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Use of Polymeric and Natural Materials for the Removal of Irradiated Direct and acid Dyes from Effluents

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Abstract

Wastewater effluents from textile plants typically contain appreciable quantities of organic dyes that are resistant to degrade by ordinary treatment processes and constitute a highly visible form of pollution in the receiving waters. Carbon absorption as well as ionizing radiation are used as treatment processes. However, each method alone did not achieve the complete removal of these pollutants. A combined treatment is more effective. The two direct dyes(Direct orange S ,Isma Fast Yellow RL) were degraded by -radiation 76% and 70% ,respectively . Also, the acid dye Sandolane Rubanole E-3GSL (Acid red 37) was degraded almost to the same extent. Addition of O_2 or H_2O_2 resulted in a remarkable enhancement in the degradation process. The effect of pH, γ-dose and dye concentration was studied. Polymeric ion exchangers proved to be more effective in the removal process than clays. However, granular activated carbon (GAC) was the best adsorbent for the direct dyes. Clays proved to be very good adsorbents for two basic dyes than their weak adsorption behavior of the direct ones.

Key Words: Direct dyes – Degradation – Radiation – Adsorption – Purification

INTRODUCTION

As a consequence of the rapid growth of the various industrial and agricultural activities, the environment is getting more and more charged with pollutants. In particular, regarding the aqueous ecosystem, the intensive use of fertilizers and pesticides and the production of large amounts of wastes, have contributed to make worse the quality of water resources. Furthermore, the chlorination of water is another factor that contributes in this respect, due to the formation of toxic by-product [1-4]. Irradiation with Υ-rays or electron beam (EB), is an efficient process for degradation of organic pollutants present in water and wastewaters and appears to be most promising technique in the future [5-14]. In this study the radiolysis of two direct and one acid dyes Direct orange S, Isma Fast yellow and one acid dye: Sandolan Rubanole E-3GSL was investigated as a function of dye

concentration, pH, irradiation dose and dose rate. Combining irradiation with conventional treatment for enhancement in the degree of degradation, addition of oxygen or hydrogen peroxide was studied. Experiments on the adsorption of the dyes onto GAC, some polymeric ion-exchange resins and polymeric membranes were carried out.

EXPERIMENTAL

Materials:

Three dyes were used in the present work, namely two direct dyes: Direct orange S (Direct orange 26) and Isma Fast yellow RL (Direct yellow 50) and one acid dye: Sandolane Rubanole E-3GSL (Acid red 37). Five adsorbent materials were used in the adsorption studies; Granular activated carbon (GAC), a strong anion exchange resin, Merck Anion Exchanger III, a strong cation exchange resin, Merck Cation Exchanger I, and two polymeric memberanes Poly Propylene (PP) films were grafted by Styrene/acrylic acid and by Styrene/acrylamide (PP-g-Sty/AAc and PP-g-Sty/AAm) All chemicals used were reagent grade and were used as received. De-ionized distilled water was used in the preparation of dye solutions without any contaminant.

Adsorbents:

Strong Anion Exchanger Merck III was supplied by Merck Laboratories, Germany. GAC was supplied by Arabic Laboratores Company, Egypt. Details of pH,UV, Υ-irradiation dose,and equilibrium studies were carried out as previously described [9, 10, 11, 12]

RESULTS AND DISCUSSION

1- Effect of concentration, Υ-irradiation dose and dose rate on the decomposition of the dyes.

