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T-26

## **Radiation Degradation of some Commercial Dyes in Wastewater**

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### **ABSTRACT**

The degradation kinetics due to irradiation of aqueous solutions of some commercial dyes, (Reactive Blue Brilliant, Reactive Yellow and Basic Blue 9 Dye (Methylene Blue 2B), was studied. Factors affecting radiolysis of the dye such as dye concentration, irradiation dose, dose rate and pH of the solutions were studied. The effects of different additives such as nitrogen, oxygen, hydrogen peroxide and sodium hypochlorite on the degradation process were investigated. The effect of irradiation dose on the different dye solutions at various concentrations, showed that the Reactive Yellow G. was very sensitive to gamma radiation. The effect of the pH of the dye solutions proved to vary according to type of the dye. Synergistic treatment of the dye solutions by irradiation and conventional methods showed that saturation of the dye solutions with nitrogen did not enhance the radiation degradation of the dyes, while addition of oxygen resulted in a remarkable enhancement of the degradation of the dyes. Also, the addition of sodium hypochlorite (5 %) and the oxidation by hydrogen peroxide resulted in more radiation degradation. Also, adsorption of the dyes onto GAC and some ion exchangers showed that GAC has the highest adsorption capacity. Radiation degradation of the toxic dye pollutants and their removal from wastewater down to concentrations not exceeding the maximum permissible concentration (MPC) according to international standards, proved to be better than conventional methods of purification alone.

*Key Words: Gamma-Irradiation / Degradation / Oxidation/ Dyes.*

### **INTRODUCTION**

The waste water effluents from textile, printing and finishing plants typically contain appreciable quantities of organic dyes that are resistant to degrade by ordinary treatment processes<sup>(1-4)</sup>. These dyes pass relatively unchanged through the usual biological waste treatment processes and constitute a highly visible form of pollution in the receiving waters<sup>(5-12)</sup>. Few alternative methods of treatment are available with carbon absorption appearing most feasible at this time. Attritional losses and expense of the carbon recycling process detract considerably from this process. Ionizing radiation may be promising for the treatment of textile dye waste effluents. However, experience has shown that radiation treatment alone of large volumes of waste effluents tends to be inefficient and uneconomic. A more promising approach arises when a combined treatment of irradiation and conventional

methods can be applied to relatively concentrated waste solutions which speed up degradation significantly.

The radiation degradation of two reactive dyes, namely Reactive Blue Brilliant, Reactive Yellow and Basic Blue 9 Dye (Methylene Blue 2B), will be studied. The factors affecting the radiolysis of these dyes such as dye concentration, irradiation dose, dose rate and pH of the dye solutions will be investigated as well as the effect of different additives such as nitrogen, oxygen, hydrogen peroxide and sodium hypochlorite on the radiation-degradation process. Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) measurements will be carried out.

## EXPERIMENTAL

### Materials:

Two reactive dyes, namely Remazol Brilliant Bright Blue, Reactive Yellow Dye (G) and Basic Blue 9 Dye (Methylene Blue 2B), were used in the present study. All chemicals were reagent grade and used as received. UV, COD and TOC measurements were carried out as previously described<sup>(13-15)</sup>.

## RESULTS AND DISCUSSION

### 1. Radiation Degradation of Dyes:

#### Effect of Irradiation Dose and Dose Rate :

The effect of irradiation dose in kGy on the dyes at various concentrations was studied. Various concentrations of Reactive dyes (Blue Brilliant Remazol and Remazol Yellow G) and Basic dye (Methylene Blue 2B) ranging from (50-150 mg/l) were subjected to different doses of gamma radiation up to 50 kGy and results are shown in Figs. (1-3). It can be seen that the decoloration of dye solutions and radiation degradation of reactive and basic dyes, the Reactive dye yellow and Basic Dye Blue are very sensitive to gamma radiation than reactive Blue Brilliant Remazol; methylene blue 2B is very sensitive to gamma radiation and dose of 20 kGy was enough for its complete destruction.

The existence of two phenyl groups only in this basic dye contributed much to its high sensitivity towards gamma radiation. Several researchers working with different Basic Blue dyes reported the same behavior<sup>(6-9)</sup>. While reactive dye Blue Brilliant Remazol showed less sensitivity towards gamma radiation than Basic Blue. The difference in the sensitivity of both reactive and basic dyes towards gamma radiation may be due to the difference in their structures as the structure of Remazol Brilliant Blue contains four benzene rings which contributes to the protection against radiations, while Methylene Blue 2B have only two benzene rings. The effect of the dose rate on the radiation degradation of the reactive and basic dyes studied was investigated at three different dose rates namely 1.22, 0.61 and 0.30

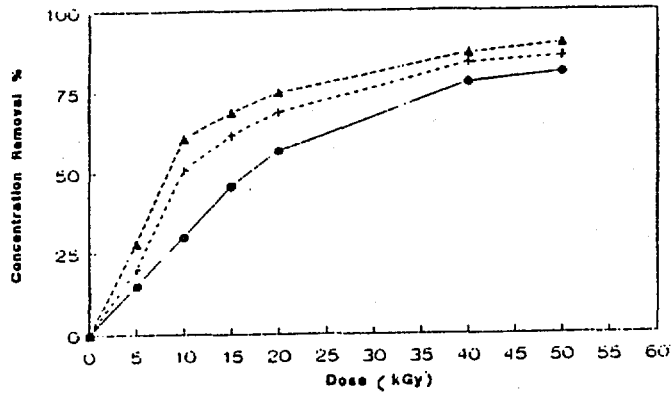


Fig. (1) Relationship between the concentration of removed Reactive Blue Dye II A and Irradiation dose at different dose rates (Gy/s).

