



Rad.C-13 "Removal of some Dyes from Industrial Effluents by Polymeric Materials and Gamma-Irradiation"

S. E. Abdel-Aal, A. M. Dessouki and Y. H. Gad
National Center for Radiation Research & Technology,
P. O. Box 29, Nasr City-Cairo, Egypt. 11731.

ABSTRACT

The radiolysis of two basic dyes (Astrazon Red 6B and Astrazon Blue BG-200%), was investigated as a function of dye concentration, pH, irradiation dose and dose rate. It was found that the Astrazon Red 6B dye showed more radiation degradation than that of the Astrazon Blue BG-200% dye. Combining irradiation with the conventional treatment resulted in an enhancement in the degree of degradation. Addition of oxygen or hydrogen peroxide showed this enhancement, while nitrogen showed no change. A pH drop was observed and may be attributed to the degradation of the dye molecules to lower molecular weight compounds such as organic acids. The primary radiolysis products as well as the secondary products are responsible for the degradation of the dye chromophore. Experiments on the adsorption or exchange the dyes onto GAC, some polymeric ion exchange resins and polymeric membranes were carried out showing that GAC having the highest adsorption capacity. Through the combined treatment of irradiation and adsorption, the total removal of these toxic dyes was achieved.

Key Words: Dyes- Removal- γ -Radiation- Adsorption- Polymeric Membranes.

Introduction

Most dyes used by textile industry are not easily degraded by ordinary treatment processes. Ionizing radiation may be promising for the treatment of the textile dye waste effluents, ⁽¹⁻⁴⁾ because the effect of radiation can be intensified in aqueous solution in which the dye molecules are degraded effectively by the primary products formed from the radiolysis of water. In the presence of oxygen, the hydrogen atom reacts rapidly with oxygen, leading to the formation of oxidizing HO₂ radical. Chemical oxidation of the organic species in the presence of oxygen is due to the interactions of oxidizing radicals with them in the aqueous solution.

EXPERIMENTAL

Materials:

Two dyes were used in the present work, namely Astrazon red 6B (Basic violet 7) and Astrazon blue BG-200% (Basic blue3). Five adsorbent materials were used in the adsorption studies; Granular Activated Carbon (GAC), a strong anion exchange resin, Merck Anion Exchanger III (it is high basic anion exchanger, it is a polystyrene derivative with anchored quaternary ammonium groups), a strong cation exchange resin, Merck Cation Exchanger I(it is a highly acidic sulphonated cation exchanger of the polymerization type based on Styrene-divinylbenzen copolymer), and two polymeric membranes 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, γ -irradiation dose, and equilibrium studies were carried out as previously described^(17, 18, 19)

RESULTS AND DISCUSSION

A- Radiation Degradation of Dyes:

The basic dyes Astrazon Blue BG-200% and Astrazon Red 6B were more sensitive to γ -radiation than acid and direct dyes. This may be attributed to the existance of six benzene rings in the structure of the dyes. It is well known fact that the existance of more benzene rings in a compound makes it more resistant to radiation effects⁽⁵⁻⁷⁾. The effect of gamma-radiation on the degradation of the dyes differed according to the type and structure of the dyes Fig (1). Astrazon Red dye showed more degradation than Astrazon Blue. Also, the dose rate study showed that here as in previous studies^(8,9) that the radiation degradation of the dyes is similar in behavior to the radiation degradation of other pollutants (pesticides). Low dose rates showed more degradation than higher dose rates. Suzuki et al⁽¹⁰⁾ working on the degradation of some anthraquinone dyes reported no dependence of the decolouration percent on the dose rate in the range 0.03- 0.55 Gy/sec. However, they reported some dependence of the radiation degradation on the dose rate in other cases. The pH of the dye solutions has a considerable effect on the degradation of the dye at various irradiation doses and it varies according to the type of the dye. It can be seen from Fig. (2) that the amount of the dye degradation was lowest at pH=10 in all cases and highest at pH= 4. It was observed that the pH of the dye solution decreases after irradiation. This drop in pH was explained on the basis of the radiolysis products forming organic acids, which lead to the decrease in the initial pH. Organic acids were detected as degradation products of the dye molecules to lower molecular weight compounds⁽⁵⁻⁷⁾.

