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Effect of Gamma Radiation in the Removal of some Hazardous Waste

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ABSTRACT

The treatment of wastewaters containing toxic pesticides poses a serious environmental problem. Many of the pesticides are not readily biodegradable and complete removal in many cases is a relatively expensive process. Ionizing radiations proved to be more effective for the treatment of these wastewaters than ordinary conventional methods. In the present study a try was made to explain the degradation kinetics due to irradiation of aqueous solutions of some active ingredient pesticides.. These pesticides are: two Organophosphorous Pesticides; Dimethoate and Sumithion and one Organochlorine Pesticide: DDT. A combined treatment of gamma irradiation and conventional methods was applied . Factors affecting the radiolysis of pesticides such as pesticide concentration, irradiation dose, dose rate and pH of the solutions were studied. The effect of different additives such as nitrogen and oxygen showed an enhancement in the degradation process. Experiments on the adsorption of pesticides on some polymeric materials and on Granular Activated Carbon (GAC), showed that GAC has the highest adsorption capacity. It may be concluded that the radiation degradation followed by adsorption of the toxic pesticide 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 the conventional methods of purification and more economical as well.

Key Words : Radiation/ Degradation/ Adsorption/ Pesticides.

INTRODUCTION

As man's requirements for water increase, the need for better methods of purification also increase. Technology has been slow to develop new methods of water treatment for the direct utilization of wastewater. Many new construction projects are at a standstill because wastewater treatment methods have not been developed to handle adequately the ever-increasing flow of waste. The treatment of pesticide wastewaters poses a serious environmental problem. Many of the pesticides are not readily biodegradable and complete removal in many cases is a relatively expensive process. On the other hand, incomplete removal is a serious health hazard.[1-6] Ionizing radiation proved to be more effective for the

treatment of these wastewaters than ordinary conventional methods. Some studies dealing with use of gamma irradiation in the treatment of wastewaters have shown that the most considerable effect, that is the effective degradation of the pesticide molecules by the primary products formed from the radiolysis of water, is accompanied by the oxidation of part of the organic substances (decrease in COD and BOD) and is a function both of pH and oxygen concentration of the solution. [7-15]

In the present study, the degradation kinetics due to irradiation of aqueous solutions of some active ingredient pesticides, in the absence of other specific pollutants of the pesticide industry. A combined treatment of gamma irradiation and conventional methods will be applied to some concentrated waste solutions in manageable volumes. The combined treatment is much more effective than either alone. Factors affecting the radiolysis of the pesticides such as pesticide concentration, irradiation dose, dose rate and pH of the solutions will be studied as well as the effect of different additives such as nitrogen and oxygen on the degradation process. Also, equilibrium isotherms and the intraparticle diffusivities will be investigated through batch experiments in analyzing the adsorption of aqueous solutions of pesticides onto Granular Activated Carbon (GAC) and two ion exchange resins.

EXPERIMENTAL

Materials:

Three pesticides were used in the present work: two organophosphorous pesticides; Dimethoate and Sumithion and one organochlorine pesticides, DDT. Three adsorbent materials were used in the adsorption studies, one of these was Granular Activated Carbon (GAC), one strong anion exchange resin Merck III and one weak anion exchange resin Merck II. All chemicals used were reagent grade and were used in the preparation of pesticide solutions without any contaminants.

Adsorption Studies

Adsorption isotherms were determined by the batch method, or bottle point method for all adsorbents. Carefully determined amounts of adsorbent equal to 0.25 gram were added to 100 ml beaker containing 25 ml of adsorbent irradiated solution with concentration 3, 4, 5, 6, 7 mg/l before irradiation, respectively. The beakers were sealed by an aluminium foil paper, stirring mechanically and then left for a period of 8 days at room temperature (25 °C). The concentration of solution was then determined, the equilibrium data from each beaker representing one point on an adsorption isotherm.

U.V., Gamma-Irradiation and Chemical Oxygen Demand and Biochemical Oxygen Demand measurements were carried out as previously described [16-18]

RESULTS AND DISCUSSION

Radiation Degradation of Pesticides

a) Effect of Irradiation Dose and Dose Rate:

The effect of irradiation dose in kGy on the different pesticide solutions at an initial concentration 5 mg/l was studied and the results are shown in Fig (1). It can be seen that the radiation degradation of chlorinated pesticides, hydrochloric acid was detected (pH decrease and Cl^- formation). Ametryn, Applaud and Aldrin insecticides were degreaded to a much lesser extent by gamma-irradiation than Chlorothalonil up to a dose of 10 KGy. The difference in behaviour of the four pesticides (pollutants) may be attributed to the difference in their structure. [10-15] Chlorothalonil was completely destroyed with the formation of hydrochloric acid which lead to a decrease in the pH of the pesticide solution, i.e. the chlorine atoms of the pollutant were very sensitive to gamma -radiation. wheras, Applaud which contains two benzene rings which may have contributed to its protection against radiation.

The effect of the dose rate on the radiation degradation of the pesticides was investigated at three different dose rates, namely 1.2, 0.6 and 0.3 Gy/Sec. (total dose of 4 KGy) and the results are illustrated in Fig. 2. The general trend for the degradation process is that the percent degradation is higher for the lowest dose rate (0.3 Gy/Sec.), followed by dose rate 0.6 Gy/Sec. and the dose rate 1.2 Gy/Sec. showed a lower degradation percent. This behavior is expected and is in good agreement with reported results.[10, 13,14]

b) Effect of pH.

