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TREATMENT OF REAL TEXTILE WASTEWATER USING ELECTRON BEAM IRRADIATION

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Abstract: Textile wastewater is known to have a large number of hazardous pollutants, intense color and high chemical oxygen demand (COD) concentration. The electron beam method is considered useful in treatment textile wastewater through chemical oxidation process. In this study, three real textile wastewaters (Sample 1: Reactive Black 5, Reactive Red 10, and Reactive Orange 13; Sample 2: Reactive Red 10 and Yellow GR; Sample 3: Reactive Black 5 and Turquoise Blue HF–G) from textile dyeing company in Ho Chi Minh city were treated by

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electron beam method. The effect of absorbed doses and hydrogen peroxide (H_2O_2) at different concentrations on the change of pH, removal capacity, COD and five day's biological oxygen demand (BOD_5) were investigated. The results indicated that color, COD, BOD_5 and pH decreased with increasing absorbed dose. A sufficient amount of H_2O_2 in the radiation process could accelerate the color removal process. In the same condition, a color removal efficiency of ~90% was obtained with EB/H_2O_2, in contrast with color loss by using EB alone (~71%). These results highlighted the potential of EB radiation technology for treatment of textile dyeing wastewater.

***Keywords*:** color removal; textile wastewater; electron beam; hydrogen peroxide.

Introduction

Reactive dye-containing textile wastewater is one of the most challenging wastewater to treat because most of the reactive dye have complex chemical structure and high water solubility.[1] Moreover, the dye structures are commonly highly resistant to biodegradation process.[2] One of the most significant concerns in wastewater treatment of a textile effluent is the color removal. Previous researches showed that conventional water treatment processes could not achieve the expected great extent of color decrease in reactive dyeing wastewater. Coagulation and adsorption sometimes could eliminate color from reactive dye compound, but this process requires chemicals (acid, coagulant or adsorbent) producing a huge toxic sludge which increases the cost of facility`s construction and running.[3,4] Biological treatment using biofiltration[5] could effectively alleviate color in textile wastewater. However, this method requires a long time due to acclimation need and dependence on the types of organisms present in water. Some oxidation processes such as ozonation, sonolysis, photodegradation, etc. could eliminate small volumes of textile wastewater; however, these methods were reported to be not effective[6-8] in practice due to high volume of the wastewater and pH dependence. Hence, the approach for the rapid and effective removal of color in reactive dyeing wastewater is necessary to be further developed. Recently, ionizing radiation method using gamma Co-60 radiation and electron beam, a kind of oxidation method which could induce oxidizing species ($^{\bullet}OH$, H_2O_2, $HO_2\bullet$…) and reducing species (e_{aq}^- and $H^{\bullet}$) through water radiolysis,[9] received considerable attention for the effective treatment of toxic organic pollutants in wastewater.

The electron beam (EB) radiation has been applied to treat textile wastewater.[10-14] The key for applying radiation techniques for waters and wastewaters purification, or degradation of pollutants to chemical forms (which are more susceptible to be removed using other methods, e.g., biodegradation), is the formation of radicals by water radiolysis or other radiation processes. The reactions with HO• radicals, hydrated electrons, and hydrogen atoms with organic and inorganic compounds and ions show the transformation of recalcitrant organics to biodegradable organics, reducing the toxic compounds to non-toxic species or degrade the complex organic compounds. EB technology is believed to be the next generation of treatment without chemical additions. Therefore, the EB systems have been designed and manufactured since 1990 in the United States. However, the radiation process normally required high absorbed doses to degrade the complex organic compounds. Thus, an additional alternative to combine with the radiation process is needed to enhance the degradation efficiency. Hydrogen peroxide (H_2O_2) could be the key to the problem. Some researchers indicated that adding small amounts of hydrogen peroxide could improve the radiation capacity for eliminating pollutants in wastewater through increasing the formation of $^{\bullet}OH$ radicals:[15,16]

$$e_{aq}^{-} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^{-} \quad (1)$$

$$H^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O \quad (2)$$

Up to now, there are only few papers focusing on the treatment of real dying wastewater. The aim of this study was to investigate the treatment of real textile dyeing wastewater released from the textile industry by electron beam radiation combined with H_2O_2. Several factors such as absorbed dose and concentration of H_2O_2 were investigated to determine the suitable operating condition.