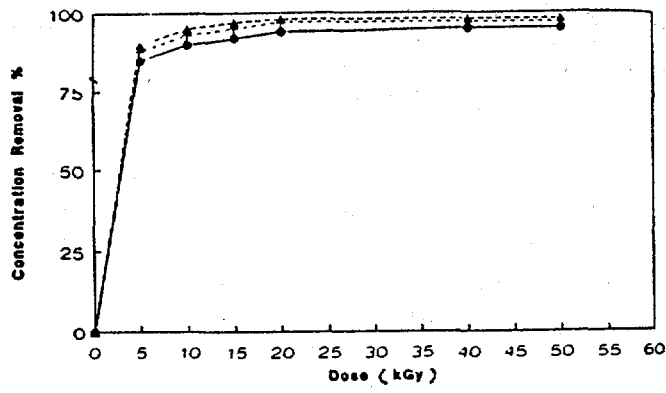


Fig. (2) Relationship between the concentration of removed Reactive Yellow Dye IIB and Irradiation dose at different dose rates (Gy/s).

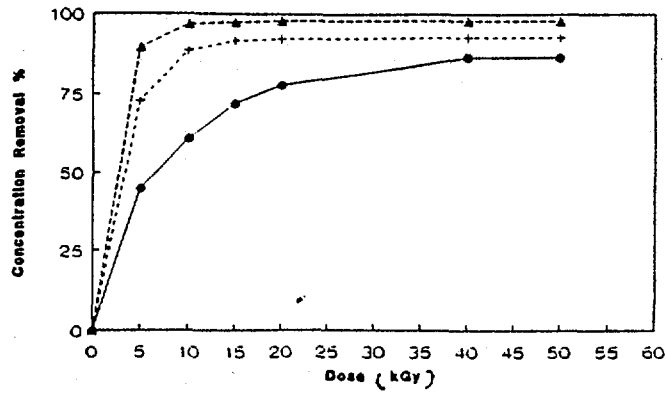


Fig. (3) Relationship between the concentration of removed Basic Blue Dye III and Irradiation dose at different dose rates (Gy/s).

- ▲-- 0.305 Gy/Sec.
- ♦-- 0.61 Gy/Sec.
- 1.22 Gy/Sec.

Gy/s. and the results are illustrated in Figs. (1-3). The general trend for the degradation process is that the percent degradation is highest for the lowest dose rate (0.30 Gy/s), followed immediately by dose rate 0.61 Gy/s and the dose rate 1.22 Gy/s showed a lower degradation percent. Suzuki et al. <sup>(8,9)</sup> working on the degradation of dyes reported also some dependence of the radiation degradation on the dose rate .

### **Effect of pH :**

Figs. (4-6) and Table (1) show the effect of pH of the dye solutions with dye concentration of 100 mg/l. The pH influence has proved to vary according to the type of the dye. For reactive dye (Blue Brilliant Remazol) and basic dye (Methylene Blue 2B) showed a remarkable decrease in pH in the neutral and acid media (pH 7 and pH 3), while in the alkaline medium (pH10) a slight decrease in pH was observed for all the dye solutions. The drop in the pH of the dye solutions may be attributed to the mechanism of the radiation degradation of the dye molecules to lower molecular weight compounds, such as organic acids. The dye molecules are degraded effectively by the primary active species formed from the radiolysis of water such as OH, H<sup>+</sup>, HO<sub>2</sub> and the solvated electron (e<sub>aq</sub>). <sup>(16)</sup>

Figs. (4-6) show the relationship between the degree of degradation of the dyes with irradiation dose at various pH values. It can be seen that the amount of the dye degraded was high at pH 3, followed by that at pH 7 and the degradation was lowest at pH 10. It seems that the formed organic acids due to the radiation degradation of the dye was somewhat neutralized by the radiolysis product. The decrease in pH and the radiation degradation of the dyes was remarkable in the case of Reactive Yellow as shown in Fig. (5). Piccinini et al. <sup>(4)</sup> reported similar radiation degradation behaviour versus pH.

## **2. Synergistic Effects on Dyes by Irradiation and Conventional Treatments :**

Radiation treatment of large volumes of waste effluents tends to be incomplete and uneconomic. <sup>(11,12)</sup> A more promising approach involving radiation treatment of wastewater arises when a combined treatment of irradiation and conventional methods can be applied. Addition of an oxidant such as oxygen, hydrogen peroxide, sodium hypochlorite coupled with gamma radiation exposure speed up any degradation of the dyes significantly. The saturation of the dye solutions with nitrogen gas did not enhance the radiation degradation of these dyes.

