) and Apollofix Yellow (AY) dye solution

Dose (kGy)	AR concentration (g/L)				
	0.050	0.075	0.100	0.150	0.200
0.0	4.80	4.80	4.80	4.80	4.80
1.0	4.78	4.52	4.50	4.70	4.54
2.0	4.27	4.18	4.11	4.08	4.02
3.0	4.38	4.15	4.07	4.03	4.00
4.0	4.20	4.11	4.05	3.99	3.95
5.0	3.81	3.96	3.94	3.99	3.93
6.0	3.93	3.95	3.84	3.94	3.90
8.0	3.95	3.85	3.80	3.84	3.84

Dose (kGy)	AY concentration (g/L)				
	0.050	0.075	0.100	0.150	0.200
0.0	5.04	5.12	5.15	5.15	5.34
1.0	4.29	4.65	4.52	4.58	4.53
2.0	4.18	4.25	4.45	4.42	4.47
3.0	4.01	4.24	4.14	4.11	4.32
4.0	4.00	4.14	4.14	4.03	4.10
5.0	4.00	4.01	3.98	3.97	3.98
6.0	3.97	3.98	3.90	3.93	3.93

Change of pH

The pH of the Apollofix dye solutions after irradiation is shown, as a function of dose, in Table 1, over the range of the dye concentrations 0.05–0.200 g/L. The pH of the 0.05 and 0.075 g/L dye solutions was lowered sharply with increasing dose up to about 2.0 kGy, while the pH of the 0.100, 0.150 and 0.200 g/L dye solutions was lowered gradually. The decrease of pH of the dye solutions was less sensitive to irradiation dose in the range 3.0–8.0 kGy. The change of pH depends on the structure of dye molecule and sulfonic and ethylsulfonic groups in Apollofix dyes which act as an acid. These findings suggest that the change in pH for dye solutions may be attributable to the oxidizing products formed by the degradation. It is known that the radiation induced oxidation of aromatic compounds results in lower molecular weight aliphatic compounds, e.g. aldehydes and organic acids [16] and that further oxidation of the organic acid formed leads to the formation of carbon dioxide [8, 12, 14].

Effect of hydrogen peroxide on decoloration

Hydrogen peroxide is a stable product which does not require any special equipment as it is an easily storable, non-corrosive and versatile liquid. Furthermore, it is totally miscible with water. Because it has no solubility limitations it turns out to be more advantageous in the oxidative process than chemicals such as sodium hypochlorite and ozone, which require more care in application [17]. The degree of decoloration and degradation behavior of AR and AY at different H_2O_2 concentrations were studied by irradiating aqueous dye solutions to a dose of 3.0 kGy for AR (0.200 g/L) and AY (0.200 g/L). The decoloration behavior vs. H_2O_2 concentration is shown in Fig. 5. The degree of

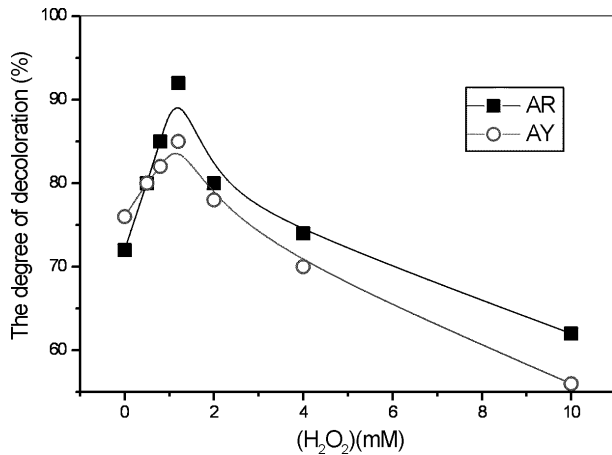
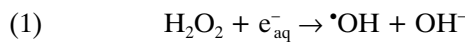
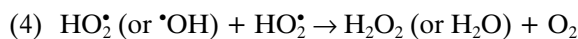
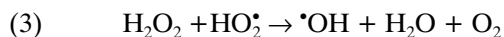
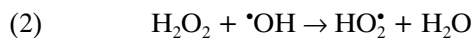


Fig. 5. Effect of hydrogen peroxide on the degree of decoloration. Irradiation dose: 3.0 kGy, [AR] = [AY] = 0.200 g/L. Dose rate: 0.14 kGy/h.

decoloration for both solutions increased with hydrogen peroxide concentration up to about 1.2 mM, suggesting that the decoloration reaction is initially promoted by addition of hydrogen peroxide. Hydrogen peroxide reacts rapidly with hydrated electron formed from the radiolysis of water leading to the formation of $\cdot\text{OH}$ radical [12]:



Therefore, the increase in the degree of decoloration by addition of hydrogen peroxide would be mainly attributable to increasing of the $\cdot\text{OH}$ radical concentration through the above reaction. This finding suggests that the $\cdot\text{OH}$ radical destroys the chromophore more efficiently than the hydrated electron does. As seen in Fig. 5 the degree of decoloration decreased above 1.2 mM hydrogen peroxide. In the case of the solution containing hydrogen peroxide, the concentration of $\cdot\text{OH}$ radical increases through reaction (1). However, as the hydrogen peroxide concentration increases, a part of the $\cdot\text{OH}$ radicals can be scavenged by the excess hydrogen peroxide through reactions (2), (3) and (4) [1, 8, 12, 14].



Therefore, the decrease in the degree of decoloration, above 1.2 mM hydrogen peroxide may be attributable to the scavenging of $\cdot\text{OH}$ radicals by the excess hydrogen peroxide through reactions (2), (3) and (4).