Experimental

Chemicals

Textile wastewater used in this study was obtained from Thu Duc textile factory, Ho Chi Minh City. They were mixtures of Reactive Black 5, Reactive Red 10 and Reactive Orange 13 (Sample 1); Reactive Red 10 and Yellow GR (Sample 2) and Yellow GR, Reactive Black 5, and Turquoise Blue HF–G (Sample 3). Hydrogen peroxide solution 30% (w/w) obtained from Merck, Germany.

Methods

1000 mL of textile wastewater (1000mL) was poured in a plastic box large enough to give a solution thickness of 2.5 cm. The radiation experiments were carried out using an electron accelerator UERL – 10 – 15S_2 in VINAGAMMA center. The absorbed doses were measured using dichromate dosimetry (ASTM International, 2004).[17]

Effect of absorbed dose

The wastewater samples were then irradiated with doses of 5-20 kGy, to investigate the impact of the absorbed doses on the characteristics of textile wastewater (pH, COD, BOD_5 and color unit).

Effect of H_2O_2 concentration at absorbed dose of 5 kGy

H_2O_2 in concentrations of 5, 10, 15, and 20 mM were added to the wastewater samples, and then the samples were irradiated with a dose of 5 kGy to investigate the effect of H_2O_2 concentration.

Effect of absorbed dose at the concentration of 10 mM H_2O_2

The wastewaters samples containing 10 mM of H_2O_2 were irradiated with various absorbed doses from 3 to 12 kGy, to investigate the effect of the oxidizer dose.

Analysis method

The absorption spectra and color were analyzed using the platinum-cobalt (Pt-Co) method[18] at a wavelength of 400 nm on a UV-Vis spectrophotometer (Shimadzu V-630). The pH values of the solution were measured using an Inolab 740 pH meter. COD and BOD_5 were determined by the permanganate method.

Results and Discussion

Effect of absorbed dose

In Vietnam, the effluent textile wastewater must obey Regulation QCVN 13–MT:2015/BTNMT, which provides the maximum acceptable values of pollution parameters before being discharged into receiving waters. Table 1 lists the changes in the pH, COD, BOD_5, and color units of textile wastewaters after being exposed to irradiation doses of 0, 5, 10, 15, and 20 kGy, in comparison with the limit acceptable values according to the fore-mentioned regulation (column 2).

The results (Table 1) showed that COD, BOD_5, and dye concentration sharply decreased with the absorbed dose for all three samples, while the pH values decreased between 1-1.5 units. It must be mentioned that the initial values (0 kGy column) are quite high and characterize filthy waters, while the EB treatment, even at low doses, drastically reduces the dyes concentrations.

Table 1. The Influence of absorbed dose on the pH, COD, BOD_5 and dye concentration of textile wastewater.

Effluent	standard*	Dose (kGy)	0	5	10	15	20
pH	5.5 – 9	Sample 1	8.93 ±0.30	7.56±0.20	7.26±0.15	8.10±0.20	7.34±0.15
		Sample 2	9.46±0.25	8.75±0.30	8.46±0.25	8.3±0.15	8.1±0.20
		Sample 3	9.38±0.20	9.26±0.30	9.19±0.15	8.98±0.25	8.90±0.30
COD (mg/l)	200	Sample 1	100±2.0	77±1.0	46±2.0	41±1.5	25±1.0
		Sample 2	150±2.0	84±1.5	61±0.5	49±1.5	35±0.5
		Sample 3	260±2.0	174±2.0	136±1.5	101±1.5	82±1.3
BOD_5 (mg/l)	50	Sample 1	67±1.5	40±1.0	35±1.5	27±1.0	23±1.5
		Sample 2	77±1.5	46±1.0	40±0.5	35±0.5	26±1.0
		Sample 3	90±1.5	68±1.0	57±1.5	45±1.0	38±0.5
Color unit (Pt–Co)	200	Sample 1	267±2.5	67±1.0	32±0.5	21±1.0	18±0.5
		Sample 2	330±2.0	61±1.5	16±1.0	10±1.0	8±0.5
		Sample 3	451±2.5	288±2.0	215±1.5	138±2.0	98±1.5

* Column B, Vietnamese technical regulation on the effluent of the textile industry.

