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Radiation-Adsorption Purification of bisolute containing pesticide and dye

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Abstract

Investigations considering the removal of pesticides and dyes separately or in their mixtures, were studied. Adsorption of the remaining part of the undegraded pollutants is carried out using granular activated carbon (GAC) and acrylamide (AAm) graft copolymer onto polyvinylalcohol (PVA).Freundlich model is used to predict the equilibrium uptake of pesticide and dye in binary and single solutions.Preliminary results show that the method of radiation combined with adsorption using GAC was effective than that of a graft copolymer. Radiation- induced decomposition of various organic materials such as pesticide (Atrazine) and dye (Cresol Red) in water represents a new and very efficient possibility for elimination of the steadily increasing pollution.

Key words: radiation-adsorption-grafting-wastewater

Introduction

As a result of strong development of various industries and the rapid growth of world population, a rather heavy overloading of water resources is observed. In addition to this, the usage of various pesticides and other chemicals contributes to contamination of ground water. The killing of microorganisms in drinking water containing humic compounds by chlorination leads to the formation of various

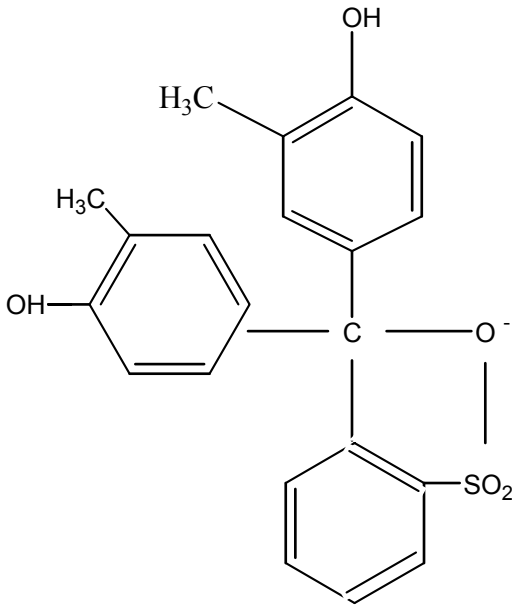
halogenated hydrocarbons[1] . Such substances are carcinogenic and are usually removed by filtration through activated charcoal which are subsequently burned up. The resulting chlorine oxides contribute to the occurrence of acid rain. Due to the above mentioned pollution sources,environmental and toxicological effects have increased considerably [2-5]. This is also reflected in the health of the population in industrial areas. Ionizing radiation (gamma, electrons , X-rays) is nowadays a very efficient tool for decomposition of organics in wastewater of various origin. Several thousands of cubic meters wastewater can be treated daily by means of an appropriate electron – accelerator[6]. In some cases the combination of a conventional water treatment (ozonation, adsorption,…etc) with the irradiation process could be very efficient, since non-degradable organics can be removed [7-10]. The present study is divided into three main parts :(1) radiation degradation of both pesticide and dye separately and in their mixture. (2) Adsorption purification of the undegraded pollutants using GAC and PVA-g_AAm.

2- Experimental

2.1 Materials

One) Pesticide: Atrazine (Herbicide) M.wt: 215.7, M.f $C_8H_{14}ClN_5$. It was supplied Crystal du pont ; Makhteshim,Agan ; Novartis, Oxon Italia. It is colourless powder. M.P 175.8 ^{0}C, B.p 205 ^{0}C. its solubility in water 33mg/l, in ethyl acetate 24,acetone 31,n-octanol 8.7(all in mg/l, 25 ^{0}C)

Two) Dye: Cresol red.M.wt 382.44 g/mol. It was supplied by s.d.fine-Chem LTD. It is a red yellow powder (pH indicator)



Cresol Red

Three) GAC : It was supplied by Chemqiet Company, Alexandria, Egypt.

Four) Acrylamide: it was supplied by Winlab.U.K, Polyvinylalcohol , was supplied by Hayshi pure chemical Industrial LTD. Japan.

2.2 –Preparation of hydrogel.

4% of PVA was mixed with 6% of AAm under vigorous stirring, the mixture was exposed to a dose 1.5m.rad using electron beam accelerator, then it was dried at room temperature.