The effect of concentration (mg/l) and gamma radiation dose in kGy on the three dyes studied (Direct Orange S, Isma Fast Yellow RL, Sandolan Rubinole E-3GSL) was carried at various concentrations (25- 150 mg/l) and the results are shown in Fig. (1) for the three dyes, respectively. Almost complete degradation was achieved for low dye concentration (25-50mg/l) and a dose of 1-2 kGy was enough to achieve this goal. However, for high concentrations (75-150 mg/l) the acid is more sensitive to radiation than and the two direct dyes. This may be attributed to the existance of six benzene rings in the structure of the yellow and orange direct dyes. It is well known fact that the existance of more benzen rings in a compound makes it more resistance to radiation effects [15]. The effect of gamma-radiation on the degradation of the dyes differed according to the type and structure of the dyes. The dose rate study showed that here as in previous studies
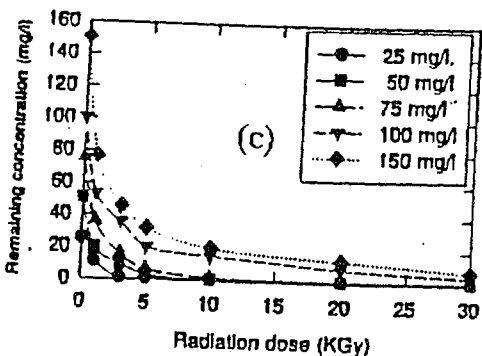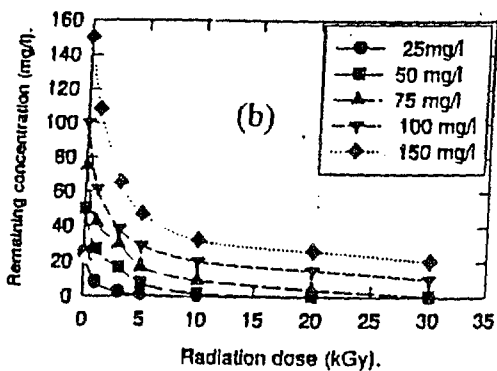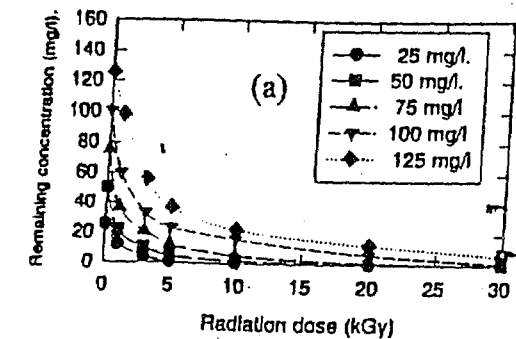
Fig.(1):

Relationship between the remaining concentration of the different dyes and gamma irradiation dose (kGy) at dose rate 2.08 kGy/h and constant pH=7.

(a): Direct orange dye. Fig.(c): Direct yellow dye.
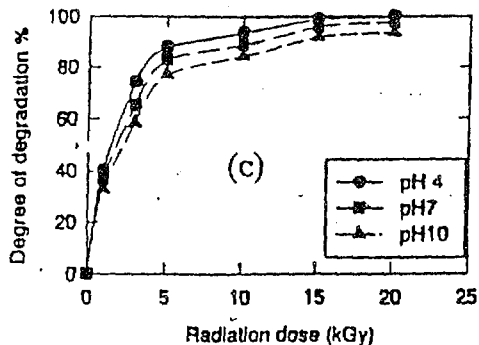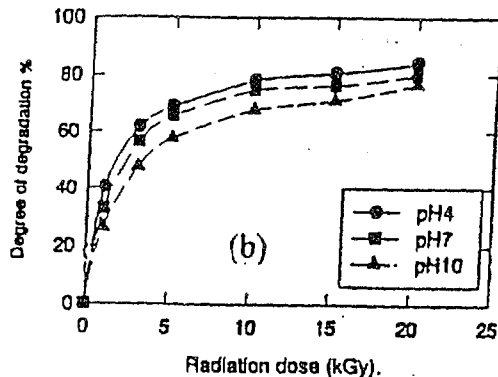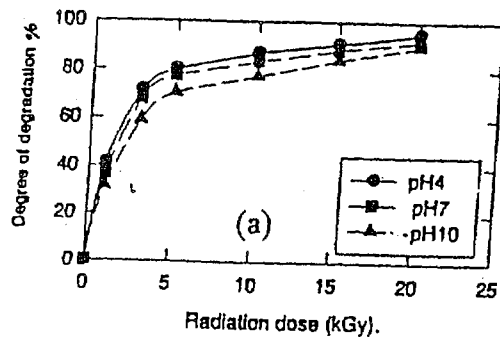(b): Acid red dye.

