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Treatment of Dyes Industrial Effluents by Ionizing Radiation

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The treatment of dyes wastewater by γ-radiation is very efficient and simple method. In the present study wastewater samples were collected from ten dyes industries and were irradiated to the absorbed doses of 2, 5, 10 and 15 kGy using Co-60 γ-radiation source. Before treatment effluents were highly polluted in term of colour intensity and chemical oxygen demand (COD) values. High energy radiation treatment has significantly improved the quality of polluted water, as its colour intensity reduced to 78 % at an absorbed dose of 15 kGy and almost complete colour removal was achieved when the samples were irradiated in the presence of hydrogen peroxide. Chemical oxygen demand decreased with the irradiation and its reduction was facilitated by irradiating the samples in presence of H_2O_2. Water quality parameters after irradiation were significantly improved. However, the treated wastewater of dyes industries could be utilized for agriculture and industrial reuse.

Key Words: Dyes, Textile, Colour intensity, Chemical oxygen demand, γ-irradiation, Hydrogen peroxide, Effluents.

INTRODUCTION

Rapid industrialization has resulted a severe threat of water pollution caused by liquid effluents expelled from industries and are get mixed with water bodies[1]. Various industries such as textile, paper, pharmaceuticals, foods, plastic, tanneries *etc*., utilize dyes and causing water pollution[2]. Huge amount of wastewater, produced by dyes and textile industries, contains dyestuff at elevated level. More than one million dyes are available on commercial scale and a small amount of dyes even at 1 mg/L concentration is highly visible in water[3]. Management of industrial effluents is a core issue presently since most of the dyes are non-biodegradable and conventional treatments owe some handicaps for their manipulation[4,5]. Usually the dye industrial effluents contains variety of compounds such as raw materials, intermediates, various chemicals, unreacted biologically resistant dyes which cause high colour intensity and elevated COD[6]. The conventional treatment methods which have been frequently used for the treatment of industrial wastewater such as reverse osmosis, filtration, coagulation adsorption, bioremediation *etc*., are insufficient and inadequate for the treatment of dyes wastewater[7]. Keeping in view the limitations of conventional methods, there is a need for an effective method/s to treat the non-biodegradable compounds present in the dyes wastewater.

Advanced oxidation processes (AOP's) have been employed for wastewater treatments which are regarded as efficient procedures for the treatment of organic compounds. During AOP's a strong oxidizing species such as hydroxyl radical ($OH^•$) produced *in situ*, which break down the complex organic molecule into less harmful smaller substances through a chain reactions. During the process of mineralization, complex organic molecule are ultimately converted into CO_2, H_2O and inorganic ions by the action of hydroxyl radical ($OH^•$) none selectively. Advanced oxidation processes comprises of UV photolytic technique, fenton process, photo-fenton process, ozonation process, sonolysis, photocatalytic approach, biodegradation and the radiation induced degradation[8]. These processes are easy to handle, produce significantly less residual effects as compared to the classical approaches and are currently being employed for colour removal, mineralization of toxic chemicals, treatment of industrial wastewater at large scale[9].

The use of ionizing radiation for the treatment of dyes wastewater is a promising method for complete degradation of pollutants present in industrial wastewater by hydroxyl radicals ($OH^•$). Previous studies have shown that the degradation of biologically resistant pollutants as well as the killing of pathogenic micro organisms found in water can be achieved by using ionizing radiation[10-14].

The present study focuses on the treatment of dyes industrial wastewaters with γ-radiation alone and combination of γ-radiation with H_2O_2. Different parameters such as pH, optical density and chemical oxygen demand were analyzed before and after treatment.

EXPERIMENTAL

Collection and treatment of samples: The wastewater samples were collected from point of discharge of dye-manufacturing units located in the premises of Faisalabad and sealed in polyethylene terephthalate (PET) bottles. The wastewater samples filled in pyrex bottle were subjected to radiation treatment by using Co-60 γ-radiation source (Issledovatel USSR) at Nuclear Institute for Food and Agriculture (NIFA) Ternab, Peshawar, Pakistan. Irradiation of collected samples were performed at ambient temperature (*ca.* 25 ºC) to the absorbed doses such as 2, 5, 10 and 15 kGy alone as well as in the presence of H_2O_2 (35 % w/w, Fluka, Germany). The dose rate of radiation source was determined by Fricke dosimetry[15].

Analyses: The double beam UV-visible spectrophotometer (U-2001 Hitachi) was used in order to find the λ_{max} and optical densities of the samples by using double distilled water as a blank. The open reflux method was carried out for the determination of chemical oxygen demand (COD) using standard method[16], while pH was determined by pH meter (Hanna HI 9813).