### **Oxygen -Saturated Dye Solutions :**

The degree of radiation degradation of the oxygen saturated Reactive and Basic dye solutions was investigated and results are shown in Figs.(7,8). The addition of oxygen resulted in an enhancement of the radiation degradation of the dye in the acidic medium. The irradiation of the dye solutions with gamma radiation leads to the formation of radical and molecular products formed from the radiolysis of water. Many authors <sup>(3-12)</sup> reported that in addition to primary OH radicals, the species (HO<sub>2</sub> and O<sub>2</sub>) contribute to the degradation process and that

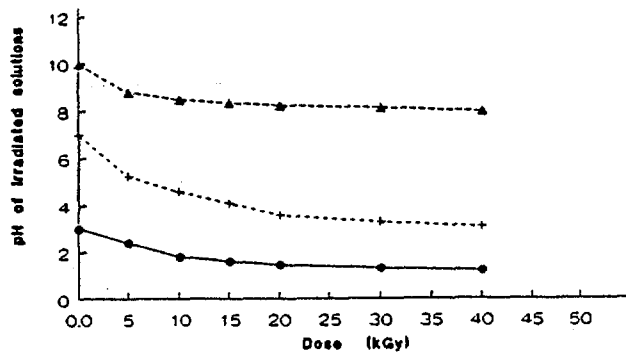


Fig. (4) ; Change in pH of irradiated Reactive Blue Dye IIA with dose. Initial pH of dye.

—●— pH 3      - - - + - - - pH 7      - - - ▲ - - - pH 10

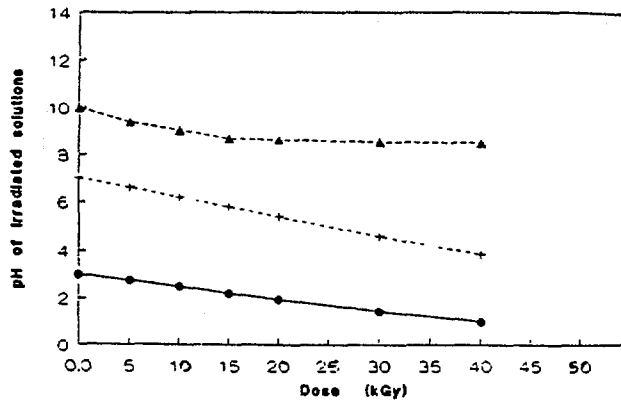


Fig. (5) ; Change in pH of irradiated Reactive Yellow Dye IIB with dose. Initial pH of dye.

—●— pH 3      - - - + - - - pH 7      - - - ▲ - - - pH 10

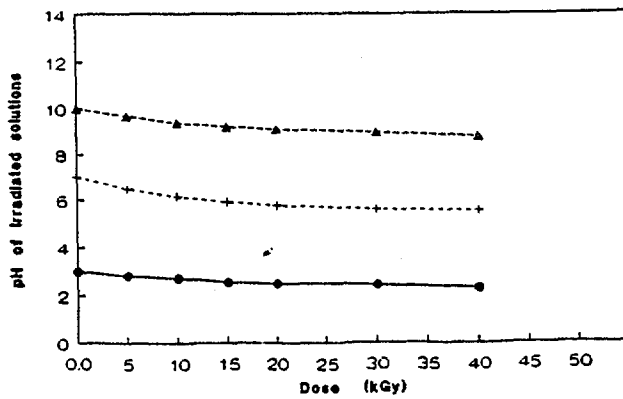


Fig. (6) ; Change in pH of irradiated Basic Blue Dye III with dose. Initial pH of dye.

—●— pH 3      - - - + - - - pH 7      - - - ▲ - - - pH 10

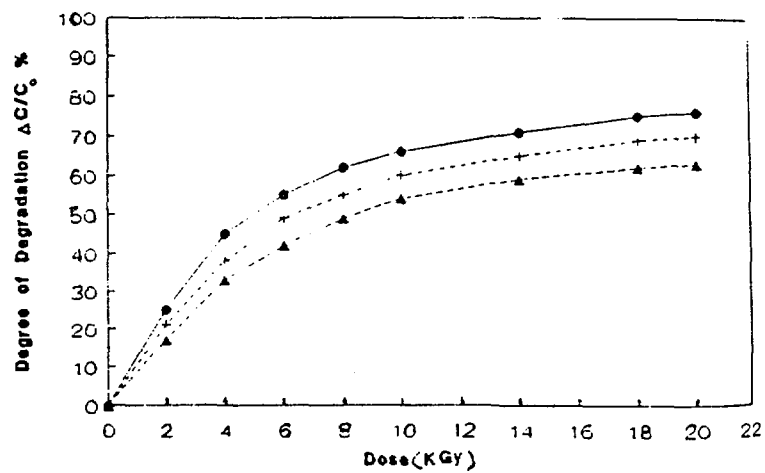


Fig. (7) : Effect of irradiation doses in  $O_2$  atmosphere on the degree of degradation percent for Reactive Blue Dye IIA at different initial pH values.