As seen in Figures 1 and 2, the degree of decolorization of samples 1, 2, and 3 increased with increasing absorbed dose. When the absorbed dose was 20 kGy, the degree of decolorization of samples 1, 2 and 3 increased to 93%, 98%, and 78%, respectively. These results were similar to those of Kim et al.[12]

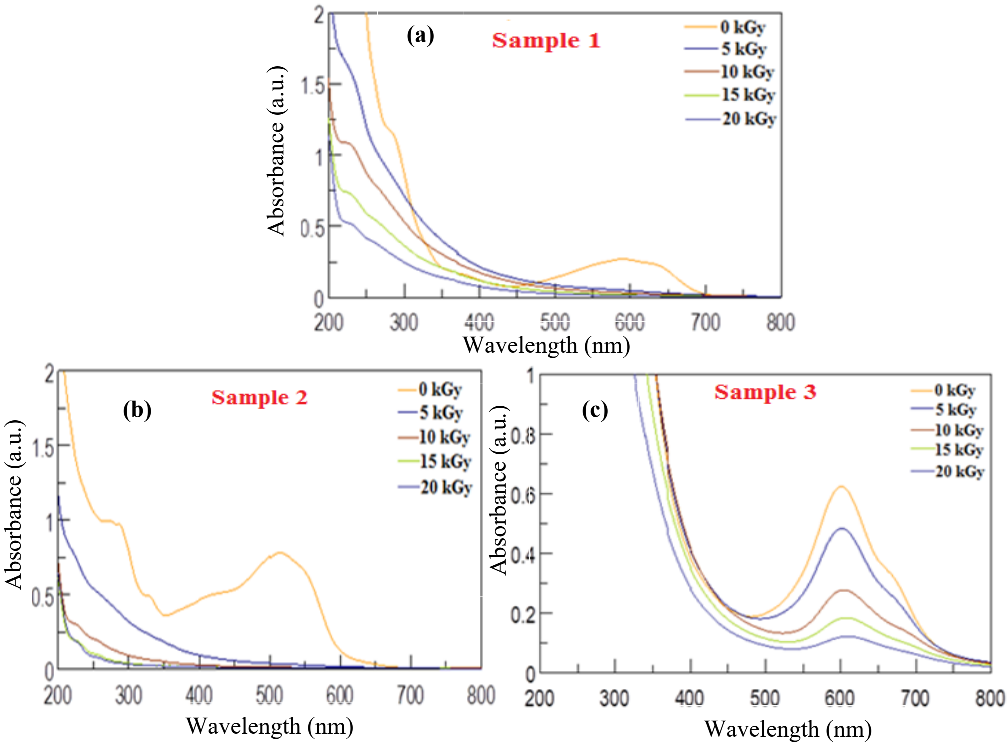

Figure 1. The UV-Vis spectrum of sample 1 (a), sample 2 (b) and sample 3 (c) after radiation with different doses.

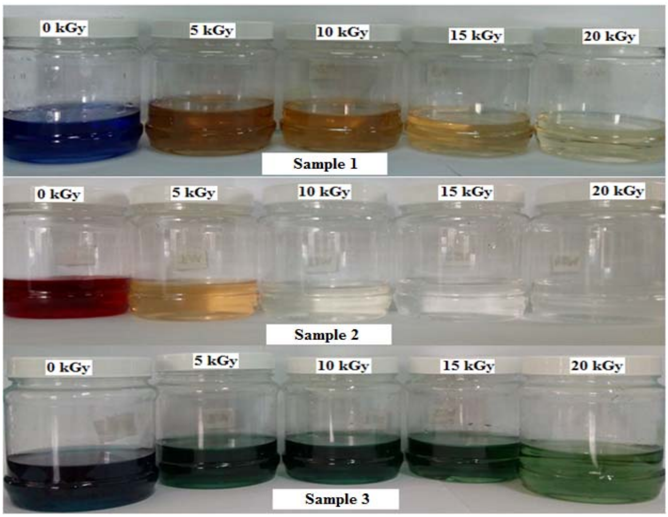

Figure 2. The color of textile dyeing wastewater after radiation at different doses.