2.3 FTIR: Infrared spectra of samples were obtained by FTIR spectrometer (ATI Mattson, Genesis series) USA.

3- Irradiation sources

Gamma-ray source: Gamma irradiation was carried out using ^{60}Co γ-ray source (gamma chamber 4000 A,India) with a cylindrical irradiation chamber, at ambient temperature (about 45 ^{0}C in the chamber) .

Electron beam accelerator (EB): The EB accelerator is obtained from high voltage Company,USA. It is a direct accelerator with energy of 1.5 M eV, beam current of 25 mA,power of 37.5 kW and variable scan width up to 90 cm.

4- **HPLc**: HPLc with constrametric 3200 series fluid metric pump provided from thermo electron company Florida (U.S.A) , connected to linear U.V visible absorbance detector. Flow rate 0.3 ml/min , wavelength 230.Mobile phase 40% water, 60% acetonitrile . Column.ODS-25U, 150 mmx 4.6m,provided from Alltech-Waukegan road.Deerfield, U.S.A.

U.V Spectrophotometry: The concentration of dye solutions was determined by measuring the absorbance at wavelength 437nm .Optical density measurments were carried out against blank of the individual solvent at room temperature (25 ^{0}C). A double- beam U.V. Visible spectrophotometer, Unicam U.V./ Vis spectrometer (UV2), United Kingdom, was used.

Adsorption study:- The adsorption isotherm was determined by immersing a given mass of adsorbents, (hydrogel and GAC) (1g) in a series of different dye and pesticide solutions before and after radiation without pH adjustment . The adsorbents (GAC and hydrogel) and the dye and pesticide solutions (100ml) of initial concentration C_0 were placed in a 150 ml beaker for 2 days at room temperature.C_e (mg/l) of dyes was measured by U.V Visible spectrophotometer at wavelength 437nm and for pesticide

by HPLc at wavelength 230nm.The amount of adsorption at equilibrium q_e (mg/g) was obtained as follows:-

$$q_e = (C_0 - C_e)\, V / W \quad \ldots\ldots (1)$$

where, C_0 and C_e are the initial and equilibrium liquid- phase concentration, respectively (mg/l) , V is the volume of the solution (l) and w is the weight of adsorbent sample (g).

Freundlich isotherm: The experimental values of the isotherm were used in the linear form of Freundlich equation, which is expressed by the following relation ;

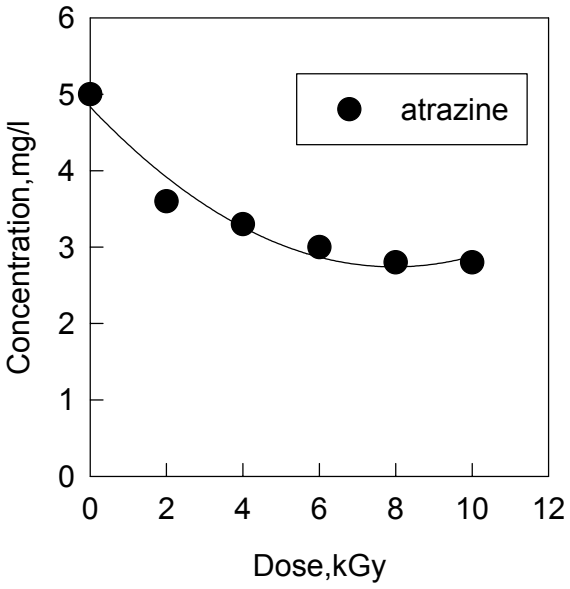
$$\text{Log } x = \log K_f + 1/n \log C_e \quad \ldots\ldots (2)$$

Where, x is the amount of adsorbate adsorbed per unit weight of adsorbent (GAC and hydrogel) at equilibrium concentration (mg/g) ,K_f ,n are empirical constants representing the adsorption capacity (mg/g) and adsorption intensity , respectively.

