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Rad.C-3 "*Degradation of Some Pesticides in Aqueous Solutions by Electron Beam and Gamma Irradiation*"

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ABSTRACT

Decomposition of two pesticides as active ingredient (Lannate and Fenvalarate) present in aqueous solution by ionizing radiations has been studied on laboratory - scale experiments. The effect of pH of the solution, the concentration of the pesticide and the irradiation dose on the degradation process was investigated carried out alone and in combination with other additives such as nitrogen, oxygen and ozone. A synergistic effect was detected which enhanced the degradation process remarkably. Lannate showed more degradation than Fenvalarte under conditions investigated. Radiation alone was not enough to achieve the complete decomposition of the pesticides. Adsorption of the undegraded pollutants was achieved using Granular Activated Carbon (GAC) and two anion exchangers (Dowex 1-X8 and Lewatit AP246). It may be concluded that irradiation followed by adsorption resulted in the removal of these organic pollutants from wastewater.

Key Words: *Pesticides, Gamma and EB - Irradiation - Decomposition - Adsorption.*

INTRODUCTION

Treatment of pesticide in 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 [1-5]. Ionizing radiation proved to be more effective for the treatment of these wastewaters than ordinary conventional methods. Some studies dealing with the use of gamma radiation in the

treatment of wastewaters have shown that the most considerable effect, that is the effective degradation of the pesticides molecules by the primary products formed during the radiolysis of water, is accompanied by the oxidation of a part of the organic substances and is a function of both pH and oxygen concentration in the solution.

In the present study, an attempt was made to explain the degradation kinetics due to the irradiation of aqueous solutions of some active ingredient pesticides, in the absence of other specific pollutants of the pesticide industry. A combined treatment by gamma radiation and conventional methods were applied which is more effective than either alone. Factors affecting the radiolysis of the pesticide such as the pesticide concentration, irradiation dose, dose rate, and pH of the solutions will be studied. The effect of different additives such as nitrogen and oxygen on the degradation process will be investigated. Also, the equilibrium isotherms and the intraparticle diffusivities will be investigated using the bath experiments for determining the adsorption of aqueous solutions of pesticides by the Granulated Activated Carbon (GAC) and two types of the ion exchange resins.

EXPERIMENTAL

Materials :

Two pesticides were used in the present study : Lannate (thiourea) and Fenvalerate (benzeneacetate). Three adsorbent materials were used in the adsorption studies, one of these was Granular activated carbon (GAC), one strong anion exchange resin Dowex 1-X8, and a weak anion exchange lewatit AP 246. All chemicals used were reagent grade and were used for the preparation of pesticides solutions without any contaminations. The solubility of pesticides is 0.4 and 0.001 g/L in water.

a) Pesticides

1. Thiourea insecticide

Lannate ($C_5H_{10}N_2O_2S$), was supplied by e.I. dupont de nemours & Co. (Inc.) It is a white crystalline solid with a melting point 78-79 ^{0}C

2. benzene acetate insecticide

Fenvalerate ($C_{25}H_{22}ClNO_2$), was supplied by shell international chemical Co. It is a viscous yellow liquid with a boiling point 300 /37 mm Hg.

Ion exchange resins

Weak anion exchanger lewatit AP 246 were supplied by Merck Laboratories, Germany. It is a polystrol drevatives with anchored quaternary ammonium group, mesh 0.1 - 0.25 mm. Strong anion exchanger Dowex 1-X8 was supplied by Dow Chemical Company. It is a polystyrene drevatives, ionic form , mesh 20-50 mm and the exchange capacity 1.4 m Eq/ml.

Granular Activated Carbon (GAC).

Untreated charcool activated granular, it is commercial synthesized, it has 8-20 mesh. It was supplied from ALEC company, Egypt.

Adsorption isotherm were determined by the batch method or bottle point method for all adsorbents. Carefully determined amounts of adsorbent equal to 0.25 g were added to 100 mL beaker containing 25 mL of the irradiated solution of concentrations of 3, 4, 5, 6, 7 mg L^{-1} before irradiation, respectively. The beaker were sealed by an aluminium foil paper, stirred mechanically and then kept for a period of 8 days at room temperature (25 ^{0}C). The concentration of the solution was then determined, the equilibrium data for each beaker representing one point on the adsorption isotherm.