B- Synergistic Effects of Irradiation and Conventional Treatments (O₂ and H₂O₂)

The addition of oxygen resulted in an enhancement of the radiation degradation of the dye solutions Fig. (3). The extent of this degradation was different for the different types of dyes. Basic Red and Basic Blue, dyes suffered the highest degree of degradation due to the presence of oxygen, while Acid and Direct dyes showed a moderate enhancement in degradation. In most cases the radiation degradation of the dyes was higher in the acidic medium followed by 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⁽¹¹⁻¹³⁾ reported that in addition to the primary OH[•] Radicals, the species (HO₂ and O₂^{•-}) 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. The mechanism of the reactions leading to dye degradation is mainly of the radical type, consequently, the observed behaviours versus pH are to be connected with the acid- base properties of both primary radical species (e⁻_{aq} and OH[•] as well as O₂²⁻ have a basic character, so that in an acidic medium a partial transformation occurs in the corresponding protonated species H⁺, H₂O⁺ and HO₂) and secondary species, i.e. the radicals produced by organic substance fragmentation, the different relative reactivity of the

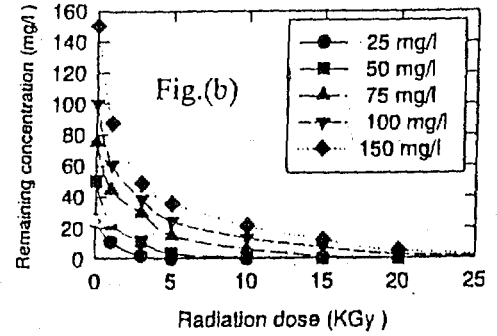
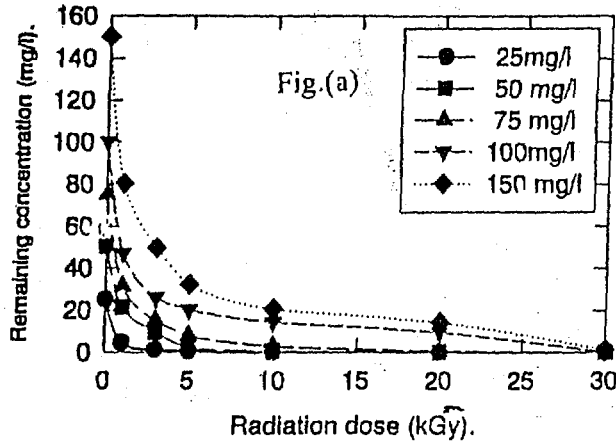


Fig.(1):

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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

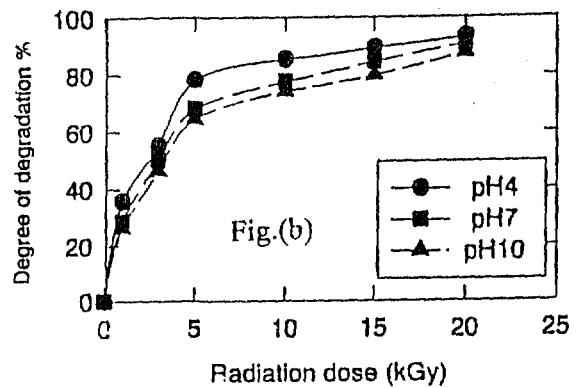
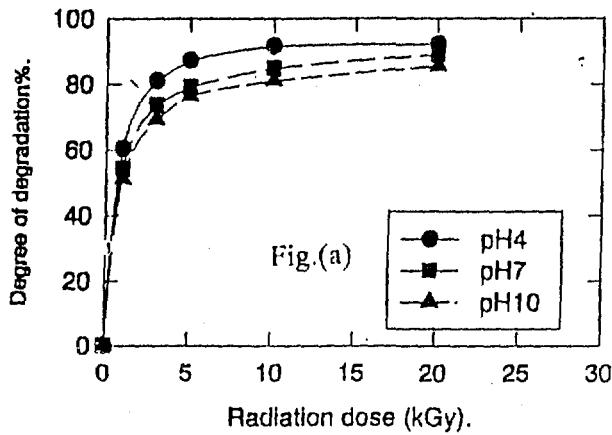