Figures (3, 4 and 5) show the effect of the pH of pesticide solutions with percent degradation at constant concentration 5 mg/l as a function of irradiation dose (2,4 and 6kGy). The pH influence has proved to vary according to the type of the pesticide . For all pesticides, very little degradation (between 2% and 6%) was observed in the alkaline medium (pH12) at all irradiation doses. The degree of degradation of pesticides in the neutral medium (pH7) was dependent on the type of pesticide and on its chemical structure. However, the percent degradation in the acid medium (pH3) was higher than that in the neutral medium in all cases. It was observed that the pH value of the pesticide solutions in the alkaline and acid medium changes slightly after irradiation, while in the neutral medium the change in pH value was remarkable. The pH value decreased as the irradiation dose increased. The drop in the pH of the pesticide solutions may be attributed to the mechanism of the radiation degradation process taking place in our studied system in which acids were detected as degradation products of the pesticide molecules to lower molecular weight compounds (such as acids). Pesticide molecules are degraded effectively by the primary active species formed from the radiolysis of water such as OH, H^+, H_2O and the solvated electron (e_{aq})[10,11,19] . The energy of gamma radiation absorbed in wastewater is converted to the active species which react effectively with very dilute pollutants such in our case. The effect of the pH of the pesticide solutions at various irradiation doses leading to the degradation of the pesticide molecules to lower molecular weight compounds and consequently the concerntration of the pesticide decreases. Also,

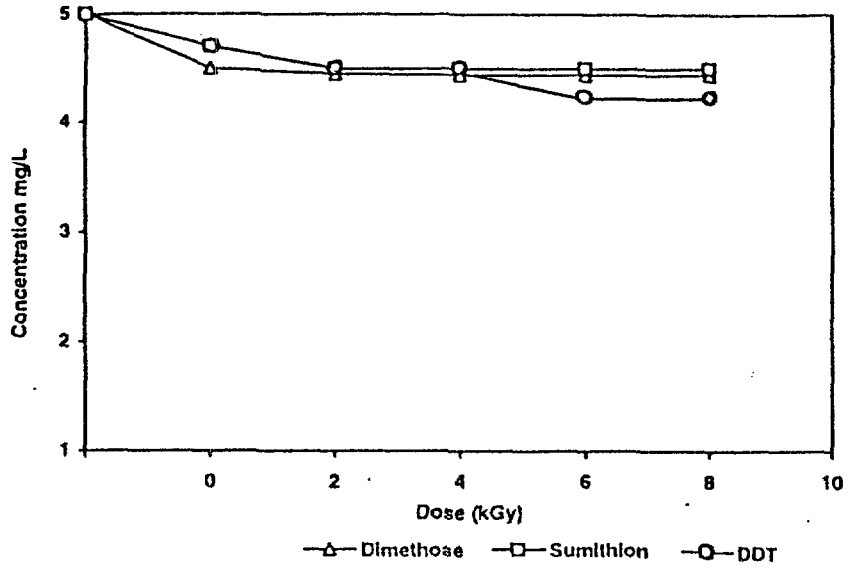


Fig. (1) Relationship Between Gamma Irradiation Doses (kGy) and the Remaining Concentration (mg/l) at Initial Concentration 5 mg/l of DDT, Dimethoate and Sumithion

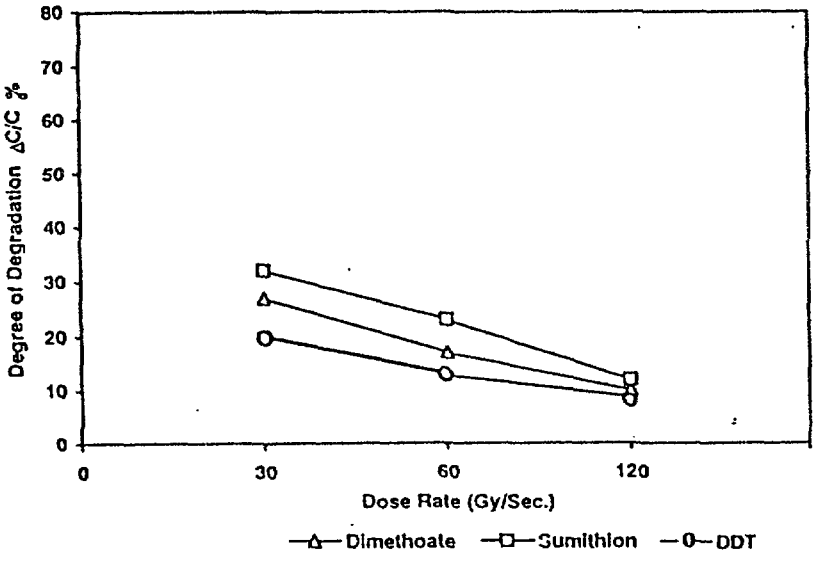


Fig. (2) : Relationship Between Gamma Irradiation Dose Rate (Gy/Sec.) and the Concentration Removal Percentage (%) for DDT, Dimethoate and Sumithion .