Fig.(2):

Relationship between the degree of degradation % of the different dyes and gamma irradiation dose (kGy) at constant initial concentration 100 mg/l and dose rate =2.08 kGy/h.

(a): Direct orange dye. (c): Direct yellow dye.
(b): Acid red dye.

[8-14] that the radiation degradation of the dyes is similar in behaviour to the radiation degradation of other pollutants (pesticides). Low dose rates showed more degradation than higher dose rate.The three dose rates used ranged (0.52-1.04-2.08 kGy/h) and experiments were carried out at pH7. However, working with other kinds of dyes. Suzuki et al [16,17] reported some dependence of the radiation degradation on the dose rate. However, the difference between the degree of degradation due to the three dose rates was remarkable in the present study.

2- Effect of pH:

The effect of the dye solutions pH on the percent degradation at constant concentration (100 mg/l) as a function of irradiation dose (1, 3, 5, 10, 20, kGy) was shown in Figure (2). The pH value of the dye solutions has a considerable effect on the degree of the dye at various irradiation doses and it varies according to the type of the dye. It can be seen from the figures that the amount of the dye degradation was lowest at pH=10 in all cases and highest at pH= 4. **Piccinini et al** [10] reported that some of the dyes are more destroyed in the basic medium, others in the acidic medium and that some others are poorly influenced by pH. The dye molecules are degraded effectively by the primary active species formed from the radiolysis of water such as $OH^.$, H^+, $HO^._2$ and the solvated electrons (e $^-$aq). The energy of gamma radiation absorbed in the wastewater and converted to these active species reacts effectively with very dilute pollutants such as in our case. The effect of the pH of the dye solutions at various irradiation doses leads to the degradation of the dye molecules to lower molecular weight compounds and consequently the concentration of the dye decreases. Also, secondary products formed due to recombination or transformation of the primary species (forming H_2, H_2O_2) also take part in the degradation process.

B- Synergistic Effects of Irradiation and Conventional Treatments :

The synergistic effect of gamma irradiation coupled with nitrogen gas bubbled in the dye solutions at various pH values (pH= 4, 7, 10) was investigated showed that the saturation of the dye solutions with nitrogen did not enhance the degradation but resulted in lowering it.

1 - Oxygen- saturated dye solutions.

The degree of radiation degradation of the oxygen- saturated dye solutions was investigated at different pH values as a function of irradiation dose and the results are shown in Fig. (3). The addition of oxygen resulted in an enhancement of the radiation degradation of the dye solutions. The extent of this degradation was different for the different types of dyes. Direct orange dye suffered the highest degree of degradation due to the presence of oxygen, while Direct Yellow and acid red dyes showed a moderate enhancement in degradation. In most cases the radiation degradation of the dyes was higher in the acidic medium followed by
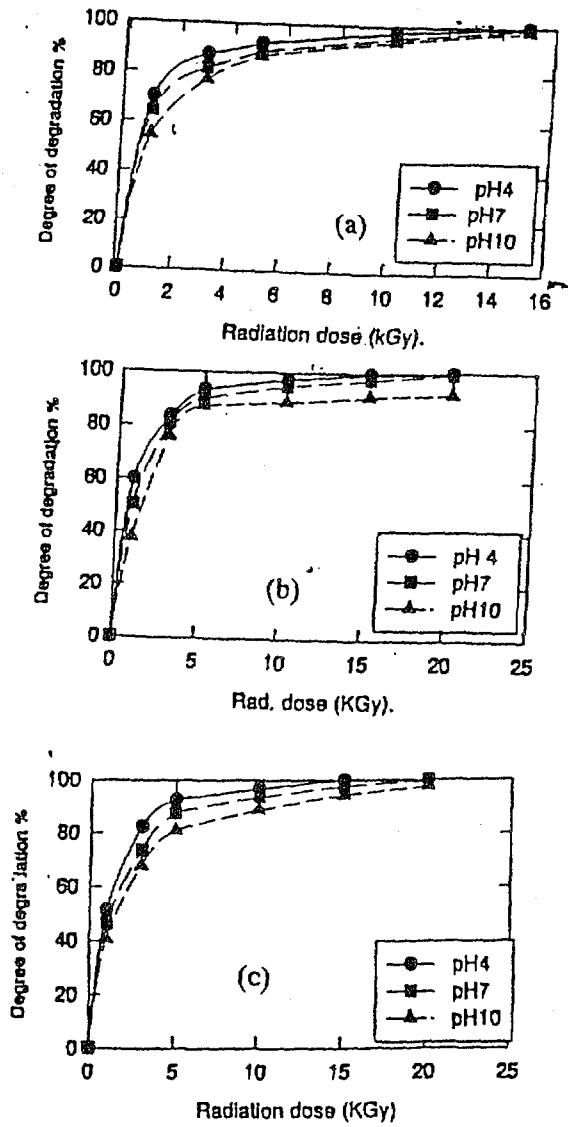
Fig.(3):