Effect of H_2O_2 concentration at absorbed dose of 5 kGy

Previous studies reported that the presence of H_2O_2 in the solution could lead to the formation of hydroxyl radical, which contributed to a high removal efficiency of COD, BOD_5 and dye concentration in some kinds of textile wastewaters.[16,19,20] To investigate the effect of different concentrations, doses between 5-20 mM were added before irradiation to the wastewater samples.

The results in Table 2 and Figure 3, 4 showed that adding small amounts of hydrogen peroxide could improve the radiation capacity eliminating the pollutants from wastewater. The pH, COD, BOD_5 and dye concentration of textile wastewater decreased fast at 5 mM H_2O_2 and absorbed dose of 5 kGy. The degree of decolorization of samples 1, 2 and 3 increased to 96%, 91%, and 53%, respectively. The results also indicated that the optimal H_2O_2 concentration was achieved at 5 mM for the samples 1 and 2 and at 10 mM for sample 3, at an absorbed dose of 5 kGy to achieve the values mentioned in QCVN 13–MT:2015/BTNMT regulation. The next experiments were run at a dose of 10 mM H_2O_2.

Table 2. The Influence of H_2O_2 concentration at absorbed dose of 5 kGy on the pH, COD, BOD_5 and dye concentration of textile wastewater.

$[H_2O_2]$ mM		0	5	10	15	20
pH	Sample 1	7.56±0.30	6.62±0.25	6.63±0.2	6.68±0.15	6.67±0.10
	Sample 2	8.75±0.20	8.20±0.30	8.00±0.15	7.90±0.30	7.60±0.20
	Sample 3	9.26±0.15	9.00±0.25	8.89±0.30	8.82±0.10	8.75±0.15
COD (mg/l)	Sample 1	77±1.5	38±0.10	84±1.6	134±2.0	179±1.5
	Sample 2	84±1.5	55±1.0	61±1.0	76±1.5	114±2.0
	Sample 3	174±2.0	131±1.5	121±1.0	115±1.5	98±1.0
BOD_5 (mg/l)	Sample 1	40±1.0	38±1.0	36±1.0	28±1.5	20±1.0
	Sample 2	46±0.6	40±1.0	37±1.5	30±1.0	25±1.5
	Sample 3	68±1.0	61±1.0	58±1.0	52±1.0	49±1.5
Color unit (Pt–Co)	Sample 1	67±1.0	10±1.0	6±1.0	5±1.5	3±1.0
	Sample 2	95±1.0	29±1.0	33±0.5	34±0.6	30±0.5
	Sample 3	288±1.0	212±1.5	210±2.0	200±2.5	196±1.0

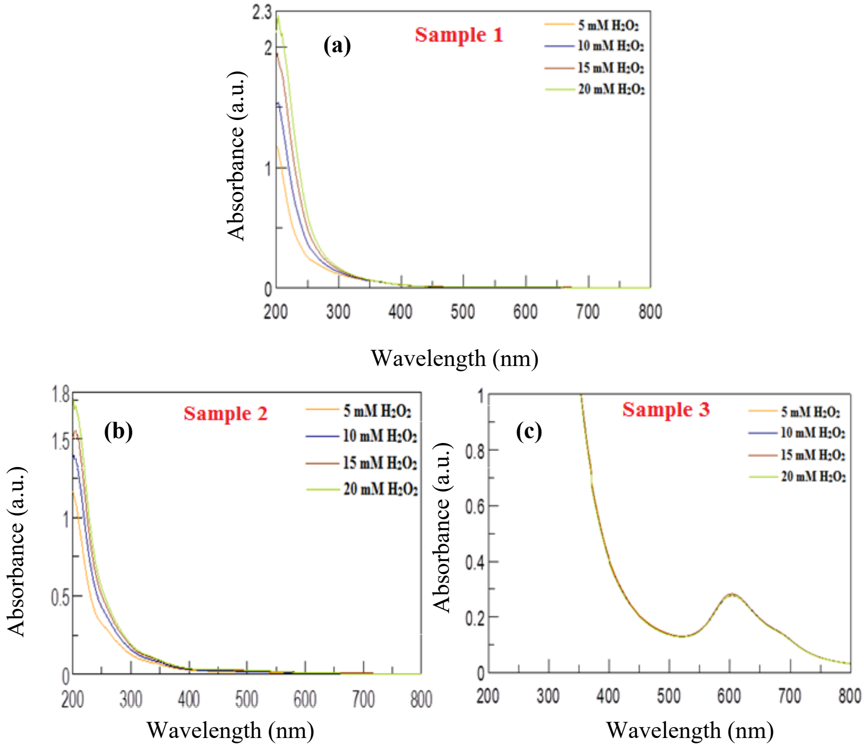

Figure 3. The UV-Vis spectrum of sample 1 (a), sample 2 (b) and sample 3 (c) after radiation with different concentration of H_2O_2 at 5 kGy.