Fig.(2):

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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

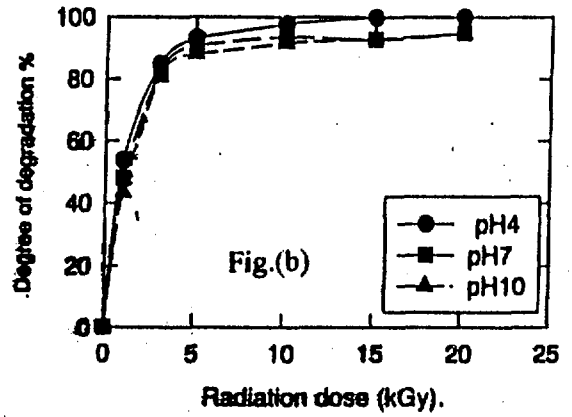
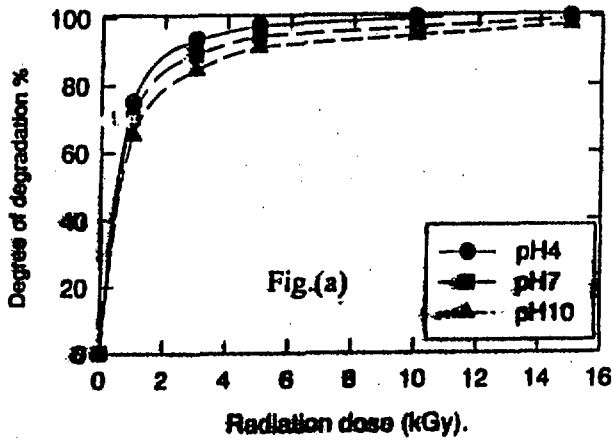


Fig.(3):

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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

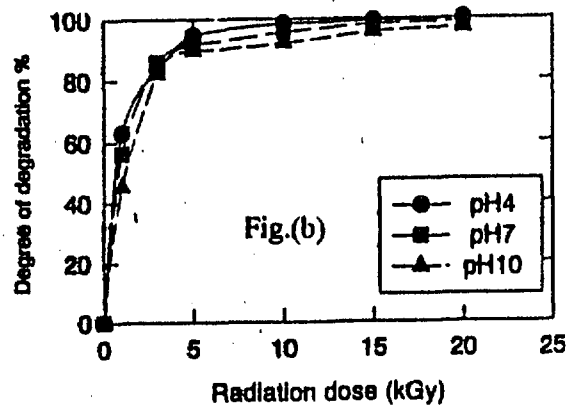
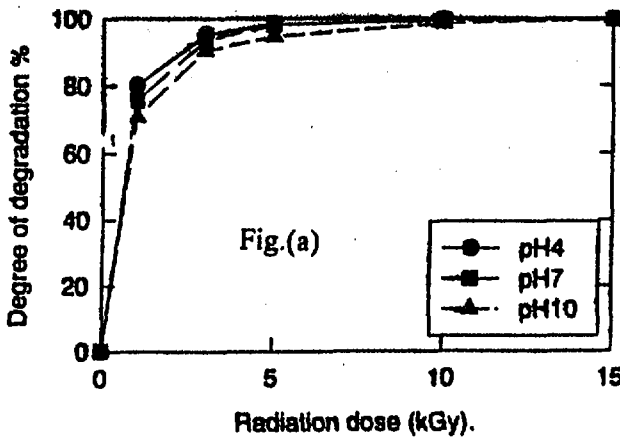