Effect of gamma irradiation doses (kGy) on the degree of degradation % of the different dyes in the presence of Oxygen at different pH values at constant initial concentration 100 mg/l and dose rate=2.08 kGy/h.

(a) : Direct orange dye.   (c): Direct yellow dye.
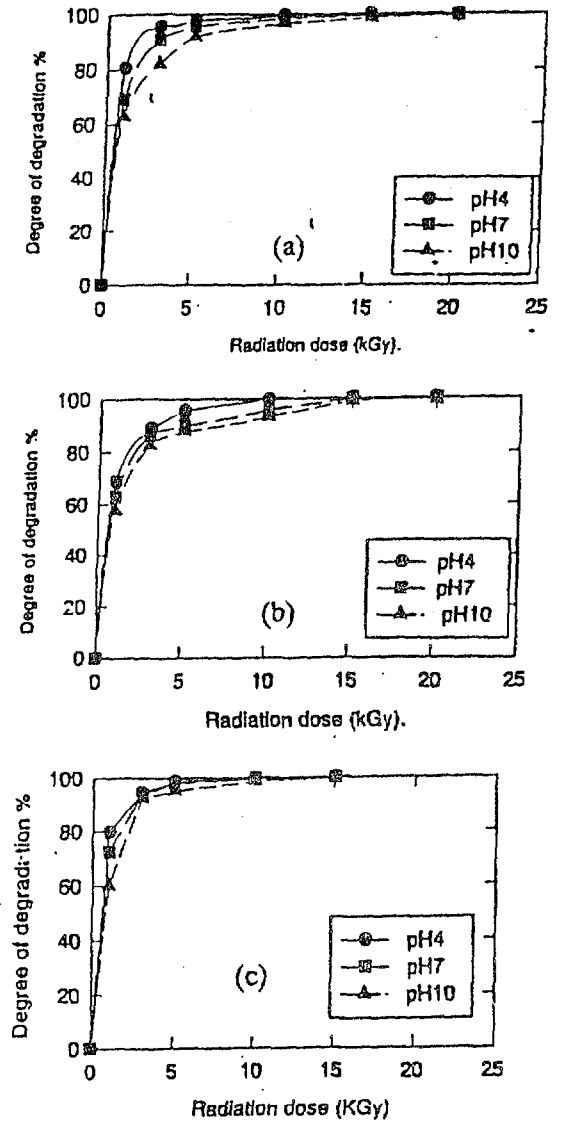(b) : Acid red dye.

Fig.(4):

Effect of gamma irradiation doses (kGy) on the degree of degradation % of the different dyes in the presence of Hydrogen peroxide (0.025M) at different pH values at constant initial concentration 100 mg/l and dose rate=2.08 kGy/h.

(a) : Direct orange dye.   (c): Direct yellow dye.
(b) : Acid red dye.