Results and Discussion

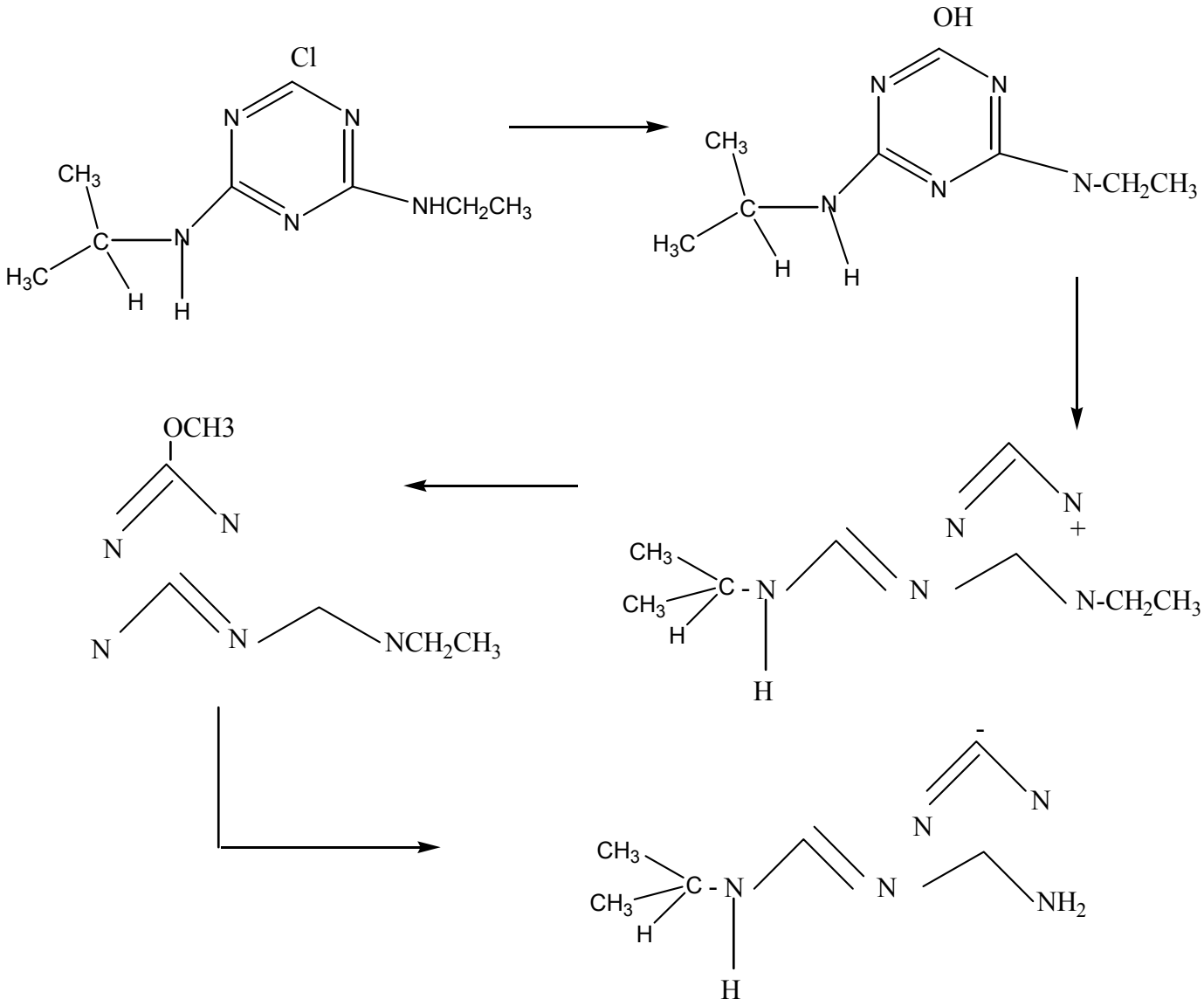
Radiation degradation of the pesticide in air- saturated solution , 5 mg/l of atrazine as active ingredient was irradiated at different radiation doses using ^{60}Co at pH 7. Fig (1) shows that the degree of degradation of atrazine is in the range from (28-44 %) with respect to the exposed dose. The decomposition process is based on the attack by the primary water radiolytic products. The irradiation of water results in the formation of electronically excited states, free radicals and ions along the path (spur) of the incident particle. The reactive species produced by irradiation may then diffuse away from the spur, or undergo geminate recombination to react their product species. Those that escape recombination may react with solutes, including pollutants present

in the water[11]. In oxygenated aqueous solutions the organic substances in the most cases will be primarily attacked by OH and HO_2(or O^-_2), as well as the primary radicals (OH,H, e^-_{aq} or HO_2) are mainly adding to organic molecules, which poses double bonds by splitting them. The resulting transients can initiate further reactions or scavenged by oxygen, leading to the formation of unstable peroxides[12] .