Results and Discussion

Irradiation of pesticides

a. Irradiation dose, and dose rate:

The effect of irradiation dose in kGy on the different pesticide solutions at an initial concentration 5 mg L^{-1} was studied at different pH values and the results are shown in Fig. 1. It can be seen that the radiation degradation of Lannate is much higher (80%) than the degradation of Fenvalerate. This may be due to the presence of three benzene rings in the case of Fenualerate, while Lannate is an aliphatic compound. It is well known that compounds with benzene rings show more radiatrion resistance, while aliphatic compounds are very sensitive to ionizing radiations [6-10]. It was also observed that more degradation happened at pH3 than the neutral medium, while the less degradation was observed in the alkaline medium for all conditions studied, (Fig. 1). The dose rate effect was also studied for three different dose rates to ellucidate its effect on the degradation process (6.8, 3.4 and 1.7 Gy/sec. - total dose 4 kGy),

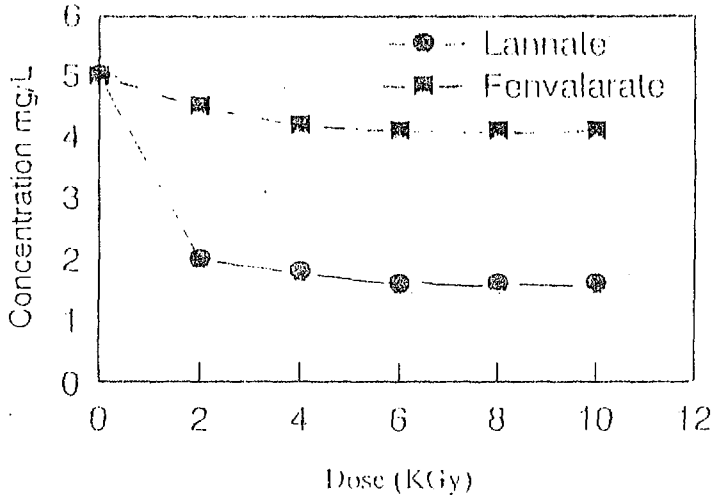


Fig (1): Relation between gamma Irradiation Dose (KGy) and remaning concentration (mg/L) for Lannate and fenvalarate

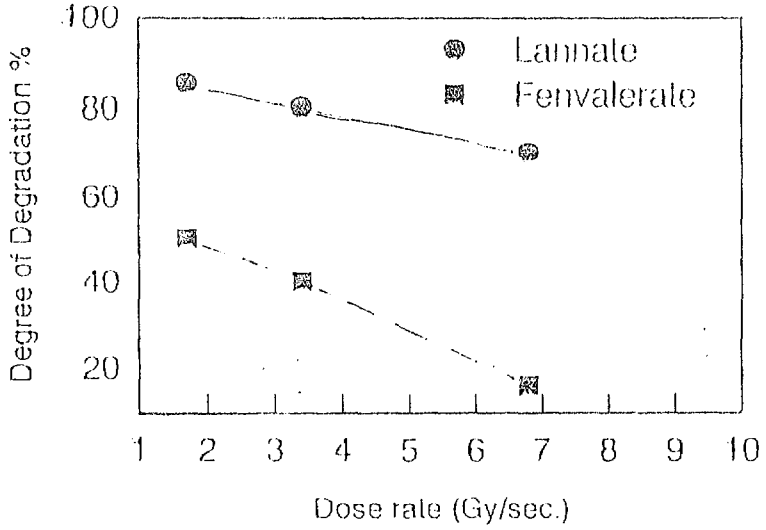


Fig (2) : Relationship Between Gamma Irradiation Dose Rate (Gy/sec.) and the Degree of Degradation(%) for Lannate and Fenvalarate at Initial Concentration 5 mg/L.

(Fig.2). A general trend for the degradation of the two pesticides showing the highest degradation occurring for the lowest dose rate. This behavior may be attributed to biomolecular radical termination which leads to a major oxidation reaction . Suzuki et al. and other authers observed the same behaviour. [11,16]

b. Effect of pH

Figure 3. shows the effect of the pesticide solution pH on the percent degradation at constant concentration 5 mg L^{-1} as a function of irradiation dose. The pH influence has proved to vary according to the type of the pesticide. For the two pesticides very little degradation was observed in the alkaline medium (pH9) at all irradiation dose. The degree of degradation of pesticides in the neutral medium (pH7) was dependent on the type of pesticide and its chemical structure. However, the percent degradation in the acidic 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 shightly after irradiation, while in the neutral medium the change in the 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 pesticide solutions may be attributed to the mechanism of the radiation degradation process taking place in the studied system in which acids were detected as degradation products of the pesticide molecules to lower molecular weight compounds (such as acids) . [6, 8, 11]

c. Synergistic effects

1. Nitrogen addition

Many previous studies by many authors [17-20] of wastewater treatment by irradiation has shown that radiation treatment of larger volumes of waste effluents tends to be incomplete and uneconomic. A more promising approach involving radiation treatment of wastewater arises when a combined treatment of irradiation and a conventional method can be applied to relatively dilute waste solutions.