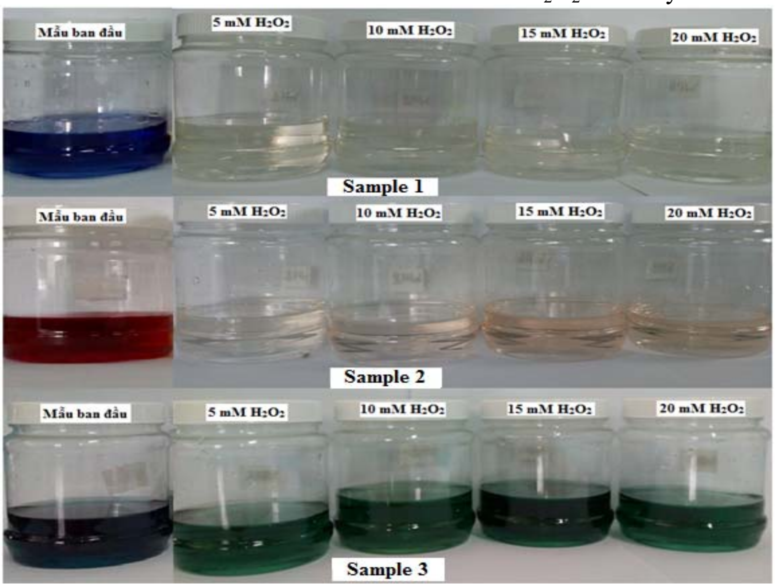

Figure 4. The color of textile dyeing wastewater after radiation with different concentration of H_2O_2 at 5 kGy.

Effect of absorbed dose at 10 mM H_2O_2

Hydrogen peroxide reacts rapidly with hydrated electron (e_{aq}^-) formed in the radiolysis of water, leading to the formation of •OH radical. Therefore, the increase in the degree of color, COD and BOD_5 removal percentage by the addition of hydrogen peroxide would be mainly attributed able to an increase in the •OH radical. The Influence of absorbed dose at the 10 mM H_2O_2 on the pH, COD, BOD_5, and dye concentration of textile wastewater was carried out and showed in Table 3 and Figure 5, 6.

The results indicated that pH, COD, BOD_5 and dye concentration of textile wastewater decreased with increasing the absorbed dose from 3 to 12 kGy at 10 mM H_2O_2 concentration. The optimal absorbed dose was of 3 kGy and 10 mM H_2O_2 for the sample 3. The same tendency had also been obtained by Vahdat et al [10].

Table 3. Effect of dose at 10 mM H_2O_2.

Absorbed dose (kGy)		3	6	9	12
pH	Sample 1	7.74±0.3	7.09±0.25	6.80±0.15	6.21±0.20
	Sample 2	8.35±0.15	8.00±0.20	7.80±0.25	7.50±0.3
	Sample 3	9.05±0.25	8.95±0.3	8.83±0.15	8.76±0.10
COD (mg/l)	Sample 1	106±2.0	66±1.0	44±1.5	30±1.5
	Sample 2	64±1.0	35±1.0	21±0.5	12±0.5
	Sample 3	145±2.0	118±1.5	102±1.5	79±1.0
BOD_5 (mg/l)	Sample 1	33±1.0	21±1.5	14±0.5	6±0.5
	Sample 2	41±1.0	29±1.5	20±1.0	14±0.5
	Sample 3	68±1.5	47±1.5	40±1.0	36±1.0
Color unit (Pt–Co)	Sample 1	5±0.5	5±0.5	4±0.5	3±0.5
	Sample 2	45±1.0	31±1.5	18±1.0	6±0.5
	Sample 3	245±2.5	175±2.0	154±2.0	90±1.5