—●— pH 3      - - + - pH 7      - - ▲ - pH 10

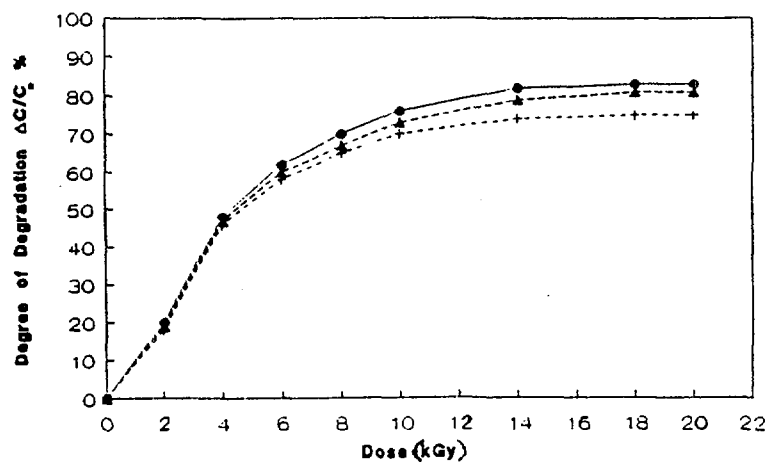


Fig. (8) : Effect of irradiation doses in  $O_2$  atmosphere on the degree of degradation percent for Basic Blue Dye III at different initial pH values;

—●— pH 3      - - + - pH 7      - - ▲ - pH 10

this process in the presence of oxygen leads to the formation of peroxides which contribute also to the degradation reactions.

The influence of dissolved oxygen is generally apparent when working in open air condition and much greater when the degradation was carried out in oxygen-saturated dye solutions. A certain dependence between oxygen concentration and pH, which leads to assume that the global effect can be better understood by a tridimensional relationship between degree of degradation, pH and oxygen concentration. (4, 6, 17)

### **Hydrogen peroxide :**

Figs. (9,10) show the degree of radiation degradation of the dyes (Reactive Blue and Basic Blue) as a function of radiation dose in kGy and at a constant dye concentration of 100 mg/l and a constant H<sub>2</sub>O<sub>2</sub> concentration of 5 mM measured at various pH values (pH = 3, 7 and 10). The results showed that for the Reactive Blue, a radiation dose of 20 kGy was needed for the destruction of the dye at pH=3. However, complete degradation of the dye was not achieved at pH=7 and pH=10. It is obvious that the degradation reaction is promoted by addition of hydrogen peroxide. Hydrogen peroxide reacts rapidly with the hydrated electron formed from the radiolysis of water, leading to the formation of OH radical. (3, 5, 16, 17)



Therefore, the increase in the degree of degradation by addition of hydrogen peroxide would be mainly attributable to increasing of the OH radical through the reaction above, in addition to the primary OH radical. This finding suggests that the OH radical destroys the dye chromophore more efficiently than the hydrated electron does.

### **Sodium Hypochlorite :**

It was found that, when dye solutions are treated with sodium hypochlorite (5%) followed by exposure to gamma radiation, the degree of radiation degradation of the dye increases. The increase is not linear over the range of radiation dose studied as show in Figs. (11,12). For the reactive blue dye, the highest degradation occurred at pH =7, followed by the acidic medium and the least degradation was observed in the alkaline medium. While basic blue dye, the highest degradation occurred at pH =10, followed by the acidic medium and the least degradation in the pH =7. The radiation degradation depends on the type and the physicochemical characteristics of the dye, a fact reported by many authors (6-11). The effect of pH on the radiation degradation may be explained in terms of the various chemical equilibria present in the system. The ionizable sites of the dye molecules are sensitive to pH, but the major differences are probably due to differences in the hypochlorite equilibria (18).

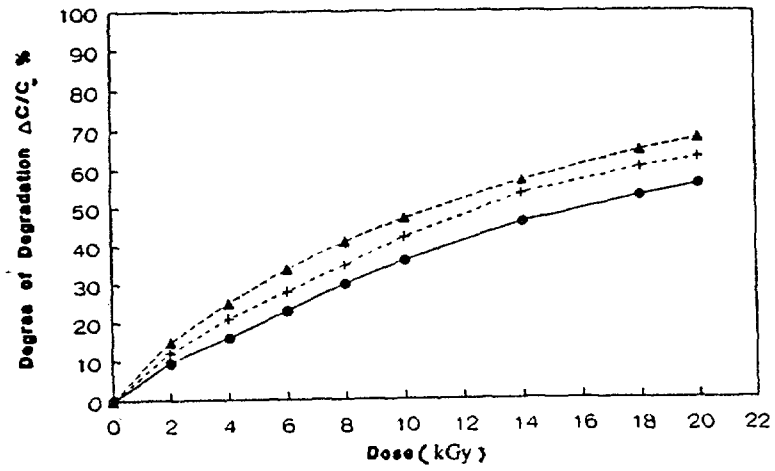


Fig. (9): Effect of irradiation dose on the degree of degradation in presence of  $H_2O_2$  (5 m mol) for Reactive Blue Dye IIA at different pH values;