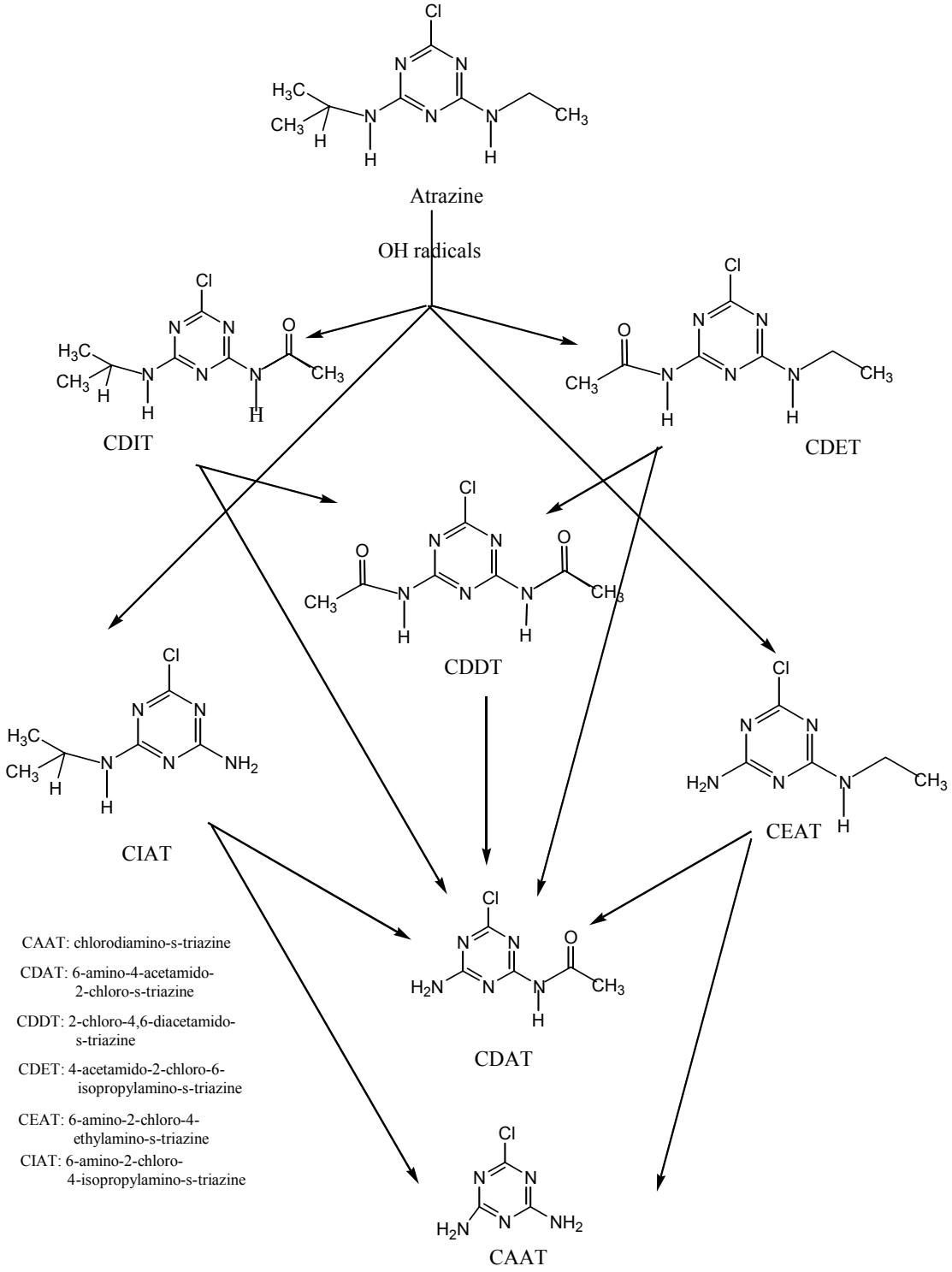


Fig(1): relation between gamma-irradiation dose carrid out in air and the remaining concentration for atrazine at pH 7.