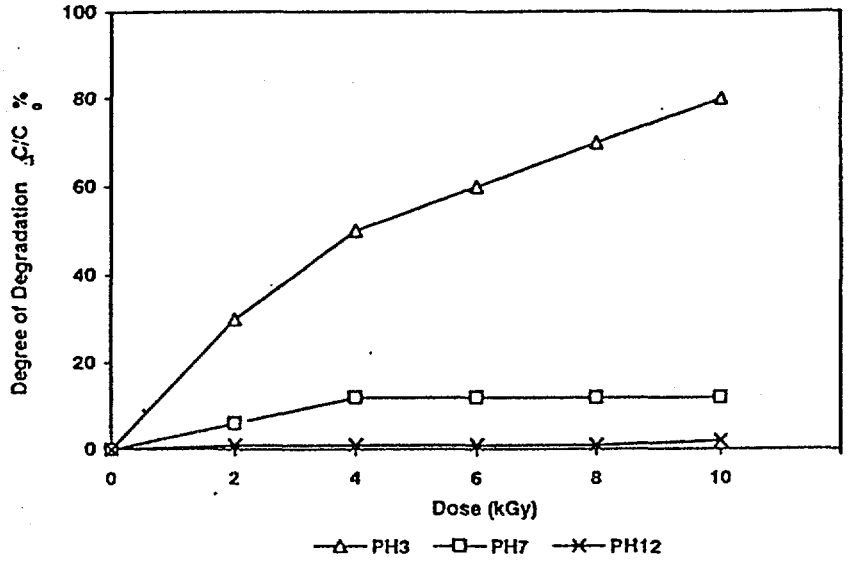


Fig. (3) : Effect of Gamma Irradiation Doses (KGy) on Both The Degree of Degradation Concentration $\Delta C/C_0$ % and The pH Value of DDT.

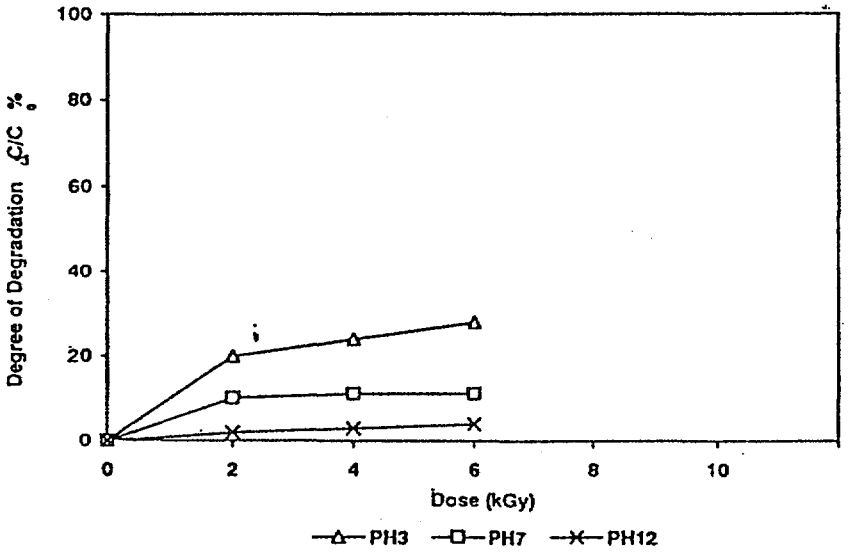


Fig. (4) : Effect of Gamma Irradiation Doses (KGy) on Both The Degree of Degradation Concentration $\Delta C/C_0$ % and The pH Value of Dimethoate.

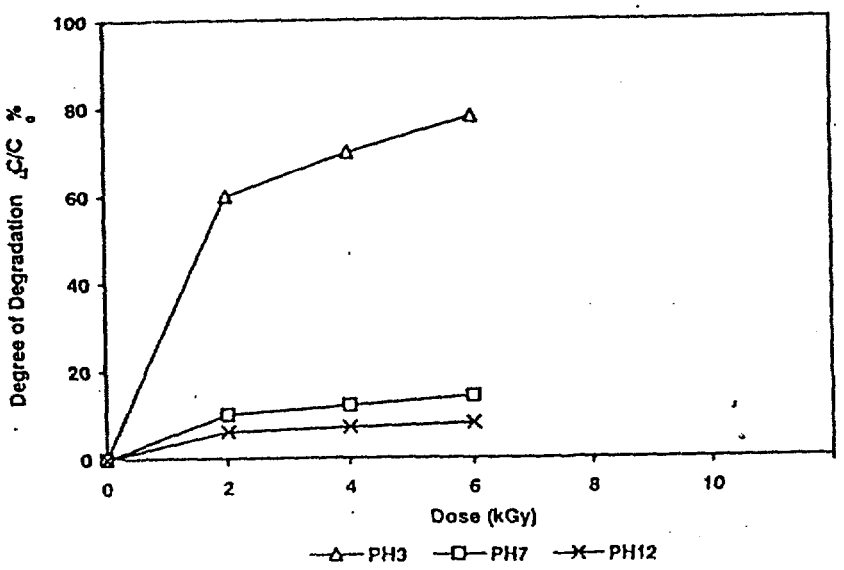


Fig. (5): Effect of Gamma Irradiation Doses (KGy) on Both The Degree of Degradation Concentration Δ C/C_0 % and The pH Value of Sumithion.