Fig.(4):

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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

various species as pH changes, involves different behaviors according to the structure of the original dye molecule. The inter-dependence between the influence of concentration of H^+ and O_2 is sufficiently clear, when taking into account the effect of dissolved oxygen already discussed, resulting in an increase in radical concentration owing to the appearance of species HO_2 and $O_2^{\cdot-}$, whose concentration are linked by acid-base equilibrium reactions.^(8,9,11)

The radiation degradation of the dye solution in the presence of 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 the dyes were very sensitive to gamma radiation in the presence of hydrogen peroxide to a large extent under 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.⁽⁵⁻⁷⁾

C- Adsorption Purification:

I- Adsorption onto GAC and Ion Exchange Resins.

Figures (5-7) 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 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 last the alkaline medium. However, complete removal of these pollutants was not achieved, although GAC is well known as very active adsorbents. 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 followed by the anion exchange Merck III. 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 were adsorbed on GAC and on the ion-exchangers. A sorbate having strong affinity with 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. Generally, the activated carbons performed best, followed by the carbonaceous adsorbents, and finally by the polymeric and resinous adsorbents. The shapes of the isotherms suggest that the polymeric and resinous adsorbents may be most competitive with activated carbon at very low waste concentrations. This is in good agreement with our results.

2-Adsorption of Dyes by Bentonite Clays:

After the treatment of clays with 1N hydrochloric acid, the dye solutions come in contact with the clays for a period of 12 days at various pH values, the results are shown in Figs. 8 and 9. It is clear that the two basic dyes showed the highest adsorption on the bentonite clays, while the least adsorption was shown by the two direct dyes for all pH values studied. This may be attributed to the difference in molecular weight, molecular size and physicochemical characteristics of the dyes: smaller molecules showed more adsorption (Basic Blue & Basic Red). The numerical values of k and $1/n$ are shown in Fig. (8, 9). Variation in the slopes ($1/n$) and intercepts of the lines (k) reflects the effect of chemical structure of the different pollutants on the adsorption process and their affinity for

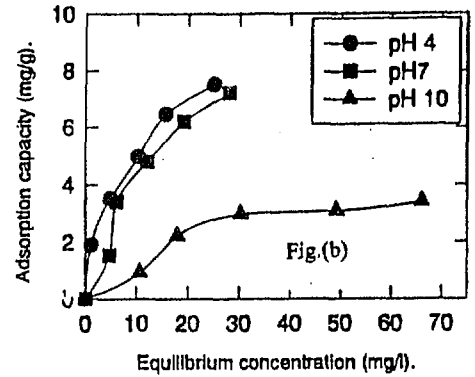
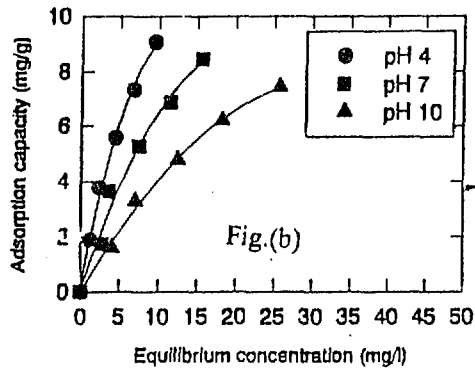
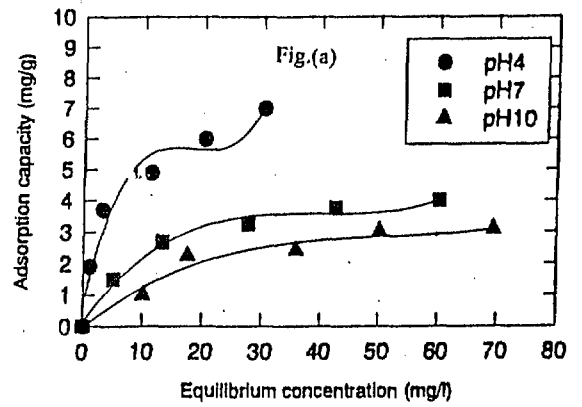
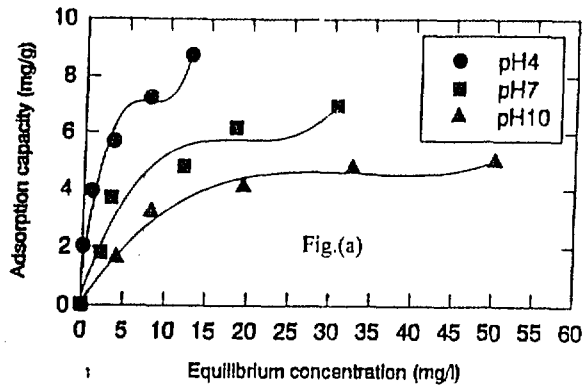