Change of COD and BOD

The pollution level of wastewaters is usually characterized by chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and dissolved carbon content. All these characteristics are group parameters, which specify the chemical and

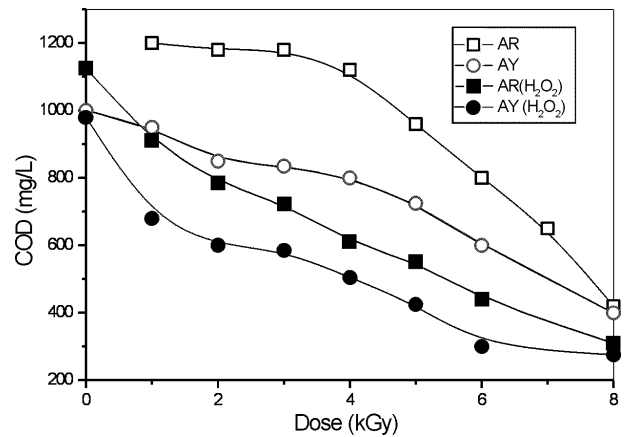


Fig. 6. COD values for AR and AY dye solutions gamma-irradiation. [AR] = [AY] = 0.200 g/L, [H₂O₂] = 1.2 mM. Dose rate: 0.14 kGy/h. (Solid symbols are used for AR and AY concentrations containing H₂O₂.)

biological oxidizability of wastewater pollutants, the total carbon content of pollutants that occur in dissolved state, respectively. Thus, COD (mg/L) is the amount of oxygen (or another oxidizing agent in terms of oxygen) required for complete oxidation of the organic matter in a test wastewater sample. BOD is the amount of oxygen consumed in the anaerobic biochemical decomposition of organic matter in the test wastewater.

The effect of irradiation dose on AR and AY dye solutions was determined by measurement of COD values with irradiation. The results are presented in Fig. 6. It was observed that COD and BOD values of AR and AY dyes studied in this work decreased with increased irradiation dose. The enhanced decrease in COD values in the presence of H₂O₂ confirms the importance of H₂O₂ in degrading the Apollifix dyes. Figures 6 and 7 show the change of COD and BOD contents of aqueous solutions of two Apollifix dyes before and after irradiation. It can be seen that the solutions of AR and AY dyes were almost completely decolorized at 2.0 kGy and 1.0 kGy doses. Simultaneously, the values of COD and BOD significantly decreased. The initial AR and AY solutions had COD

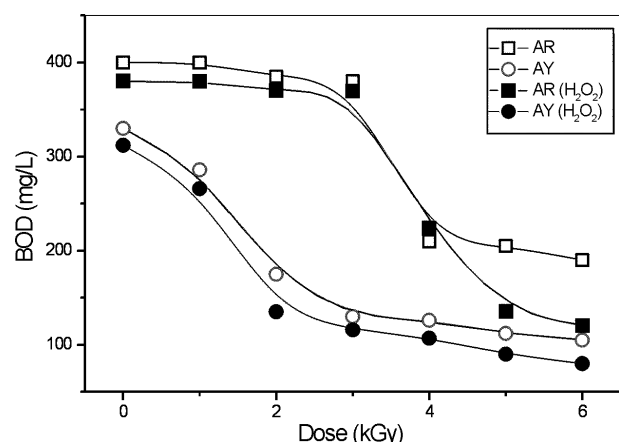


Fig. 7. BOD values for AR and AY dye solutions gamma-irradiation. [AR] = [AY] = 0.200 g/L, [H₂O₂] = 1.2 mM. Dose rate: 0.14 kGy/h. (Solid symbols are used for AR and AY concentrations containing H₂O₂.)

values equal to 1200, 1000 mg/L, and BOD values equal to 400, 330 mg/L, respectively. The gamma-irradiation caused a decrease in the COD and BOD of the two dye solutions. In the presence of H_2O_2 , the COD values decreased from 1200 to 310 mg/L and from 1000 to 275 mg/L and BOD values decreased from 400 to 120 mg/L and from 330 to 80 mg/L in the irradiation range 1.0–6.0 kGy for AR and AY, respectively. The BOD contents for AR and AY dye solution was almost constantly maintained up to 3 kGy irradiation dose in the system of γ and H_2O_2/γ and then decreased to 6 kGy irradiation dose. For AY dye solution, BOD contents were decreased from 1 kGy to 6 kGy irradiation dose range in the system of γ and H_2O_2/γ . It appears that the H_2O_2/γ system produced only biodegradable components like organic acids, however the biodegradable components were not decomposed to products with dose employed.

Conclusions

The decoloration and degradation of Apollofix dyes in aqueous solutions are easily decolorized by gamma-irradiation, which may be, therefore, promising for the treatment of textile dye wastewater. Decoloration and degradation of textile wastewater can be carried out but necessary dose varies with the types of the waste. The decoloration and degradation of different type of textile dyes in aqueous solutions was investigated in the presence of H_2O_2 , ozone by using gamma-rays and UV in the different studies. Water soluble, direct acid, reactive dyes and water insoluble disperse dyes were decolorized by ozone and H_2O_2 [17] as were dyes containing azo, anthraquinone and phthalocyanine chemical groups. Gamma-irradiation process is an excellent remover of low solute concentrations. The combination effect of some oxidants and gamma-irradiation was higher than that when using only gamma-irradiation or only H_2O_2 /ozone, and this technique may prove to be practical for use in all industries. In this study, the destruction of the skeleton of the dye molecule, or decoloration and degradation of the Apollofix dyes in aqueous solutions can be achieved by gamma-irradiation alone or by gamma-irradiation of aqueous dye solutions which contain 1.2 mM concentration of H_2O_2 .

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