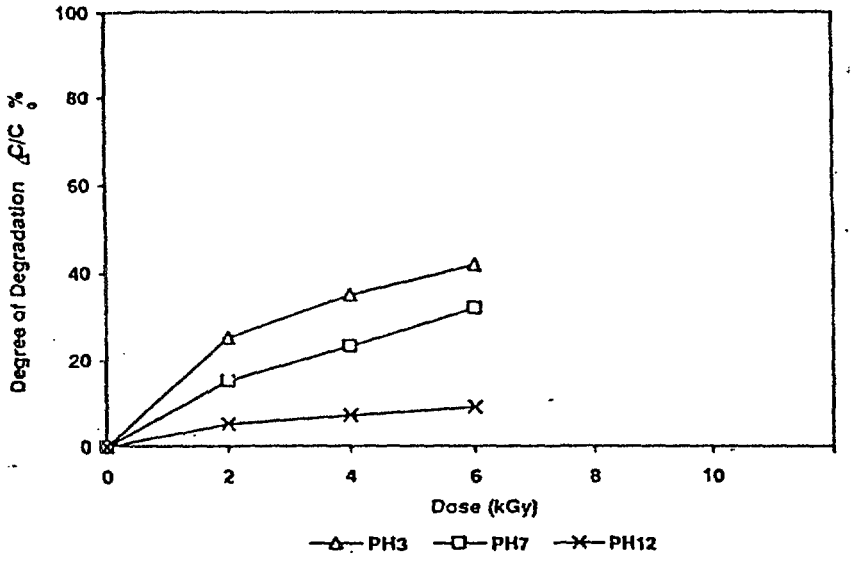


Fig. (6): Synergistic Effect of Gamma Irradiation Coupled With Nitrogen Gas on The Degree of Degradation for DDT.

secondary products formed due to recombination or transformation of the primary species (forming H_2 and H_2O_2) also take a part in the degradation process. In the presence of organic substances reactions occur with the primary species of various types : demolitions , polymerizations, hydroxylations, reductions and in the presence of dissolved oxygen, oxidations caused by HO_2 and O_2 species. One can conclude that the radicals are to be considered as mainly responsible for pesticide degradation, they lead in fact to the formation of organic radicals that are able in turn to react or transform and form either simpler products of a greater molecular complexity at a different oxidation stage. [12,13] These reactions occurring in this system can be amplified by the use of a combined treatment of gamma irradiation and additives such as oxygen and nitrogen.

c) Effect of Additives

Previous attempts by several authors[8-10, 13-16] of wastewater treatment by irradiation, has shown that radiation treatment of large volumes of waste effluents tends to be incomplete and uneconomic. A more promising approach involving irradiation of wastewater arises when a combined treatment of irradiation and a conventional method can be applied to relatively dilute waste solutions. Simultaneous addition of an oxidant such as oxygen coupled with radiation exposure speed up the degradation of the pesticides significantly. Also, the addition of nitrogen to pesticide solutions coupled with radiation treatment was investigated in the present study.

1) Nitrogen Saturated Pesticide Solutions

The synergistic effect of gamma radiation coupled with nitrogen was studied for the pesticide solutions at pH 7 and the results are shown in Figs.(6, 7 and 8). It was observed that more degradation of the pesticides occurred in the presenc of nitrogen than in the case radiation degradation of these pesticides carried out in air. However, the extent of degradation of the different pesticides varied according to the type and structure of the pesticide, so that some of these pesticides are more destroyed in acid and alkaline medium in the presence of N_2 (such as Dimethoate and Aldrin), some pesticides showed more destruction when irradiated in the presence of nitrogen in neutral medium , while others suffered more degradation in acid medium.

2) Oxygen saturated pesticide solutions:

The degree of radiation degradation of the oxygen saturated pesticide solutions was investigated at different pH values as a function of irradiation dose and the results are shown in Figs. (9, 10 and 11). The addition of oxygen resulted in an enhancemenof the radiation degradation of the pesticide solutions. The extent of this degradation was different for the different types of pesticide. As shown in the figures, Dimethoate and Sumithion pesticides solutions suffered the highest degree of degradation due to the presence of oxygen, while DDT showed a moderate enhancement in degradation.This rise in degree of degradation of the pesticides was higher than that caused by the presence of nitrogen which in turn was higher than that of the radiation degradation carried out in air. In most cases the radiation

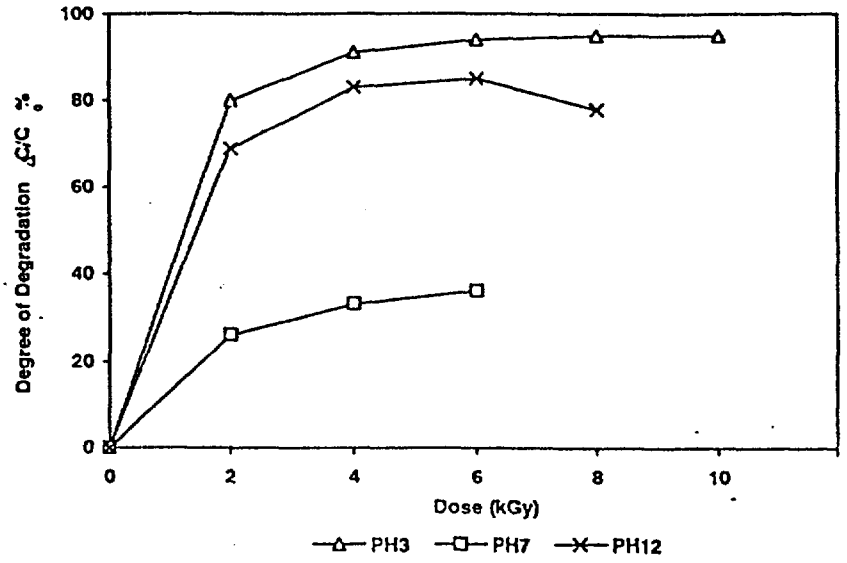


Fig. (7): Synergistic Effect of Gamma Irradiation Coupled With Nitrogen Gas on The Degree of Degradation for Dimethoate.