RESULTS AND DISCUSSION

The data shows that the optical density of the wastewater samples were in the range of 0.89-2.522, while the COD values were ranging from 675-2210 mg/L as shown in Table-1. The pH values of ten collected samples lie in different ranges which are shown in Table-1. The treatment efficiency was evaluated by analyzing the absorbance and COD of wastewater samples after treatment. The synergetic effect of H_2O_2 along with γ-radiation was also investigated. The effect of different operational parameters is discussed as:

TABLE-1
WATER QUALITY PARAMETERS OF DYES INDUSTRIES BEFORE TREATMENT

S. No.	λ_{max} (nm)	Absorbance	COD (mg/L)	pH
Sample 1	472	1.582	790 ± 35.5	9.7 ± 0.045
Sample 2	530	2.522	657 ± 30.15	1.9 ± 0.001
Sample 3	394	1.787	895 ± 40.10	1.7 ± 0.001
Sample 4	492	1.696	939 ± 46.50	1.8 ± 0.001
Sample 5	576	1.298	677 ± 25.60	1.6 ± 0.001
Sample 6	624	1.650	1156 ± 57.8	8.5 ± 0.04
Sample 7	488	0.890	1345 ± 67.25	9.1 ± 0.046
Sample 8	514	1.760	1290 ± 64.50	10.2 ± 0.05
Sample 9	615	2.120	1762 ± 88.10	4.5 ± 0.025
Sample 10	601	2.180	2210 ± 110.50	11.5 ± 0.05

Effect of γ-radiation on colour removal of dyes wastewater: The colour intensity is an important parameter to evaluate the degree of pollution in wastewater. When the polluted samples were irradiated to the absorbed doses of 2, 5, 10 and 15 kGy, observed decrease in optical density values were 17, 44, 78 and 95 %, respectively as shown in Fig. 1. It is revealed from the data that an absorbed dose of 15 kGy completely decolourized dyes wastewater which has harmony with the previously study[17]. When the dyes wastewater samples are irradiated, energy absorbed by the water molecules resulting in the formation of reactive species such as hydroxyl radicals

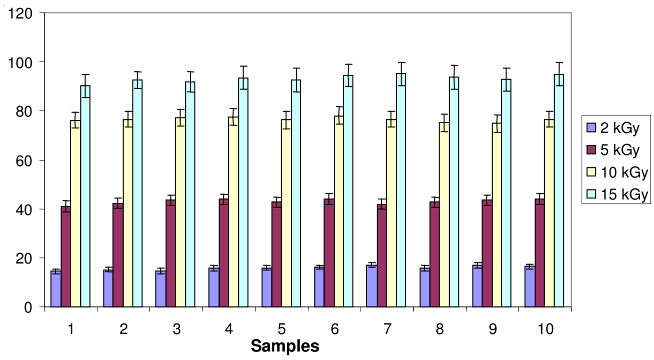

Fig. 1. Effect of γ-radiation on absorbance of dyes wastewater samples

($OH^•$), hydrogen radicals ($H^•$) and hydrated electron (e_{aq}^-). The $OH^•$ radicals react with the chromophoric groups and then degrade the dye molecules which results in the reduction of colour intensity. Irradiation in presence of O_2 enhances the oxidative degradation of pollutants none selectively[18].

Effect of γ-irradiation on the reduction of chemical oxygen demand (COD): Chemical oxygen demand (COD) is an imperative factor to analyze the degree of pollution in term of organic pollutants present in wastewater. The COD values of dyes wastewater samples were in the range of 657-2210 mg/L which indicated that the collected wastewater samples were highly polluted. Upon γ-irradiation, considerable improvement was observed because the COD values decreased sharply with the radiation absorbed doses. The COD values reduced to the level of 11, 34, 41 and 72 % when wastewater samples were treated to 2, 5, 10 and 15 kGy absorbed doses as presented in Fig. 2. It was found that COD reduction was rather difficult as compared to colour removal since effective decrease can be achieved when the complex organic molecules break down into small molecules upon irradiation which is also reported[19].

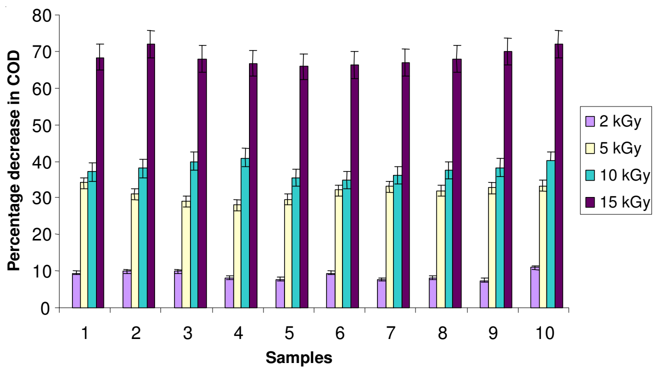

Fig. 2. Effect of γ-irradiation on COD of dyes wastewater samples

Effect of H_2O_2 and irradiation on colour and COD reduction: Although the radiation treatment has significant effect on colour and COD reduction but when H_2O_2 was added in wastewater samples before irradiation the efficiency of the treatment was enhanced considerably. The degree of decolourization has been attained up to 25, 60, 85 and 100 %, while decrease in COD values were 15, 41, 55 and 80 % for the irradiated samples to the radiation absorbed doses of 2, 5, 10 and 15 kGy in presence of H_2O_2 (Figs. 3 and 4). It is clear from the results that reduction of colour intensity and COD