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that in neutral medium and the degradation carried out in alkaline medium proceeded with the least degree. 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 authers [7-9] reported that in addition to the primary $OH^.$ radicals, the species (HO_2 and O_2^-) contribute to the degradation process and that 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.

2 - Effect of hydrogen peroxide:

The radiation degradation of the dye solution in the presence of 0.025 M H_2O_2 as a function of irradiation dose in kGy at a constant dye concentration of 100mg/l at various pH values (4, 7 and 10) is shown in Fig. (4). The results showed that all the three dyes were very sensitive to gamma radiation in the presence of hydrogen peroxide to a large extent at all conditions studied. A dose of 5 kGy was enough for almost the complete degradation of these pollutants at pH= 4, but this was not achieved at pH= 7 and 10. It is obvious that the degradation reaction is promoted by addition of hydrogen peroxide. Hydrogen peroxide reacts rapidly with the hydrated electrons (e^-aq) formed from the radiolysis of water, leading to the formation of $OH^.$ radical.[5,6]

C- Adsorption Purification:

The adsorption of the pollutants on GAC, two ion exchange resins and two polymeric membranes was investigated at various pH values using equilibrium studies. The concentration of the dyes ranged from 10-100 mg/l.

1- Adsorption onto GAC and Ion Exchange Resins.

Figure (5) show the relation between the adsorption capacity (mg/g) of Granular Activated Carbon and the equilibrium concentration (mg/l) for the dyes at different pH values (4, 7 and 10), respectively. The highest adsorption capacity onto GAC was shown by the two dyes with different percentages depending on the physicochemical characteristics of these pollutants and their chemical structure. More adsorption was shown at pH=4, followed by the neutral medium and at the last the alkaline medium. However, complete removal of these pollutants was not achieved, although GAC is well known as a very active adsorbent. When resinous adsorbents such as **Merck I** (a strong cation exchanger) and **Merck III** (a strong anion exchanger) were used for the adsorption of the pollutants, less removal was observed Merck I showed better adsorption capacity for the dyes (Fig.6) followed by the anion exchanger Merck III (Fig.7). Due to the degree of purification that can be achieved by adsorption, this process is often used in the case of synthetic polymeric ion-exchangers. This is the first general trend in the adsorption studies. Also, it was observed that more cationic species
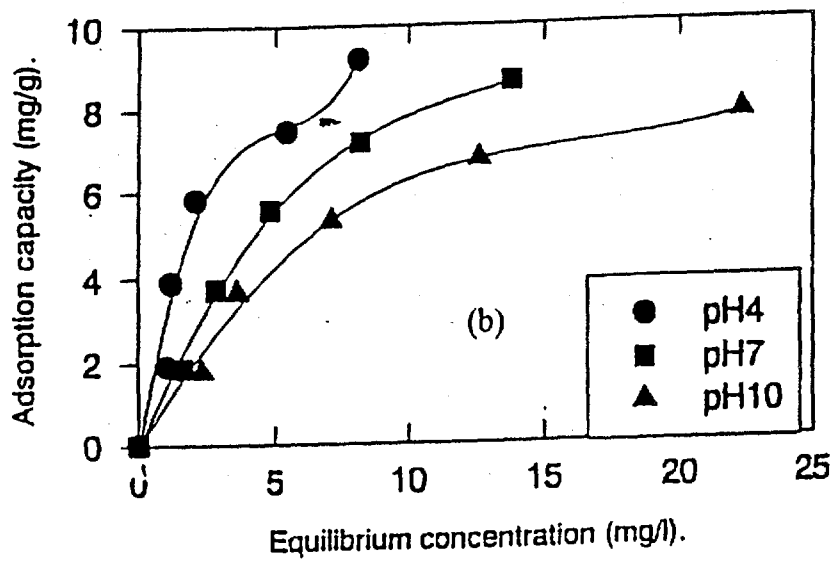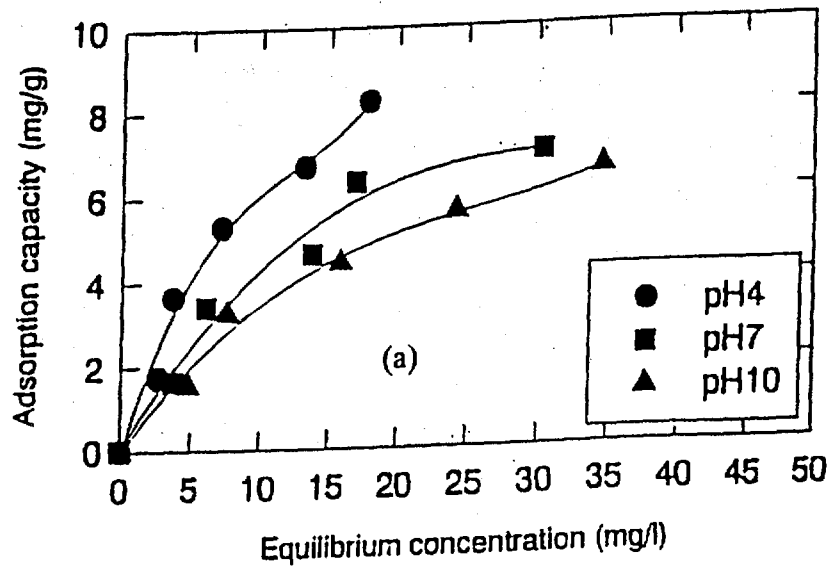
Fig.(5): Relationship between the adsorption capacity (mg/g) of Granular Activated Carbon and the equilibrium concentration (mg/l) of the different dyes at different pH values.