For two pesticides, no complete destruction was achieved by irradiation alone. A synergistic effect of gamma radiation coupled with nitrogen was studied for the two pesticides at different pH values and the results are shown in Fig. 4. It was observed that higher degradation of the pesticides occurred in the presence of nitrogen than in the case of radiation

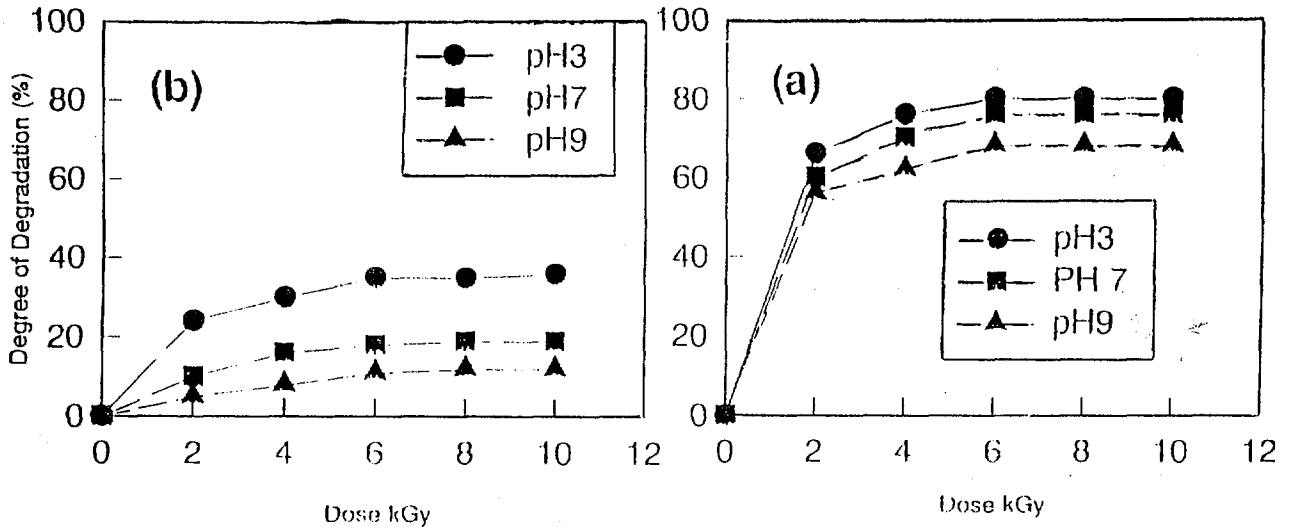


Fig. (3): Effect of irradiation dose on the degree of degradation at various pH values for Lannate(a) and Fenvalarate(b)

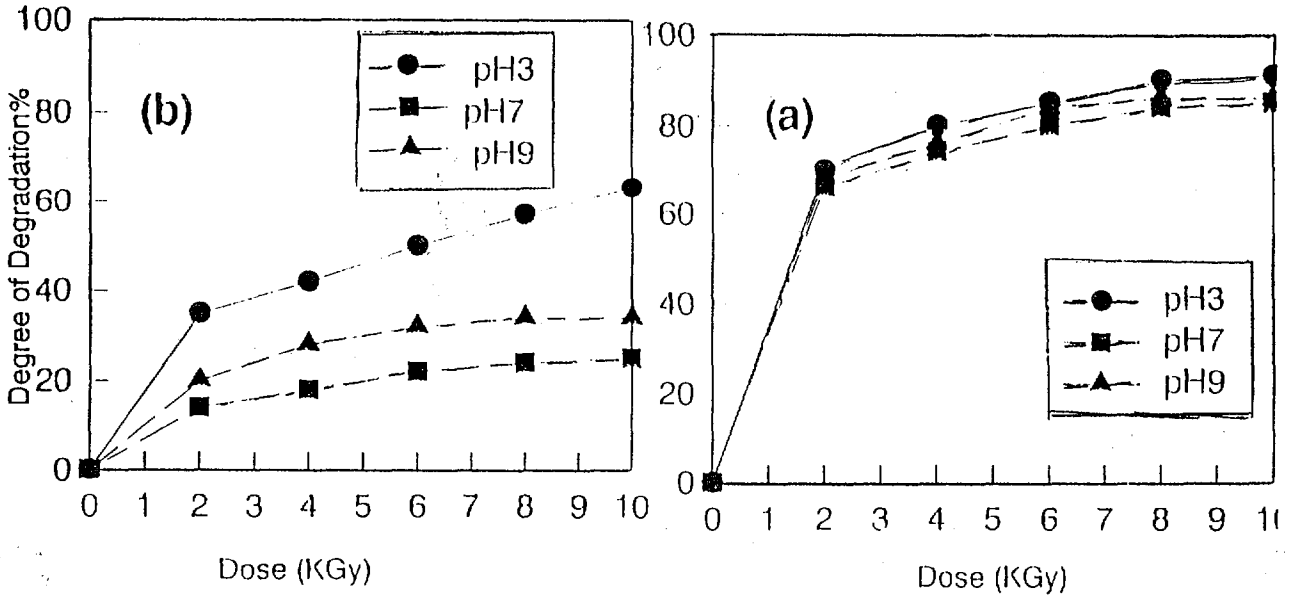


Fig (4) : Synergistic Effect of Gamma Irradiation Coupled with Nitrogen Gas on the Degree of Degradation for Lannate(a) and Fenvalerate (b) at different pH values.