—●— pH 3      -+--+ pH 7      --▲-- pH 10

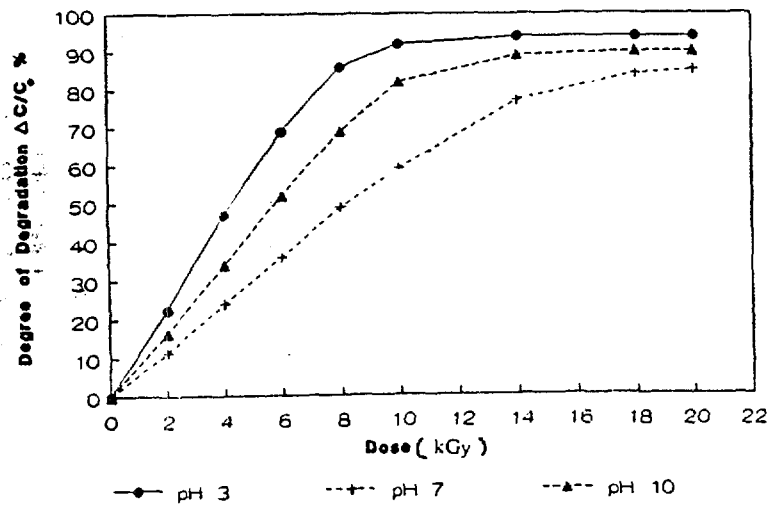


Fig. (10): Effect of irradiation dose on the degree of degradation in presence of  $H_2O_2$  (5 m mol) for Basic Blue Dye III at different pH values;

—●— pH 3      -+--+ pH 7      --▲-- pH 10



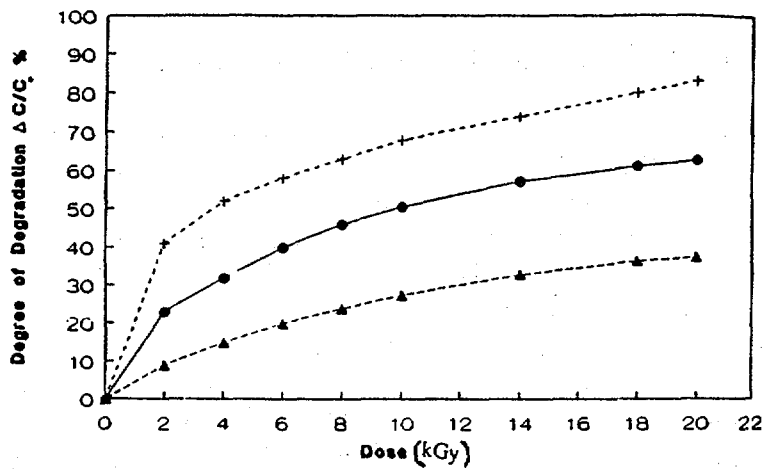


Fig. (11) Effect of irradiation dose on the degree of degradation in presence of 1 ml NaOCL (5%) for Reactive Blue Dye IIA at different pH values;

● pH 3      +--- pH 7      ▲--- pH 10

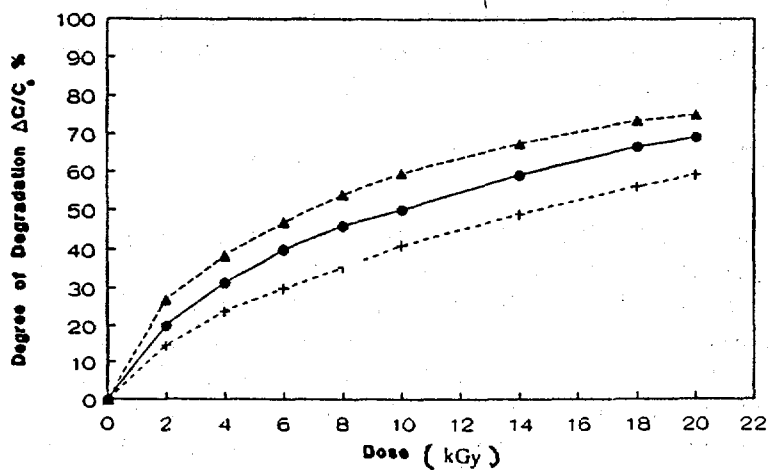


Fig. (12) Effect of irradiation dose on the degree of degradation in presence of 1 ml NaOCL (5%) for Basic Blue Dye III at different pH values;

● pH 3      +--- pH 7      ▲--- pH 10

## **Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD):**

Some studies dealing with the use of gamma irradiation in the treatment of waste water containing dyes and other pollutants have shown that the most considerable effect, that is the degradation, is accompanied by the oxidation of part of the organic substances (decrease in TOC and COD) and is a function both of pH and oxygen concentration of the solution. Changes of Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and pH values of the dye solutions as a function of irradiation dose is tabulated in Table (2). A reduction in TOC and COD was observed for the dyes studied. This reduction increased with the increase of gamma dose. This reduction in TOC was almost similar for the dyes used and was accompanied by a decrease in the pH values of the dye solutions as shown in Table (1). The decrease in TOC was reported by Suzuki and Nagai <sup>(6)</sup> to be almost equal to the increase in the amount of inorganic carbon in the solution suggesting that the dye molecule is degraded almost completely to carbon dioxide in the presence of enough oxygen.

To evaluate globally the amount of oxidation in the dye molecules, COD determination was made on solutions before and after the irradiation, the relative results are only indicative of the oxidation amount, as probably only a part of the organic matter is oxidized by the dichromate, because of the high resistance of such dyes. Chemical Oxygen Demand (COD) was determined for a number of irradiated samples and the results are shown in Table (2). In general, it was found that significantly higher doses were required for appreciable changes in COD. The COD reduction was explained by oxygen addition reactions following reactions of the radiolytic species. The oxidation reactions can only proceed as long oxygen is available in the solution. The tendency of TOC reduction, the COD reduction and the change of pH values for the two dye solutions was similar to each other.