Fig.(5):

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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue 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.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

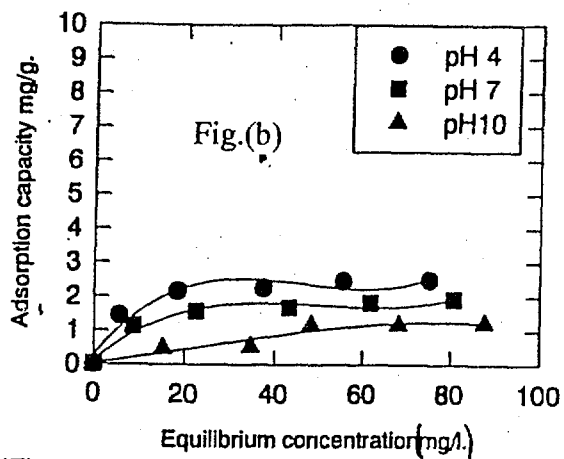
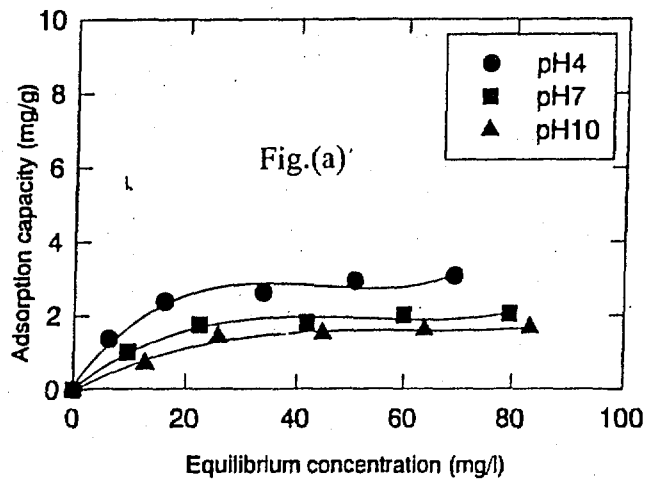


Fig.(7): Relationship between the adsorption capacity (mg/g) of Anion Exchange Resin and the equilibrium concentration (mg/l) of the different dyes at different pH values.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

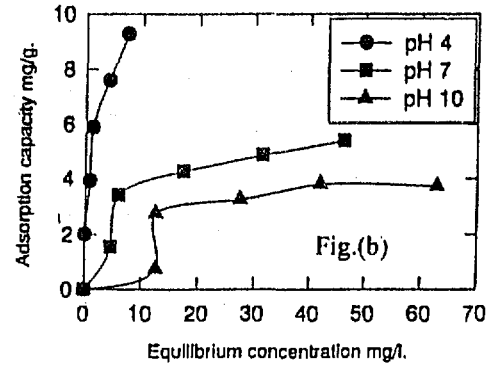
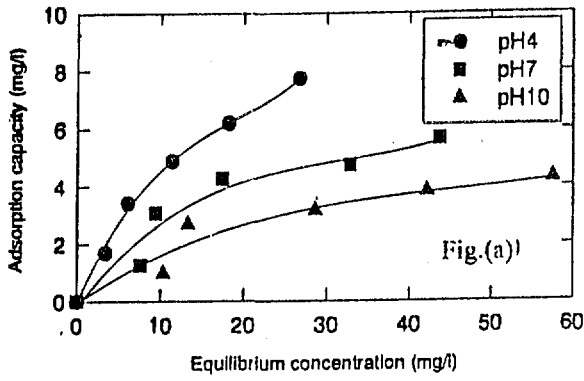