degradation of these pesticides that carried out in air. However, the extent of degradation of the different pesticides varied according to the type and structure of the pesticide. This degradation effect may be attributed to oxygen and oxidizing species formed by the reaction of OH radicals with hydrogen peroxide accumulated during irradiation. [11]

$$H_2O_2 + {}^{\bullet}OH \text{ -----> } HO^{\bullet}_2 + H_2O \quad (1)$$

$$H_2O_2 + HO^{\bullet}_2 \text{ -----> } OH + H_2O + O_2 \quad (2)$$

$$HO^{\bullet}_2 + HO^{\bullet}_2 \text{ -----> } H_2O_2 + O_2 \quad (3)$$

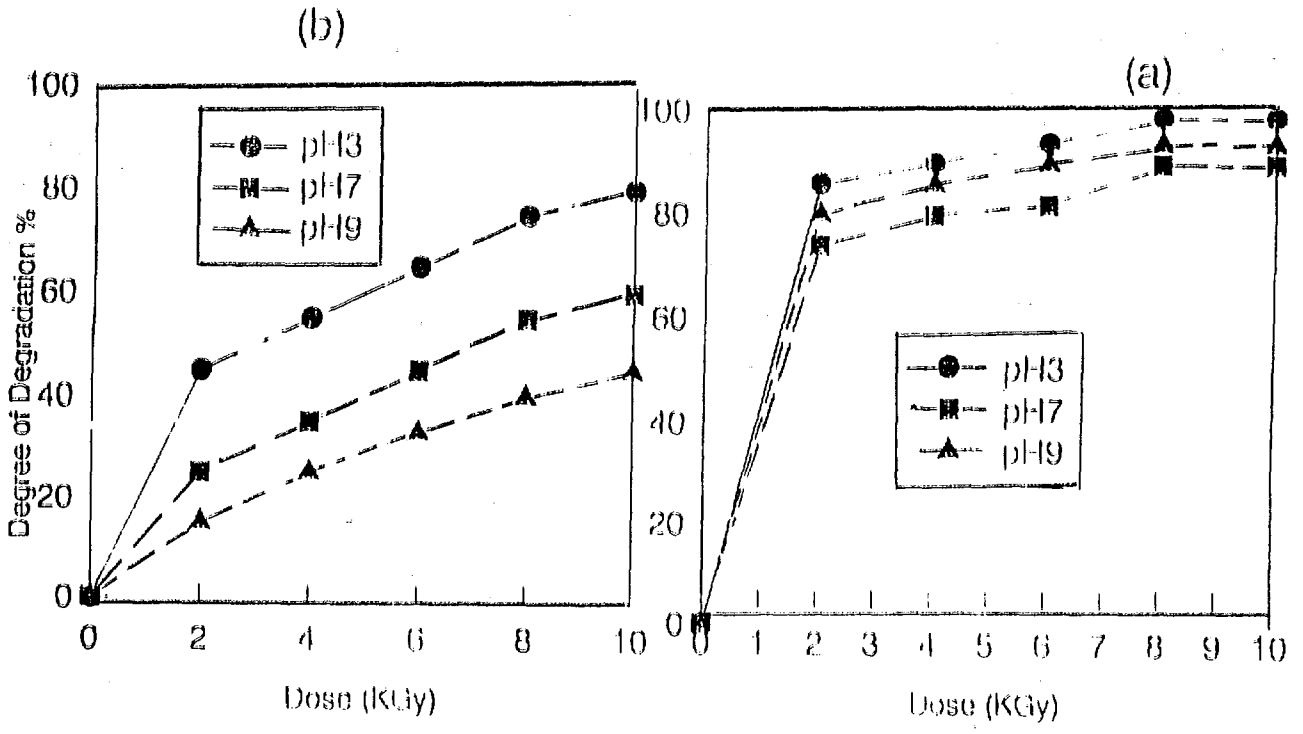
$$^{\bullet}OH + HO^{\bullet}_2 \text{ -----> } H_2O + O_2 \quad (4)$$

as well as the small amount of dissolved oxygen (about 5 X 10^{-4} g/L) that cannot be removed with nitrogen bubbling. [21]

b . Oxygen addition

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 result are shown in Fig. (5). The addition of oxygen resulted in an enhancement of the radiation degradation of the pesticide solutions. The extent of this degradation was a different for the two pesticides. Lannate pesticide solution suffered the highest degree of degradation due to the presence of oxygen, while Fenvalerate showed a moderate enhancement in degradation. In the two cases radiation degradation of the pesticides was higher in the acidic medium followed by that in neutral medium and the degradaion carried out in alkaline medium proceeded in the least degree.

The irradiation of the pesticide solutions with gamma radiation leads to the formation of radicals and molecular products formed from the radiolysis of water. According to Suzuki et al. [18,19] 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. It is well known that the oxidation of aromatic compounds induced by ionizing radiations gives some lower molecular weight aliphatic products as aldehydes and organic acids and then proceeds the further oxidation of the organic acids. The radiation initiation oxidation of organic compounds was reported by Hoigne [20], who showed that the reaction of hydroxyl radicals with solutes as



Figo (5): Synergistic Effect of Gamma Irradiation Coupled with Oxygen Gas on the Degree of degradation for Lannate (a) and Fenvalerate (b) at different pH values.