## **Adsorption Purification of Surface Water From Dyes :**

Adsorption onto solid adsorbents has great environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment sequence. Figures (13-18) show the relationship between the adsorption capacity (mg/g) of Granular Activated Carbon (GAC), and Strong Cation Exchanger Merck I for the Reactive and Basic dyes and the equilibrium concentration at different pH values (pH 3, 7 and 10). The initial concentration ranged between 2 and 100 mg/l, a volume of 100 ml of the different concentrations was always used with 1 gm of the adsorbent.

Basic Blue Dye showed somewhat higher adsorption capacity on GAC and Merck I than Reactive Blue Dye at all pH values which may be due to the difference in physico-chemical characteristics. The general trend is that better adsorption capacity for all adsorbents was observed at pH 3, followed by the neutral medium pH 7 then at last the alkaline medium pH 10 <sup>(13-15)</sup>. This may be due to the fact that the uptake by changing the buffering pH value is greatly affected by the ions of buffer solution of the dyes since, it helps the migration of these charged molecules to be diffused onto the macroporous. Granular Activated Carbon (GAC)

**Table (1): Effect of gamma irradiation doses on the initial pH values of different dyes**

Dose kGy	Reactive Blue Dye			Reactive Yellow Dye			Basic Blue Dye		
	pH <sub>3</sub>	pH <sub>7</sub>	pH <sub>10</sub>	pH <sub>3</sub>	pH <sub>7</sub>	pH <sub>10</sub>	pH <sub>3</sub>	pH <sub>7</sub>	pH <sub>10</sub>
0	3.00	7.0	10.0	3.00	7.0	10.0	3.0	7.0	10.0
5	2.70	5.8	9.10	2.80	6.8	9.2	2.8	6.4	9.5
10	2.00	4.9	8.70	2.50	6.1	9.1	2.6	6.2	9.2
15	1.80	4.3	8.20	2.10	5.9	8.9	2.5	6.0	9.0
20	1.68	4.0	8.10	1.95	5.3	8.8	2.3	5.7	9.0
30	1.65	3.8	8.05	1.75	4.5	8.7	2.1	5.3	8.8
40	1.60	3.7	8.00	1.50	3.6	8.6	2.1	4.9	8.5

**Table (2): Changes of TOC, COD and pH by gamma-irradiation**

Dyes	Dose	Reduction %		pH
	kGy	TOC	COD	
Reactive Blue	0.0	-	-	6.38
	1	16	11	3.12
	3	24	19	3.31
	5	34	32	3.47
	10	61	65	3.50
	30	79	79	3.58
	50	92	83	3.64
	Basic Blue 9	0.0	-	-
1		22	18	3.16
3		30	29	3.24
5		41	61	3.31
10		77	75	3.47
30		85	81	3.63
50		96	89	3.63

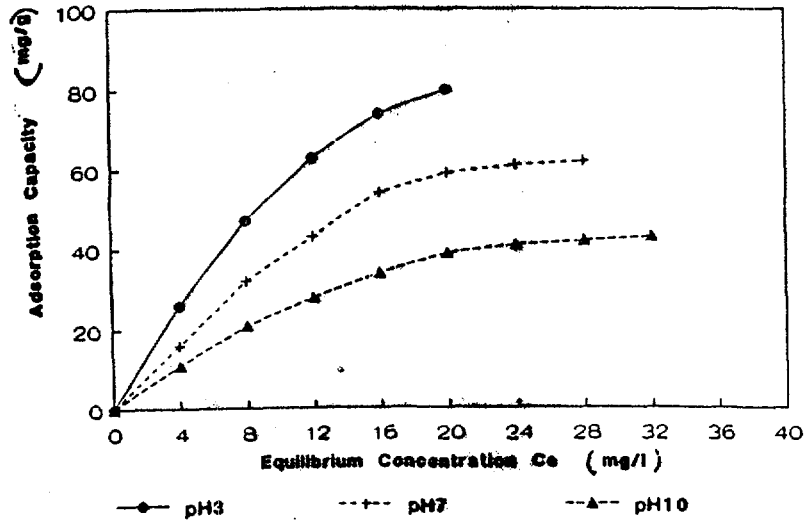


Fig. (13): Relationship between the adsorption capacity and equilibrium concentration for Reactive Blue Dye IIA in presence of GAC at different initial pH values;