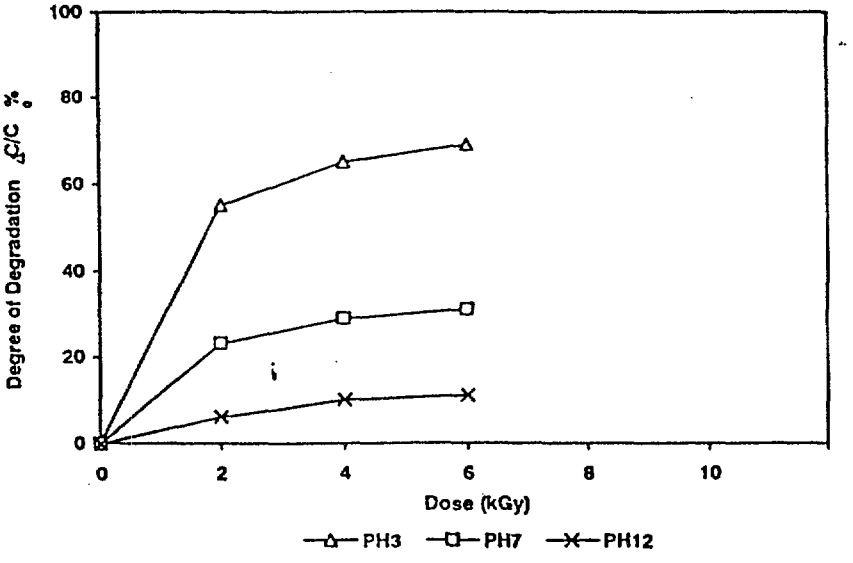


Fig. (8): Synergistic Effect of Gamma Irradiation Coupled With Nitrogen Gas on The Degree of Degradation for Sumithion.

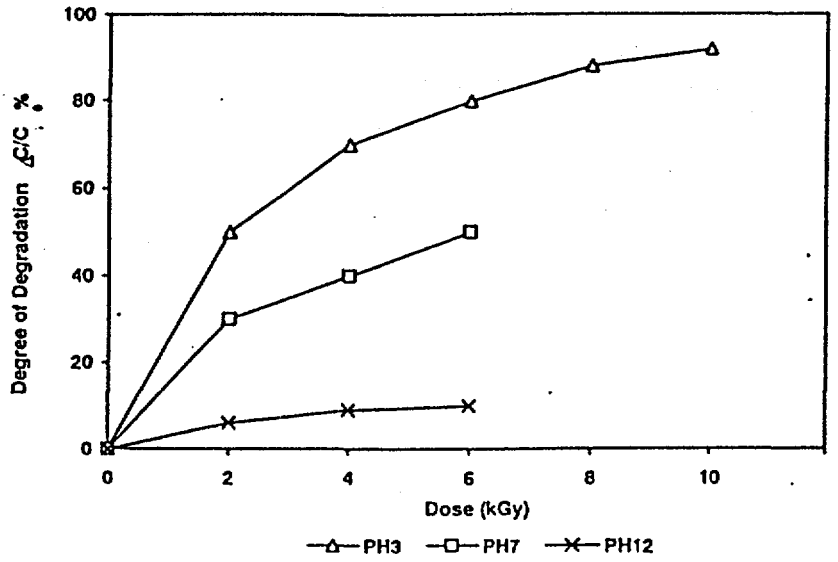


Fig. (9): Synergistic Effect of Gamma Irradiation Coupled With Oxygen Gas on The Degree of Degradation for DDT

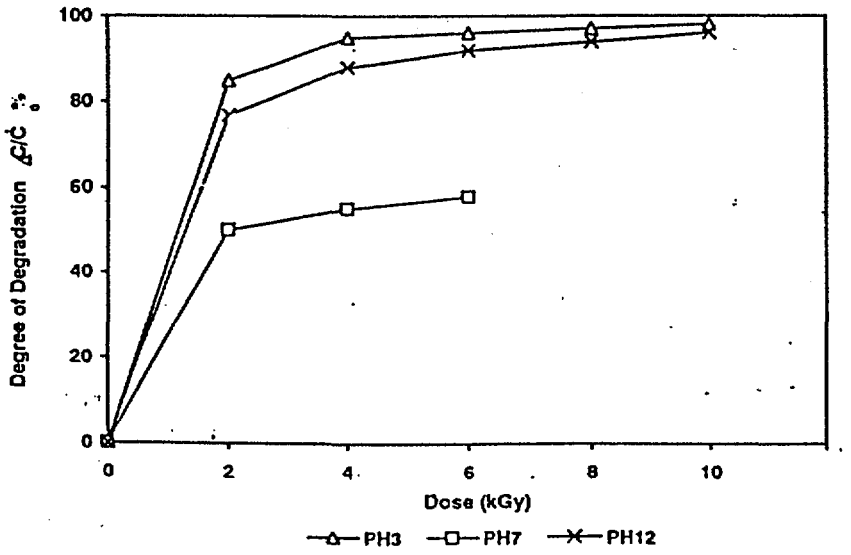


Fig. (10): Synergistic Effect of Gamma Irradiation Coupled With Oxygen Gas on The Degree of Degradation for Dimethoate.

degradation of the pesticides was higher in the acidic medium followed by that in neutral medium and then that carried out in alkaline medium. The irradiation of the pesticide solutions with gamma radiation leads to the formation of radicals and molecular products formed from the radiolysis of water. [11-13] According to **Suzuki et al.**[10, 11] who reported that in addition to the primary OH radicals, these 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. Results in Table 1, show that the pH of the oxygen saturated solutions was lowered steeply at radiation dose 4 kGy in case of DDT and Sumithion and 2 kGy for Dimethoate. These results suggest that the formation of acid is promoted by oxygen.