Fig.(8):

Relationship between the adsorption capacity (mg/g) of Bentonite Clay and the equilibrium concentration (mg/l) of the different dyes at different pH values.

Fig.(a): Basic red dye.

Fig.(b): Basic blue dye.

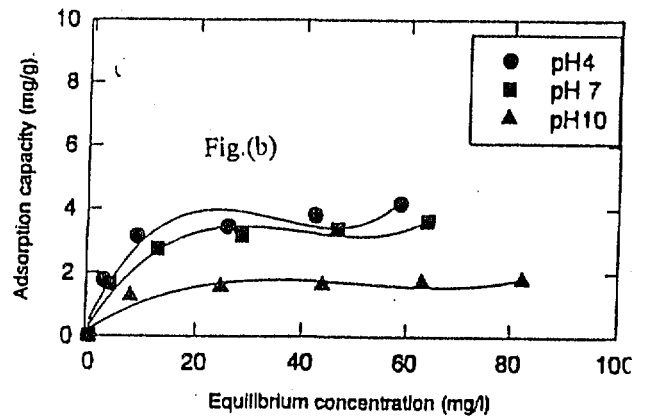
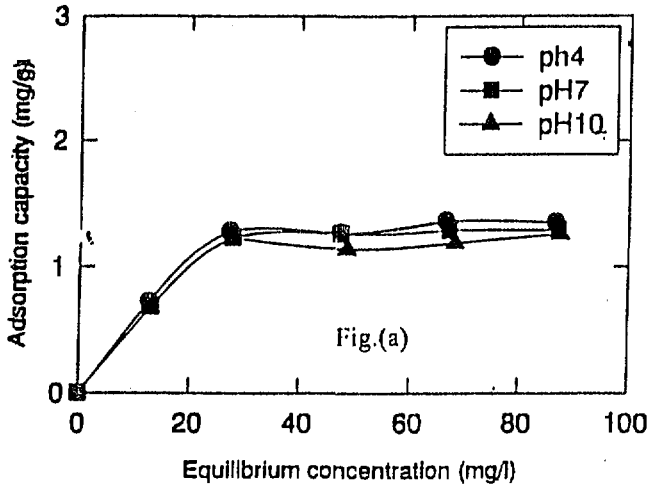


Fig.(9):

Relationship between the adsorption capacity (mg/g) of Bentonite Clay and the equilibrium concentration (mg/l) of the different dyes at different pH values.

Fig.(a): Direct orange dye.

Fig.(b): Direct yellow dye.

adsorption. In general, as the (k) value increases, the adsorption capacity of adsorbent for a given compound increases. The slope of the isotherm line may also characterize the adsorption process. Steeper slopes indicate relatively good adsorption of the compound when present in high concentration. Slight slopes indicate comparable adsorption over the entire range of concentrations. Consequently, the adsorption parameters (k, 1/n) describe on a quantitative basis the adsorption process and account for the variation in adsorbent doses required for the removal of dyes⁽¹⁴⁾

3-Adsorption onto Polymeric Membranes:

Membranes seem to be the most promising technology in water treatment technologies. Their best advantage is their ability to produce water with a constant and well adjusted quality. At a time where the demand for quality is a major drive, membranes thus have a clear advantage over all other technologies. They remove a wide range of substances, from particles to ions, including bacteria and viruses. Theoretically they could remove everything. They can operate without chemical addition to water, are reliable, compact, and to automate⁽¹⁵⁾. Their major disadvantages are still their rather high capital and operation costs, and the fact that they are prone to fouling, which requires often a high level of pretreatment and regular chemical cleaning. They may also have a rather important reject stream whose disposal creates problems. PolyPropylene (PP) films were grafted by styrene / acrylic acid (pp-g-st /AAc) and by styrene / acrylamide (pp-g-st /AAm) to obtain membranes to be used in the removal of the different dyes from wastewater. Fig. (10) 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 figures 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 functional groups grafted on the trunk polymer.

D- Radiation - Adsorption Purification:

Radiation adsorption purification is one of the new directions in the radiation purification field. This method combines radiation treatment of the organic pollutants coupled with the conventional adsorption purification by equilibrium batching method. Granular Activated Carbon (GAC), two ion-exchange resins (previously used in the adsorption section) and one bentonite clay were used as adsorbents for the dyes. All experiments were carried out at different pH values (4, 7 and 10). The irradiation dose was 3 kGy for all types of the pollutants as well as the equilibrium concentration 20-35 mg/l for the dyes. It can be observed that very high percent removal was achieved which ranged between 97- 100 % using the different adsorbents as shown in Table (I). 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. Adsorption from solutions can be highly pH dependent, as discussed earlier⁽¹⁶⁻¹⁹⁾. From the economic and practical standpoint, a fluid should always be evaluated at ambient pH. In other words, the pH of a solution is significant for its effect on the adsorbent as well as on the adsorbate. Both adsorbate and adsorbent may have chemical characteristics that are affected by the concentration of hydrogen ions [H⁺] in the solution. Some adsorbents have affinity for [H⁺] or [OH⁻] ions can directly affect the solution pH and therefore the solubility and the adsorption capacity.

Adsorbent	Name Of dye	pH 4		pH 7		pH 10	
		after radiation	after adsorption	After radiation	after adsorption	after radiation	after adsorption
		GAC	Basic red	18.1	0	25.5	.01
Basic blue	45.9		0	51.9	0	54.9	.06
Cation exchange resin	Basic red	17.8	0	24.8	0	30.9	.3
	Basic blue	44.6	.06	50.7	.03	55.2	21.1
Anion exchange resin	Basic red	17.4	.01	25.1	4.6	31.2	.11.9
	Basic blue	45	19.9	50.3	29.7	55.4	41.5
Bentonite clay	Basic red	17.7	0	25.2	0	31.3	.1
	Basic blue	45.4	.03	51.2	.15	54.1	15.8
	Direct orange	28.1	.01	32.2	.02	41.3	25.93
	Direct yellow	35.2	21.6	40.8	27.2	47.6	34.7