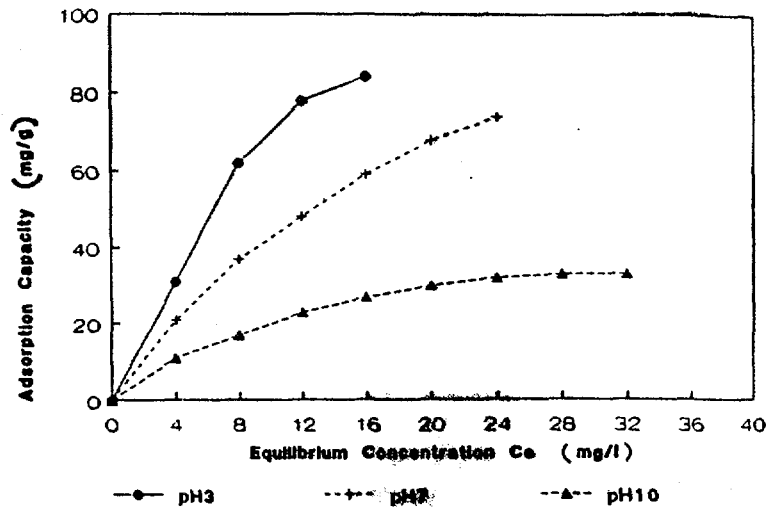


Fig. (14): Relationship between the adsorption capacity and equilibrium concentration for Reactive Blue Dye IIA in presence of strong cation exchange resin (Marck I) at different initial pH values;

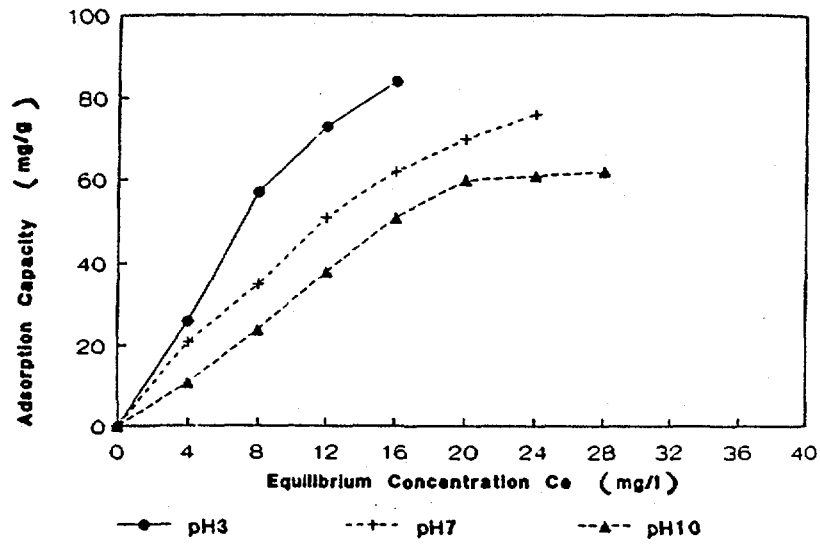


Fig. (15) :Relationship between the adsorption capacity and equilibrium concentration for Reactive Yellow Dye IIB in presence of GAC at different initial pH values;

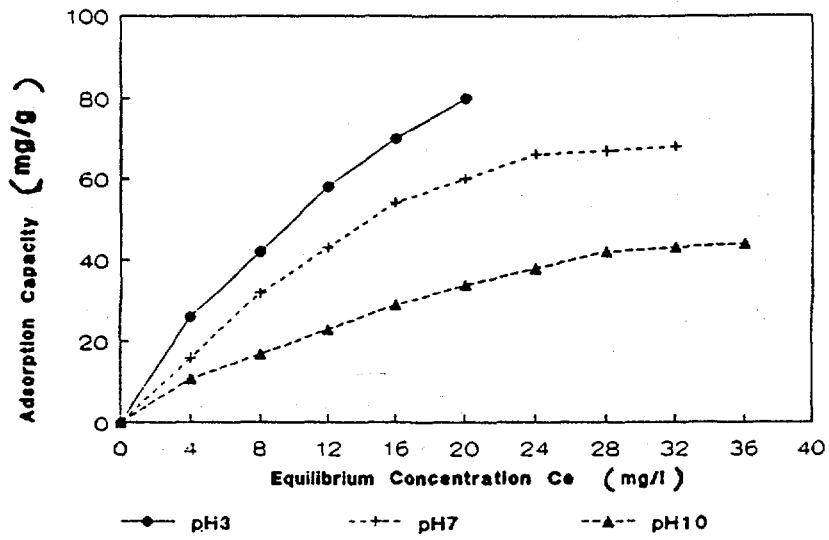


Fig. (16) :Relationship between the adsorption capacity and equilibrium concentration for Reactive Yellow Dye IIB in presence of strong cation exchange resin (Merck I) at different initial pH values;

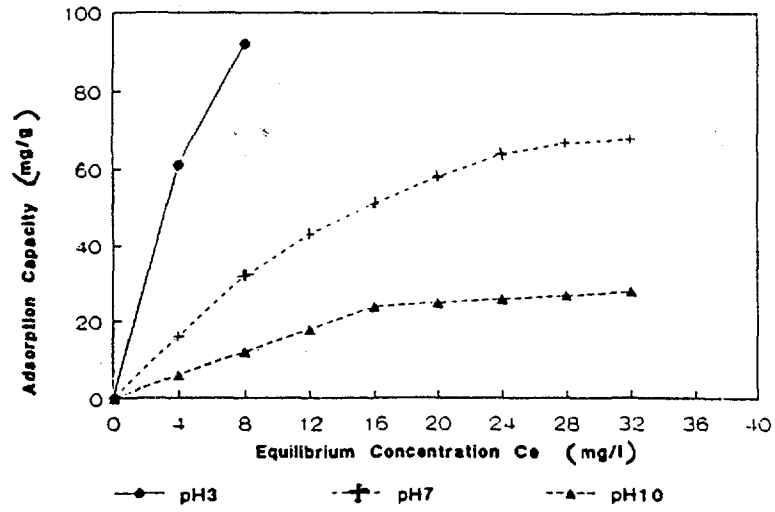


Fig. (17): Relationship between the adsorption capacity and equilibrium concentration for Basic Blue Dye III in presence of GAC at different initial pH values;