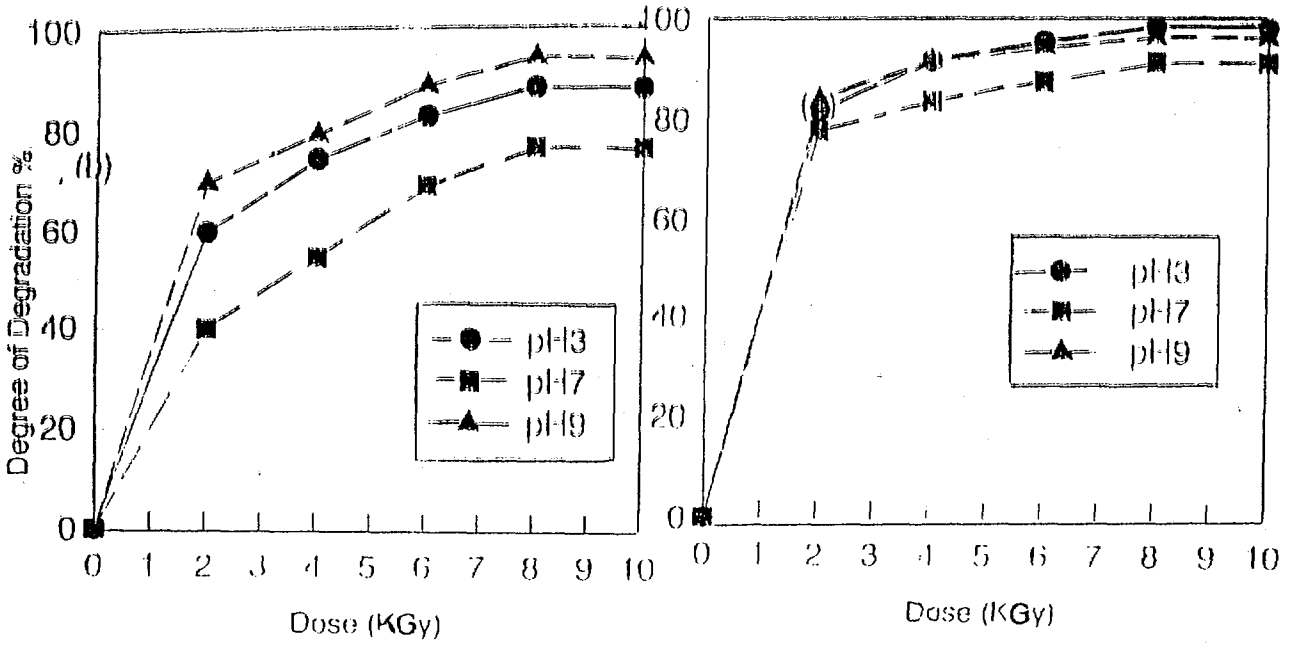


Fig (6): Synergistic Effect of Gamma Irradiation Coupled with Ozone Gas on the Degree of Degradation for Lannate (a) and Fenvalerate (b) at Different pH values.

well as the secondary oxygen addition to radicals lead to oxidized products. The yields achieved by hydroxylation were calculated from the amount of OH radicals formed. This hydroxylation lower the Chemical Oxygen Demand (COD) values of wastewater, by 43 mg/L^{-1} per Mrad [17].

3. Ozonolysis

The ozone saturated pesticide solution were also studied and the results are shown in Fig. (6). The addition of ozone resulted in an enhancement of the radiation degradation of the pesticide solutions. The extent of the degradation depends on the type and structure of the pesticide. It is well known that ozone is a powerful oxidant and it can react with organic and inorganic molecules in solution both directaly and indirectly via its aqueous phase degradation products such as the hydroperoxyl and hydroxyl radicals.[22 23] Thus, in the presence of water in either the gas or aqueous phase, ozone will photolyze to produce hydroxyl radicals, which are stronger oxidizing agent. Therefore, the combined ozone/gamm process greatly enhances the degradation of organic compound more than ozone process alone. From the above results, it can be concluded that the degree of degradation is in the following order

O_3 > O_2 > N_2 > air.