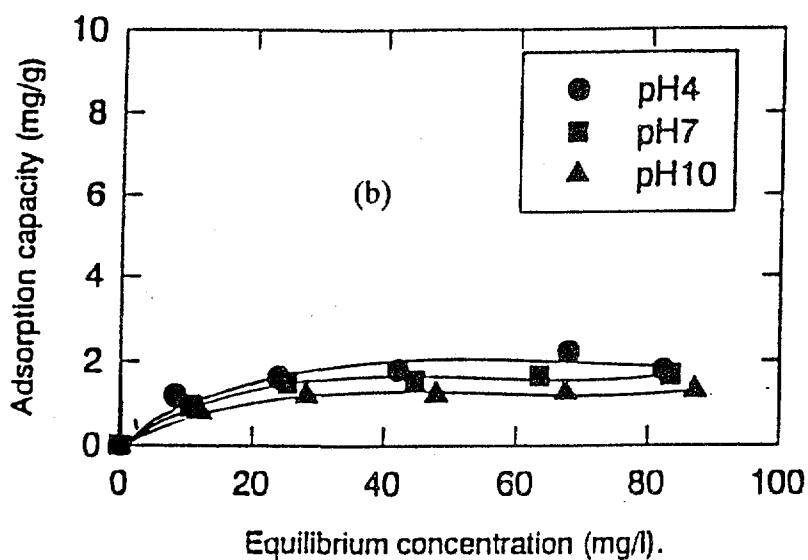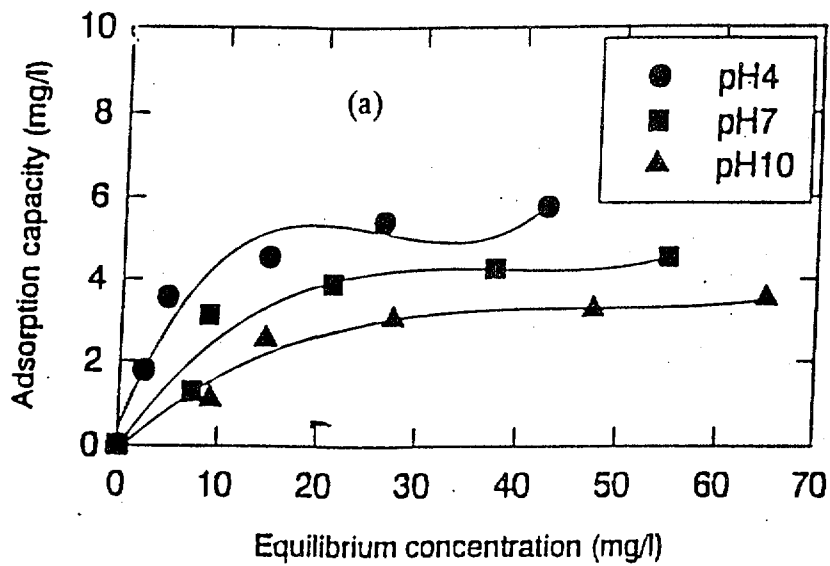(a) : Direct yellow dye.   (b): Acid red dye.