Adsorption Purification of Surface Water from Pesticides.

The radiation purification process by using gamma radiation minimized the amount of pesticide pollutants in surface water. However, this process was not enough to remove these pollutants to reach the maximum permissible values of these pesticides in surface water. Hence, adsorption purification process by using GAC and some synthetic polymeric ion exchangers was used to improve the process of purification of surface water.

Figures (12, 13 and 14) show the relationship between the adsorption capacity (mg/g) of Granular Activated Carbon (GAC), the strong Anion Exchanger Merck III and the weak Anion Exchanger Merck II for the different pesticides and the equilibrium concentration at pH7. The initial concentration differed for the different pesticides, since the degradation due to γ-radiation (4 kGy) was different for them as shown in Table 3.

The results show some general trends:

a - Granular Activated Carbon (GAC) showed the highest adsorption capacity compared to the other resinous adsorbents. The higher adsorption capacity of GAC than the ion exchanges may be due to the very high surface area of GAC (1100 m^2/g) and the high porous nature which causes internal and external distribution within the carbon particle more than it does in the case of polymeric ion exchange resins.

b -Merck Anion Exchanger II, a weak anion exchanger showed better adsorption capacity than the strong anion exchanger Merck III. A sorbate having strong affinity with the sorbent surface and weak affinity with solvent usually represents a strongly adsorbed species, therefore, the sorbate has a high adsorption capacity. This may be explained that there is a strongly adsorbed species which always has a greater tendency to occupy the adsorption sites than the weakly adsorbed species does. Noll et al.[27] 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[38] who reported that when adsorption forces predominante, the resins do not contain charged or chemically active groups. The main differences between them exist in the specific surface area and the mean pore size, so the adsorption behavior is controlled to a large extent by kinetic forces.

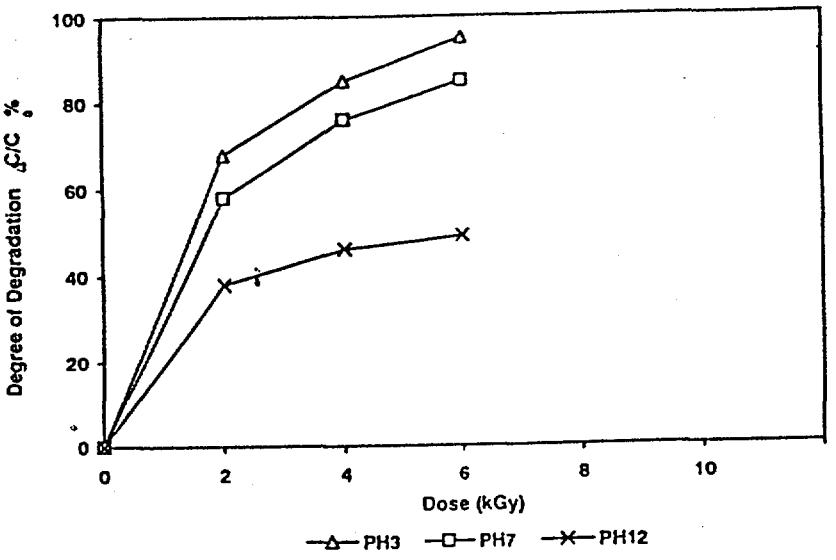


Fig. (11): Synergistic Effect of Gamma Irradiation Coupled With Oxygen Gas on The Degree of Degradation for Sumithion

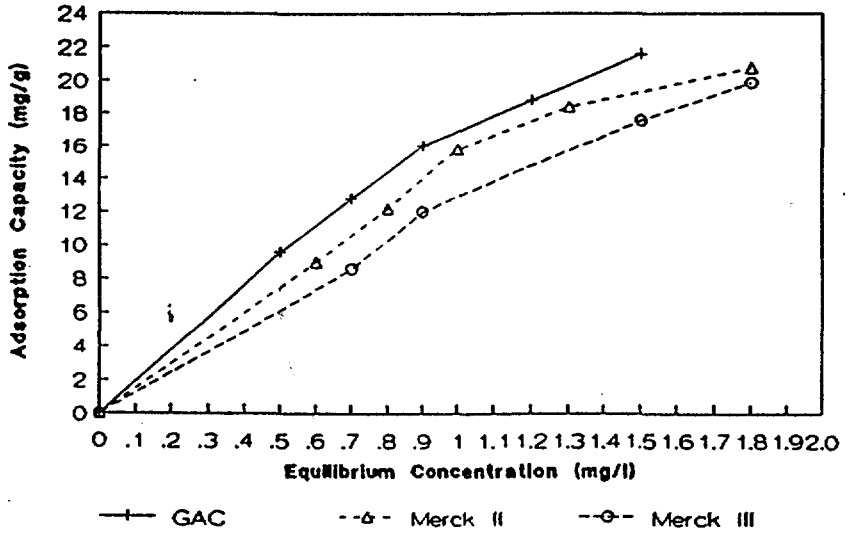
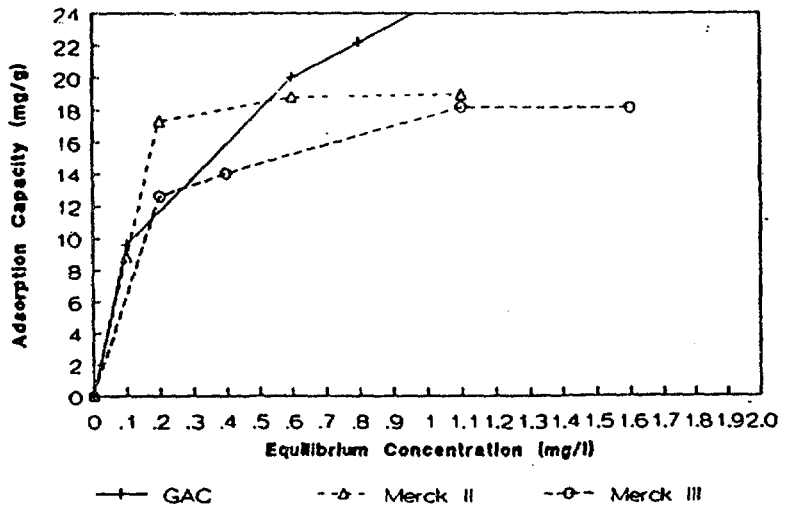