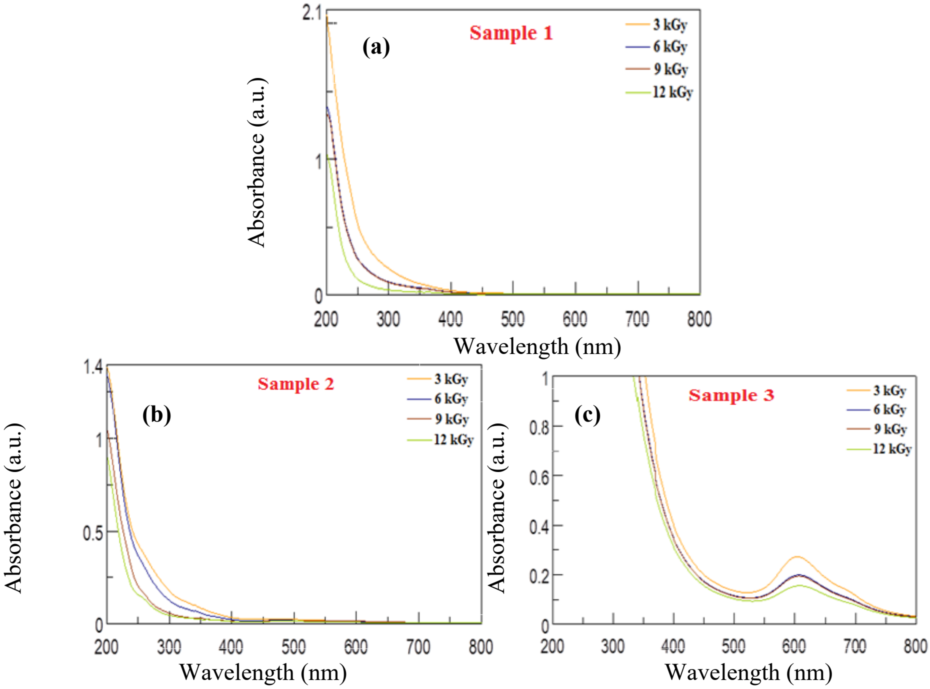

Figure 5. The UV-Vis spectrum of sample 1 (a), sample 2 (b) and sample 3 (c) after radiation with different doses at 10 mM H_2O_2

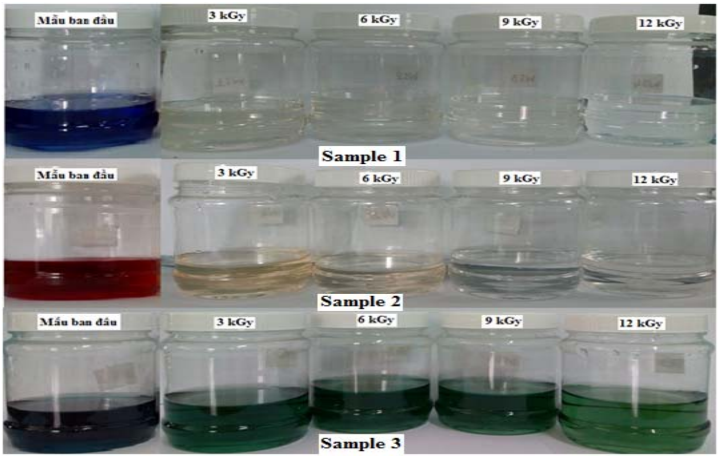

Figure 6. The color of Textile dyeing wastewater after radiation with different doses at 10 mM H_2O_2

Conclusions

The obtained results presented that electron beam treatment is highly efficient for the removal of color, COD, and BOD_5 from real textile dyeing wastewater in Ho Chi Minh city. The effluent meets the Vietnamese technical regulation on the effluent of textile industry (QCVN 13–MT:2015/BTNMT). The efficient H_2O_2 concentration was determined to be 5 mM at an absorbed dose of 5 kGy, or of 10 mM and absorbed dose of 3 kGy, respectively, for initial dye concentrations (Pt-Co) of 267 (Sample 1) and 330 (Sample 2), respectively. For Sample 3. the initial dye concentration of 450 (Pt-Co), the suitable H_2O_2 concentration was found to be10 mM and absorbed dose of 5 kGy. These results showed that electron beam radiation technology could be a potential and promising method for dye removal from textile wastewater.

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