Fig.(6): Relationship between the adsorption capacity (mg/g) of Cation Exchange Resin and the equilibrium concentration (mg/l) of the different dyes at different pH values.

(a) : Direct yellow dye.　　　　　(b) : Acid red dye.

were adsorbed on GAC and on the ion-exchangers. A sorbate having stronge affinity with the solvent the solvent usually represents a strongly adsorbed species, therefore the sorbate has a high adsorption capacity. This may be explained that there is a strong adsorbed species, which always has a greater tendency to occupy the adsorption sites, than the weakly adsorbed species does. Noll et al [18], reported a similar explanation in their work with the system phenol + p-chlorophenol onto XAD-4 resin and phenol + p-chlorophenol onto carbon F-400. A further explanation was given by Malissa [19] who reported that when adsorption forces predominate, the resins do not contain charged or chemically active groups. Van Vliet et al [20], reported that widely differing adsorption isotherms were obtained for phenol on a sereis of synthetic adsorbents and two activated carbons.

2-Adsorption onto Polymeric Membranes:

Poly Propylene (PP) films were grafted with styrene / acrylic acid (pp-g-st /AAc) and by styrene / acrylamide (pp-g-Sty /AAm) to obtain membranes to be used in the removal of the different dyes: (Acid Red and Direct Yellow) from wastewater. Fig. (8) show the adsorption capacity (mg/g) of these grafted membranes as a function of equilibrium concentration (mg/l) for the different pollutants at pH= 7. It can be seen from the figure that PP-g-Sty /AAc showed less adsorption capacity than the PP-g-Sty /AAm membranes, for all pollutants. This may be due to the different functional groups grafted on the trunk polymer.

3- Radiation &Adsorption Purification:

Granular Activated Carbon (GAC), two ion-exchange resins (previously used in the adsorption section were used as adsorbents for the dyes (Direct Yellow and Acid Red at different pH values (4, 7 and 10) and irradiation dose 3 kGy. The equilibrium concentration 20-35 mg/l for the dyes as shown in tables 1and 2. It can be observed that very high percent removal was achieved which ranged between 97- 100 % using the different adsorbents as shown in Table (1).It was also observed that the best conditions for the adsorption was at pH= 4 for all the dyes. The irradiation of the dyes followed by adsorption achieved the highest purification grade under MPC (Maximum Permissible Concentration) according to the FAO regulations.