4. Electron Beam Irradiation

Industrial effluents containing pesticides at initial concentration of 5 mg/L and different pH values were irradiated using an electron beam 1 Mev to study the compounds degradation. The samples were irradiated with different doses ranging between 2 and 10 kGy. Electron beam irradiation treatment efficiency was evaluated by U.V. measurement of the samples before and after irradiation. Fig. (7) shows the relationship between the electron beam irradiation dose the degree of degradation of two pesticides at various pH values. It can be seen that at a dose of 4 kGy the pesticide lannate reached a maximum degradation of 86% which is a little higher than when irradiation was carried out with gamma- rays. However, electron beam irradiation proved to be much effective than gamma irradiation in case of Fenvalerate. The degree of degradation using gamma rays was 35 % and by using electron beam machine it rose to 80% at pH3. The efficiency of electron beam irradiation is obviously much greater than the degradation of gamm-irradiation may be explained by the high effective

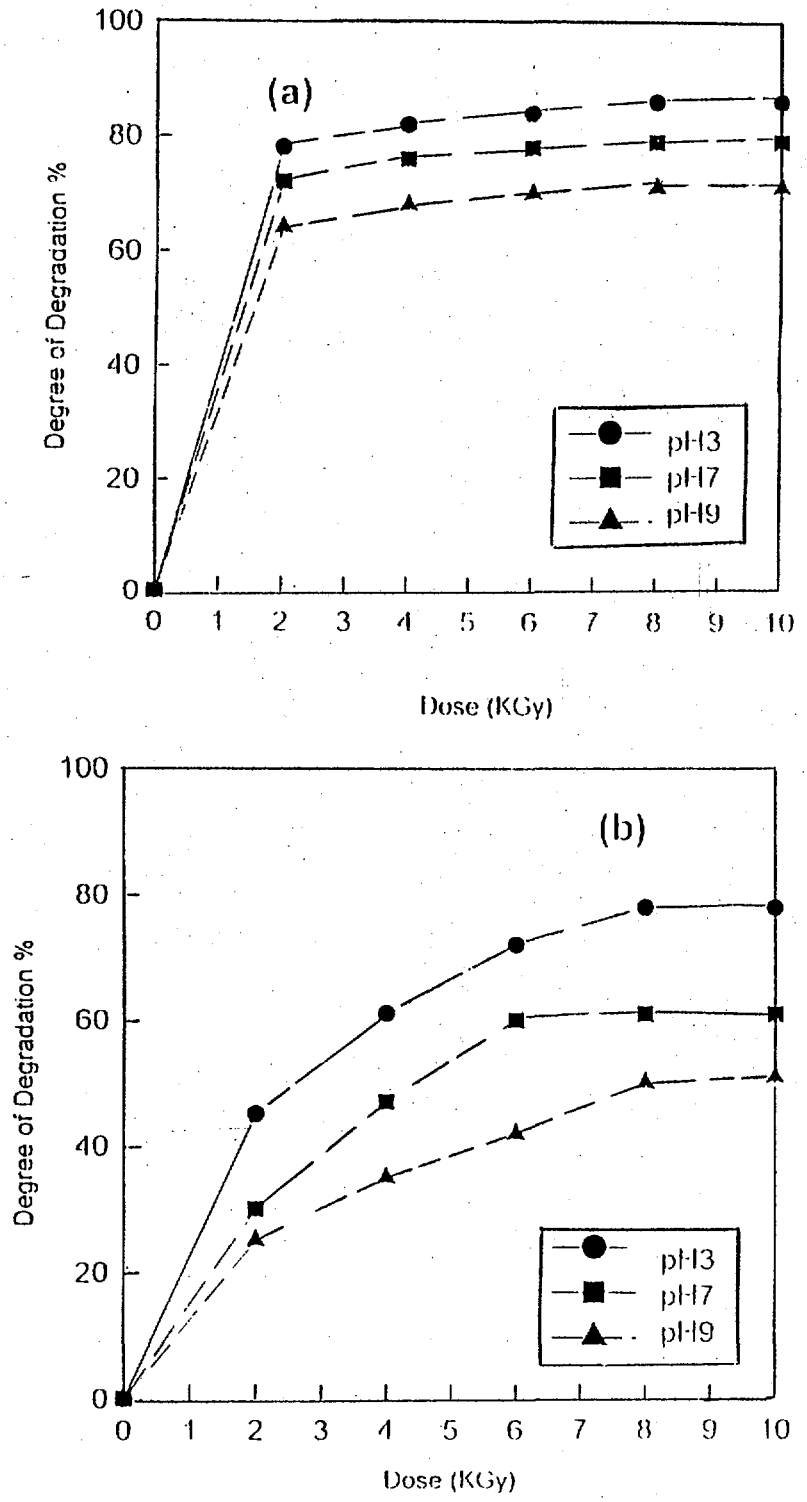


Fig (7): Effect of Electron Beam Irradiation Dose on both the Degree of Degradation % and the pH value of Lannate (a) and Fenvalarate (b).

energy of the electron beam accelerator adsorbed by the pesticides in a very short time compared with the energy and time of gamma irradiation.[24,25,26]

Radiation Adsorption Purification

Adsorption experiments were carried out with three different adsorbents (GAC, Dowex, Lewatit) and at different pH values to study the adsorption behaviour of two pesticides. Moderate adsorption was observed in both cases (46%) and (52%) respectively. It seems that adsorption also is not enough alone to achieve the complete removal of these toxic pollutants. Therefore, radiation adsorption purification was tested in Fig. (8 and 9), shows the relationship between the equilibrium conc. mg/L of the pesticide solutions and the adsorption capacity mg/g for the three adsorbents.