Fig (12): Relationship Between Equilibrium Concentration (mg/l) of DDT Solution and The Adsorption Capacity (mg/g) of GAC, Merck III and Merck II.



Fig(13): Relationship Between Equilibrium Concentration (mg/l) of Dimethoate Solution and The Adsorption Capacity (mg/g) of GAC,Merck III and Merck II.

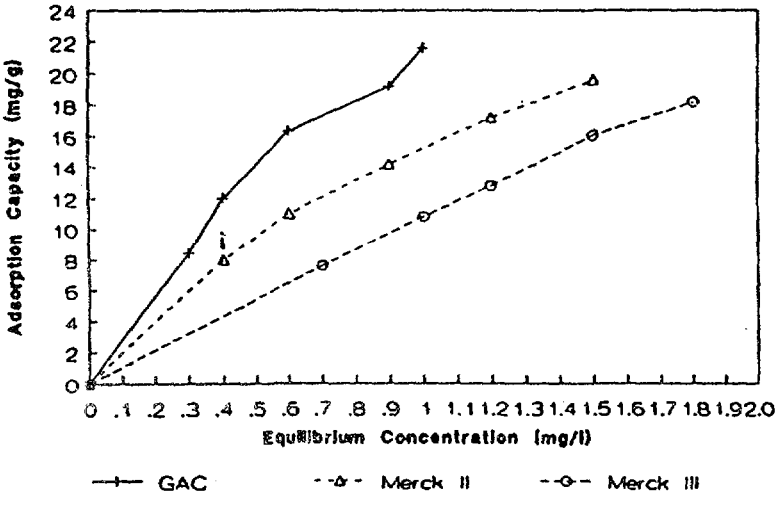
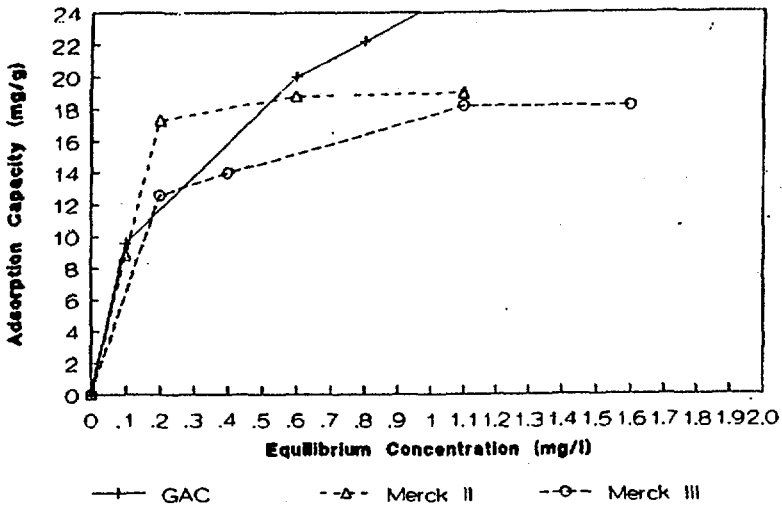


Fig (14): Relationship Between Equilibrium Concentration (mg/l) of Sumithion Solution and The Adsorption Capacity (mg/g) of GAC,Merck III and Merck II.



Fig(13): Relationship Between Equilibrium Concentration (mg/l) of Dimethoate Solution and The Adsorption Capacity (mg/g) of GAC,Merck III and Merck II.

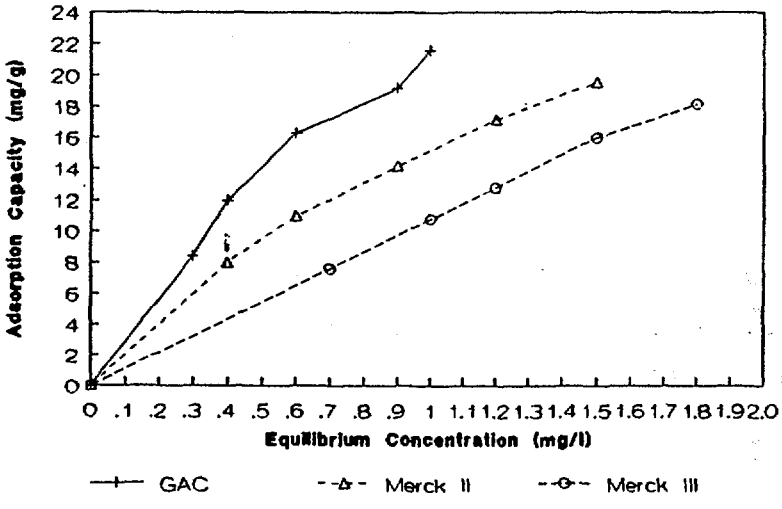


Fig (14): Relationship Between Equilibrium Concentration (mg/l) of Sumithion Solution and The Adsorption Capacity (mg/g) of GAC,Merck III and Merck II.