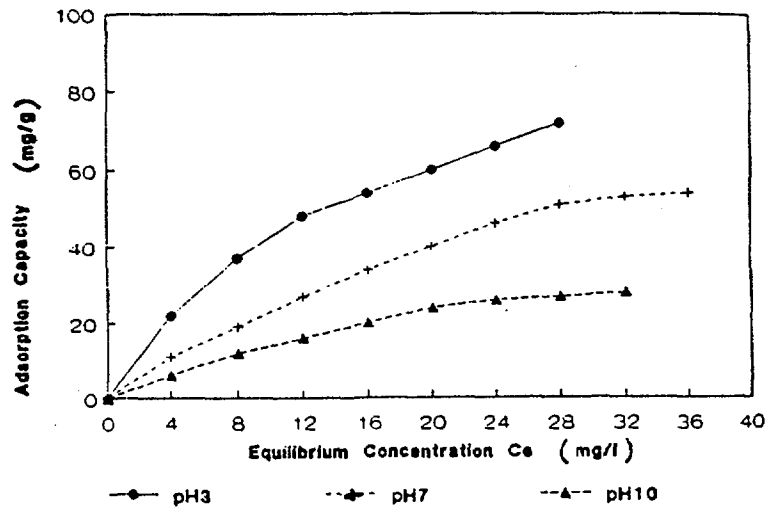


Fig. (18): Relationship between the adsorption capacity and equilibrium concentration for Basic Blue Dye III in presence of strong cation exchange resin (Merck I) at different initial pH values;

showed the highest adsorption capacity for Reactive and Basic Dyes compared to the ion exchange resins used. This may be attributed to the very high surface area of GAC (1100 m<sup>2</sup>/g) and the high porous nature which causes internal and external distribution within the carbon particle more than the case of the synthetic polymeric ion exchangers.

It may be concluded that the radiation degradation of toxic dye pollutants and their removal from wastewater down to concentration not exceeding the maximum permissible to be better than the conventional methods of purification alone. A combination of the radiation degradation and adsorption process at the end of a treatment sequence may be the best way for the complete removal of many organic pollutants.

## REFERENCES

1. D.C. Hinge, Experiences in the Continuous Monitoring of River Water Quality, *J. Instn. Water Engrs. Scits.*, 34, 546 (1980).
2. J. Dojlido and G.A. Best, "Chemistry of Water and Water Pollution", Ellis Horwood, New Work (1992).
3. M. Washino, *Radiat. Phys. Chem.*, 18, 383 (1981).
4. N. Piccinini and F. Ferrero, *Int. Atomic Energy Agency, Vienna, Symposium on : Radiation for a Clean Environment*, 249 (1975).
5. N. Takeshi and N. Suzuki, *Int. J. Appl. Radiat. and Isotopes*, 27, 699 (1976).
6. N. Suzuki, T. Nagai, H. Hotta and M. Washino, *Int. J. Appl. Radiat. Isotopes*, 26, 726 (1975).
7. N. Suzuki, and H. Hotta, *Bulletin of the Chemical Society of Japan*, 50, 1441 (1977).
8. N. Suzuki, M. Tejiro, S. Akihisa, S. Hashimoto and W. Kawakami, *Int. J. Appl. Radiat. and Isotopes*, 29, 103 (1978).
9. N. Suzuki, O. Tokunaga and M. Washino, *Bulletin of the Chemical Society of Japan*, 51, 1337 (1978).
10. R.D. Morris and T.F. Craft, *International J. of Appl. Radiat. and Isotopes*, 24, 245 (1973).
11. Craft, T. F. and Eichholz, G. C. *Int. J. Appl. Radiation Isotopes*, 22, 543 (1971).
12. Craft, T.F. and Eichholz, G.C. *Nucl. Technol.*, 18, 46 (1973).
13. A.M. Dessouki, S.E. Abdel-Aal, *Radiation Technology for Conservation of the environment, IAEA Symposium in Zakopane, Poland, September (1997)*.
14. S.E. Abdel-Aal, A. M. Dessouki and S. A. Ismail, *Arab J. of Nuclear Sciences and Application*, 31 (2), 117 (1998).
15. A.M. Dessouki, S.E. Abdel-Aal and S.A. Ismail, *9th Tihany Symposium on Radiation Chemistry, Budapest -Hungary, August (1998)*.
16. A. Swallow, J., "Radiation Chemistry", Wiley, New York (1973).
17. K.H. Gregor, *Hoellriegelskrouth, Fed. Rep. Germany*, 71, 976 (1990).
18. Stallmann, *Use of Metal Complexes in Organic Dyes and Pigments, J. Chem. Educ.*, 37, 220 (1960).