The following general trends have been observed:

1. Granular Activated Carbon (GAC) showed the highest adsorption capacity in comparison with the other resinous adsorbents. The higher adsorption capacity of GAC than that of the ion exchangers may be due to the very high surface area of GAC (1100 $m^2 g^{-1}$).
2. Lewatit, a weak anion exchanger showed better adsorption capacity than the strong anion exchanger Dowex 1-X8. This may be explained by the fact that there exists a strong adsorbed species which always has a greater tendency to occupy the adsorption sties than the weakly adsorbed species does. Noll et al. [27] reported a similar explanation in their work with the system phenol + p-chlorophenol or the XAD-4 resin and phenol + p-chlorophenol on carbon F-400. A further explanation was given by Malissa [28] who reported that when adsorption forces predominate, the resined 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 behaviour is controlled to a large extant by kinetic ferces.
3. All the studied pollutants reached maximum permissible values after treatment with radiation followed by adsorption.

Although, the role of the adsorbent is very essential to the adsorption process, the physico-chemical characteristics of the adsorbate plays also an important role in this process. For example, pesticides of similar chemical structure and solubility show the same adsorption behaviour.

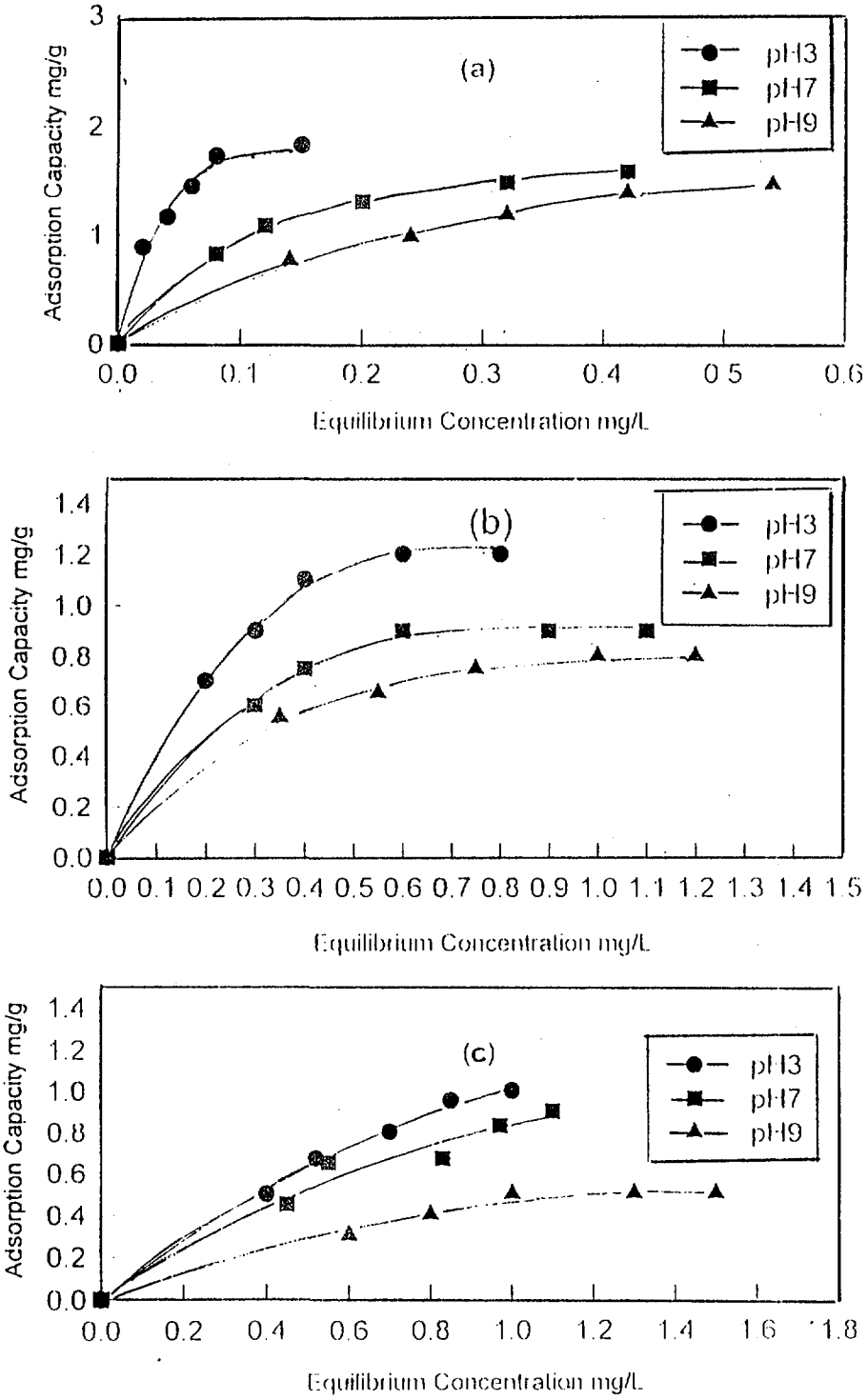


Fig.(8): Relationship Between Equilibrium Concentration (mg/L) of Lannate Solutions and the Adsorption Capacity (mg/g) of GAC (a) , Lewatit (b) and Dowex (c) at different pH Values.