Conclusion

It can be concluded that the radiation treatment of the pollutants was not enough to achieve it's complete degradation. Also, adsorption purification alone was not enough for the complete removal of these hazardous wastes. The new trend for using the combined treatment of irradiation followed by adsorption achieved this goal and almost complete removal of these pollutants and their radiolysis products (fragments) were all removed by the adsorbents.
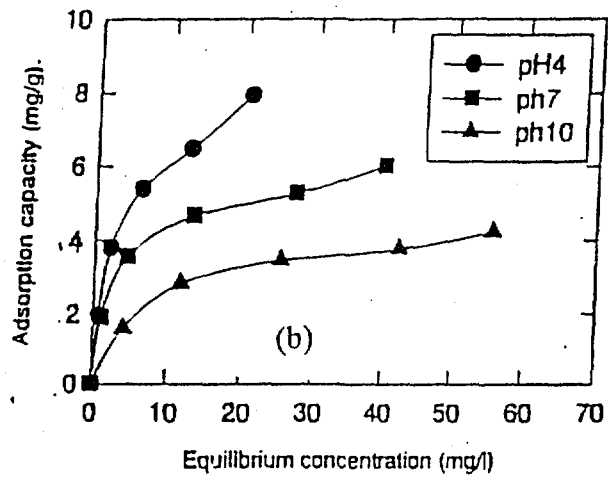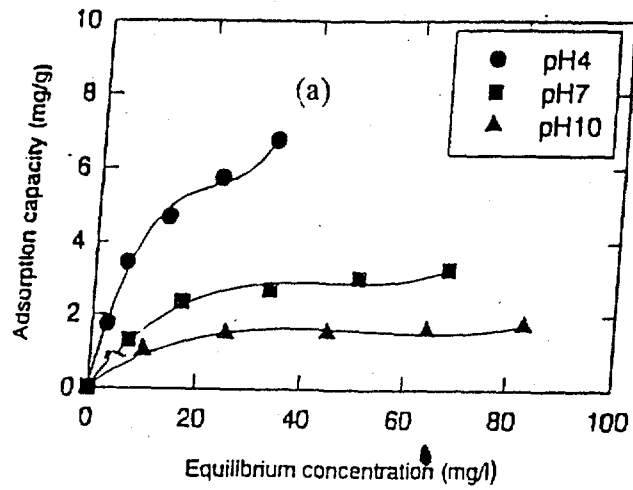
Fig.(7): Relationship between the adsorption capacity (mg/g) of Anion
Exchange Resin and the equilibrium concentration (mg/l) of the
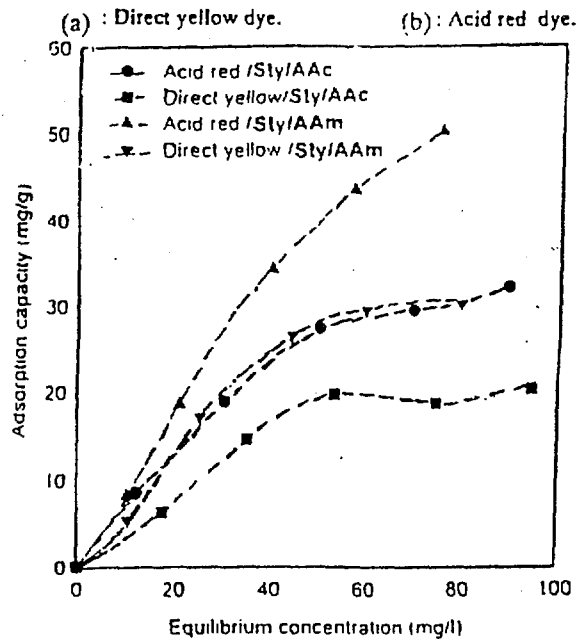different dyes at different pH values.

(a) : Direct yellow dye.   (b) : Acid red dye.

Fig.(8):Relationship between the adsorption capacity
(mg/l) of PP-g-Sty/AAc and PP-g-Sty/AAm
for the acid red and direct yellow dye at pH=7.

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Table (1):- The remaining concentration (mg/l) after the radiation & adsorption treatment of the different dyes by radiation dose (3 kGy) then adsorption on different adsorbent materials at different pH values and initial concentration 100 mg/l.

Adsorbent	Name of Dye	pH 4		pH 7		pH 10	
		After radiation	After adsorption	After radiation	After adsorption	After radiation	After adsorption
GAC	Direct yellow	35.7	0.0	40.2	0/04	48.5	0.1
	Acid red	33.9	0.02	37.4	0.06	42.9	0.01
Cation exchange Resin	Direct yellow	35.7	0.01	39.8	0.03	49.1	13.2
	Acid red	33.6	15.2	38.4	21.6	43.4	29.8
Anion exchange resin	Direct yellow	35.1	0.06	40.4	7.8	48.9	20.2
	Acid red	32.4	0.0	38.9	0.0	43.8	1.2

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