Table (1) :Change of pH by γ- irradiation in the presence of O_2 and in the presence of N_2

Pesticide	Dose in kGy	pH in presence of O_2	pH in presence of N_2
DDT	0	7.00	7.00
	2	5.70	6.20
	4	5.60	6.00
	6	5.00	5.70
	8	4.70	5.60
	10	4.50	5.40
Dimethoate	0	7.00	7.00
	2	5.35	6.29
	4	4.41	5.65
	6	4.03	5.00
	8	4.40	6.00
	10	4.15	5.10
Sumithion	0	7.00	7.00
	2	4.30	5.50
	4	4.10	5.30
	6	3.80	5.10
	8	3.70	5.00
	10	3.60	4.80

T able (2): Efficiency of combined treatment: γ-irradiation (4 kGy) followed by adsorption on Granular Activcated Carbon.

Pesticide	pH		COD mg O_2/1		BOD mg O_2/1	
	Raw waste water	Treated effluent	Raw waste water	Treated effluent	Raw waste water	Treated effluent
DDT	7.2	6.4	741	22	-	12
Diemthoate	7.2	6.9	98	50	-	5.4
Sumithion	7.1	6.3	757	30	-	18

c-Chlorinated hydrocarbons such as Chlorothalonil showed the best removal percent, followed by Applaud, Aldrin, and finally Ametryn. All the studied pollutants reached maximum permissible value (MPV) after treatment with radiation followed by adsorption.

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD).

Changes of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and pH values of the pesticide solutions as a function of radiation-adsorption processes is tabulated in Table (2). A reduction in COD was observed for all three pesticides studied. In general, it was found that significantly low doses were required for appreciable change in COD (4 kGy). The COD reduction was explained by oxygen addition reactions following reactions of the radiolytic species. The oxidation reactions can only proceed as long as oxygen is available in the solutrion. The tendency of the COD reduction and the change of pH values for all the pesticide solutions was similar to each other.

Table (2) shows the results of Biochemical Oxygen Demand (BOD) which show that the raw wastewater did not show any biological activity due to the existence of these toxic pollutants in high concentration. However, after treating the pesticide solutions with γ-radiation followed by adsorption which resulted in a high reduction in the amount of these toxic pollutants, some biological activities appeared. Accordingly, the biological oxygen demand increased and reached the value of irrigation water. [6, 9] Hay[9] reported that BOD is directly related to the quantity of dissolved oxygen in the wastewater and to the radiation dose.

It may be concluded that a combination of radiation degradation and adsorption process at the end of the treatment sequence may be best way for the complete removal of these organic pollutants.

REFERENCES

1. D.C. Hinge, Experiences In The Continuous Monitoring of River Water Quality, J. Instn. Water Engrs. Sci., 34, 546 (1980).
2. T.H.Y. Tebbutt, "Principles of Water Quality Control", Pergamon Press, New York. (1982).
3. H. Malissa., J. Anal Chem., 1, 49, (1990).
4. K.E.Noll, V. Coumaris and W. S. Hou, "Adsorption Technology for Air and Water Pollution Control," Lewis Publishers Inc. (1992).
5. J. Dojlido and G.A. , "Chemistry of Water And Water Pollution", Ellis Horwood, New York, (1992)..
6. F. Hamoda and M. S. Al-Awadi., The Second Midlle East Conference On Wastewater Management. Cairo, Egypt, 19 (1995).

7. C. Cappadona, P. Guarine and E. Caldearo, Radiation For a Clean Environment Symposium in Munich, Germany, P. 265 (1975).

8. D. M. P. Rohrer, Radiation For a Clean Environment Symposium in Munich, Germany, P. 241 (1975).

9. W.C. Hay, Radiation For a Clean Environment, Proceedings of a Symposium in Munich, Germany, P. 433 (1975).

10. N. Suzuki, T. Nagai, H. Hotta and M. Washino, Bulletin of the Chemical Society of Japan, 48, 2158 (1975).

11. N.Piccinini and F.Ferrero, Int. Atomic Energy Agency, Vienna, 249 (1975).

12. N.B.El-Assy and A.A. Abdel-Fattah, Egyptian J. of Radiat Sci. and Applications, 4, 229 (1986).

13. N. Suzuki, M. Teijiro Akihisa, S. Hashimoto and W. Kawakami, Int. J. Appl. Radiats and Isotopes, 29, 103 (1978)..

14. S. Hashimoto, T.Miyata, N. Suzuki and W. Kawakami, Radiat. Phys. Chem, 13, 107 (1979).

15. M. Washino, Radiat. Phys. Chem, 18, 83 (1981).

16. A.M.Dessouki, S.E.Abdel-Aal, Radiation Technology for Conservation of the environment, IAEA Symposium in Zakopane, Poland, September (1997).

17. S.E. Abdel-Aal, A. M. Dessouki and S. A. Ismail, Arab J. of Nuclear Sciences and Application, 31 (2), 117 (1998).

18. A.M. Dessouki, S.E. Abdel-Aal and S.A. Ismail, 9th Tihany Symposium on Radiation Chemistry, Budapest -Hungary, August (1998).

19. A.J. Swallow, "Radiation Chemistry", Wiley, New York (1973).