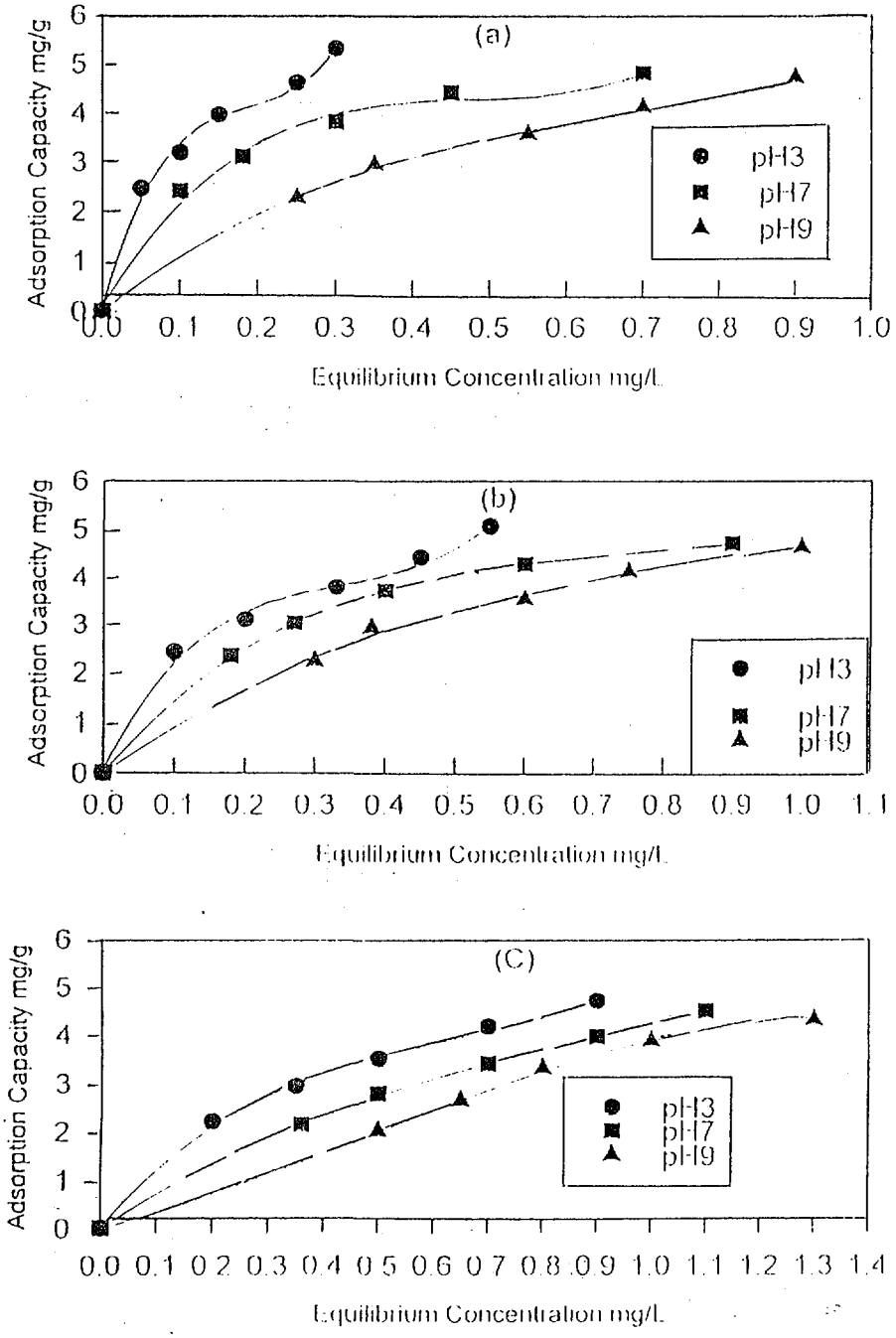


Fig.(9): Relationship Between Equiplibrium Concentration (mg/L) of Fenvalerate Solutions and the Adsorption Capacity (mg/g) of GAC (a), Lewatit (b) and Dowex(c) at Different pH Values.

For example, pesticides of similar chemical structure and solubility show the same adsorption behaviour.

Some studies dealing with the use of the combination of gamma irradiation and adsorption in the treatment of wastewater containing pesticides and other pollutant have shown that the degradation is accompained by the oxidation of part of the organic substances and is a function both of pH and oxygen concentration of the solution. It may be concluded that the radiation degradation of toxic pesticide pollutants and their removal from wastewater down to concentration not exceeding the maximum permissible concentration, MPC, according to the international standards proved to be better than the conventional methods of purification alone.

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