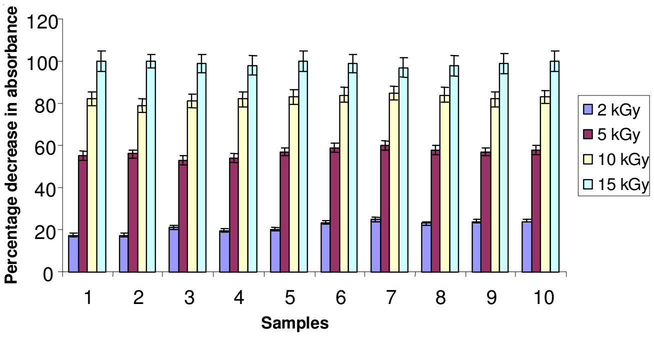

Fig. 3. Combined effect of γ-irradiation and H_2O_2 on absorbance of dyes wastewater samples

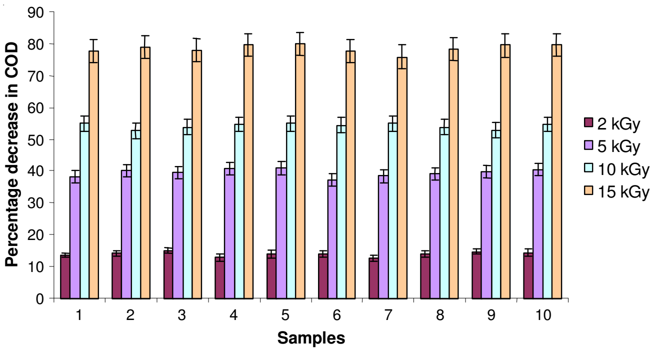

Fig. 4. Combined effect of γ-irradiation and H_2O_2 on COD of dyes wastewater samples

became pronounced in presence of H_2O_2. Since hydrogen peroxide is a good scavenger of the reducing species such as hydrogen radical ($H^•$), hydrated electron (e_{aq}^-) and promote the generation of hydroxyl radical ($OH^•$) which are regarded as the most reactive oxidizing species to treat the wastewater[20]. It is reported that large number of $OH^•$ radicals are generated when the irradiation is carried out in presence of hydrogen peroxide which might facilitate the oxidation process that leads to the degradation of complex molecules[21-23].

Effect of γ-radiation on pH of dyes wastewater samples: The results shown in Fig. 5 reveal that after treatments there is a considerable decrease in pH of dyes wastewater. The complex dye molecules present in the wastewater undergo radiolytic degradation and low molecular mass carboxylic acids, aldehydes *etc*., are formed *via* intermediates, which further decompose into carbon dioxide and water. The decrease in pH is attributed

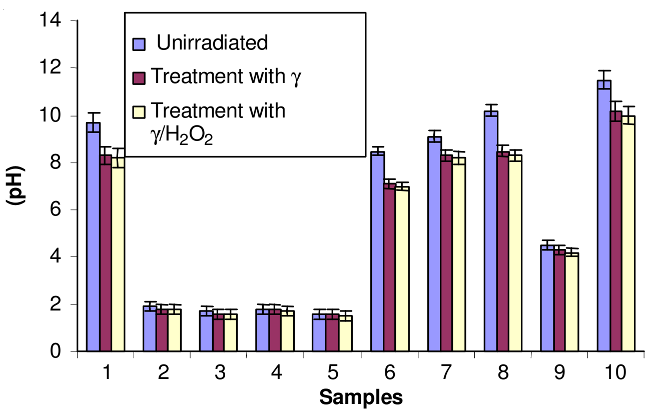

Fig. 5. Effect of γ-radiation and H_2O_2 treatment on pH of dyes wastewater samples

to the formation of these simpler compounds during the radiation treatment. It was observed that the decrease in pH was non-significant in wastewater samples having acidic pH but the notable decrease was found in wastewater samples which had alkaline pH due to the formation of low molecular mass carboxylic acid.

Conclusion

The advanced oxidation process using γ-irradiation in combination with hydrogen peroxide is an effective method to treat the industrial effluents. The treatment using high energy radiation holds good for the removal of colour intensity as well as reduction of chemical oxygen demand of highly polluted wastewater. Furthermore, it is safe and environmental friendly methods, beyond the risk of induction of radioactivity and further treatment for management of sludge is not required. The treated water may also be used for agriculture and industrial reuse.

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