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

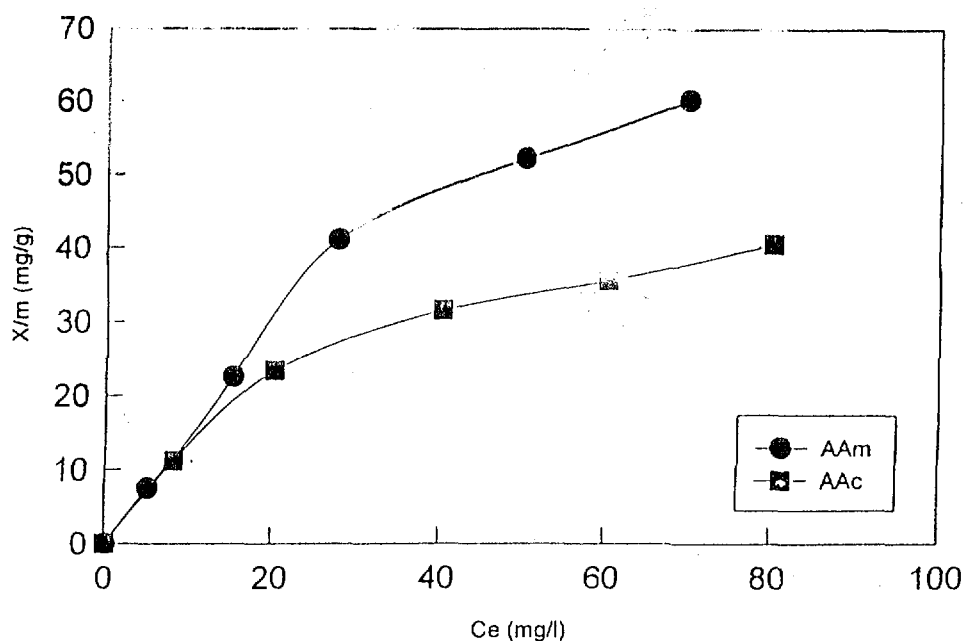


Fig.(10): Relation between the adsorption capacity (mg/g) of PP-g-Sty/ AAm & PP-g-Sty/AAc and the equilibrium concentration (mg/l)of the basic red dye at pH =7

Conclusion

It can be concluded that the radiation treatment of the pollutants was not enough to achieve its 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 of the pollutants, new compound such as acids...etc.) were all removed by the adsorbents. This means that the radiolysis products which may be also toxic, were completely removed as well as the original pollutants and were removed from the polluted solutions down to concentrations not exceeding the maximum permissible concentration (MPC) according to the international standards.

References

1. Rook, J. N. Water Treatment Exam. 23, 234 (1974).
2. Hutzinger, O.; Frei, R., Merian, E. and Pocciari, F. Chlorinated Dioxines and Related Compounds-Impact on the Environment, Pergamon Press, Oxford (1982).
3. Getoff, N., Water Res. 40, 585 (1989).
4. Quit R. M. Radiation Phys Chem. 47, 835 (1996).
- 5- Spinks, j. and Woods , R." An Introduction to Radiation Chemistry ", J. Wiley , New York (1964).
- 6- Swallow , A. J., " RadiationChemistry "" , Wiley , New York (1973).
- 7- Henglein , A.; Schnable. W. and Wendenburg, J., "Einführung in die Strahlenchemie ", Verlag Chemie, Weinheim, Germany (1973).
- 8- Suzuki. N. Nagai , T.; Hotta .H. and Washino. M., Bulletin of the Chemical Society of Japan , 48, 2158 (1975).
- 9- Suzuki, N.; Teijiro, M.; Akihisa, S.; Hashimoto, S. and kawakami, W., Int. J. Appl. Radiat. and isotopes . 29, 103 (1978).
10. Suzuki, N.; Tokunaga , O. and Washino , M., Bulletin of the Chemical Society of Japan , 51, 1337 (1978).
- 11- Washino, M., Rdiat. Phys. Chem., 18, 383 (1981).
12. Piccinini, N. and Ferrero , F., Int. Atomic Energy Agency Symposium, Vienna, 249, (1975).
- 13- Gregor, K.H., Hoellriegelskrouth, Fed. Rep. Germany, 71, 976 (1990).
- 14-El- Dib, M. A. and Aly, O. A., Journal Water Rsearch, 11, 617 (1976).
- 15-Pollard, E., Davidson, W. L., J. Applied Nuclear Physics, Wiley, New York, p. 127. (1942).
- 16- Dessouki, A. M., and Abdel-Aal, S. E., International Atomic Energy IAEA Symposium on " Radiation Technology for conservation of the Environment", Zakopane, Poland (1997).
- 17- Dessouki, A. M., Abdel-Aal, S. E. and S. A. Ismaail 9. Th. Tihany Symposium on Radiation Chemistry, Budapest- Hungary August (1998).
- 18- Dessouki, A. M., Aly, Sokker. H. F. H. H., Czechoslovak Journal of Physics, 49, 521 (1999).
- 19-Abdel- Aal, S., E., Ph.D. Thesis , Ain- shams University –Cairo (1996).