According to Arantegui et al [13] the possible pathway of photo degradation of atrazine is :



Unlike photochemical reactions, a high- energy electron is capable of initiating secondary reactions as it dissipates its energy.The products of atrazine oxidation by means of OH radicals according to Torrents et al[14] are represented as follows:



Fig(2) shows the effect of pH on the degradation of atrazine. The result showed that the degradation of atrazine is high in acidic medium, followed by alkaline medium which is higher than that in neutral medium, where the reaction chemical yields are strongly depending upon the pH of the aqueous solution,since in acidic media e^-_{aq} is converted into H-atom

$$e^-_{aq} + H^-_{aq} \rightarrow H \quad \text{.....(3)}$$

on the contrary, in basic solutions the H-atoms are transferred into e^-_{aq}

$$H + OH^-_{aq} \rightarrow e^-_{aq} \quad \text{.....(4)}$$

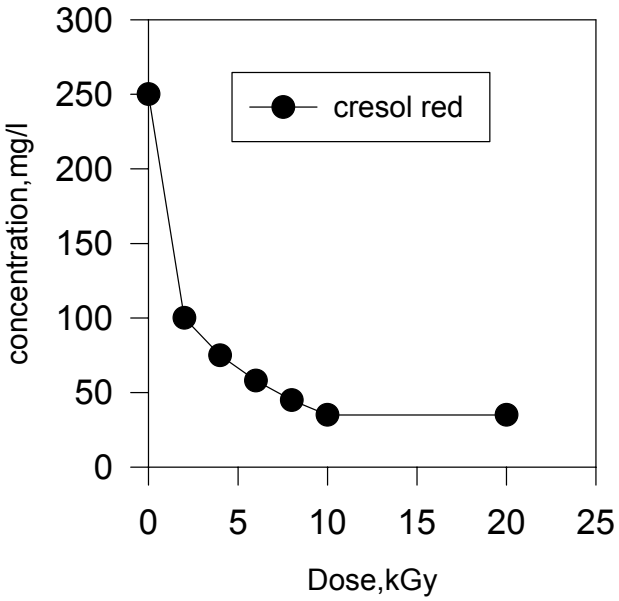
In addition to this the OH-radicals dissociate :

$$OH \leftrightarrow O^-_{aq} + H^+_{aq} \quad \text{..... (5)}$$

In the presence of air both H and e^-_{aq} , are scavenged by oxygen leading to the formation of peroxy-radicals[12] .

$$H + O_2 \rightarrow HO_2 \quad \text{.....(6)}$$

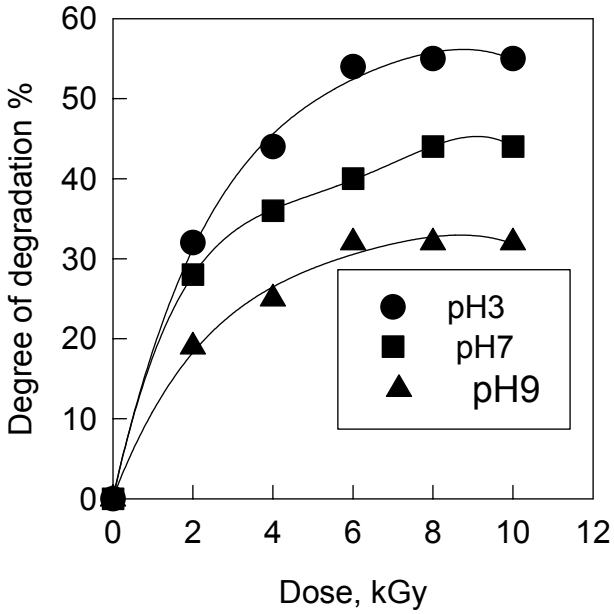
Table (1) shows the effect of radiation doses on the degree of decomposition of atrazine at different concentrations. It can be seen that no influence of the concentration of atrazine on its decomposition.



Fig(2): Relation between gamma-irradiation dose carried out in air and remaining concentration for cresol red at pH 7.

Effect of radiation dose on air saturated dye solutions:

The effect of radiation dose in KG y on the decolouration and degradation of dye solution was studied. 250 ppm of dye solutions was subjected to different irradiation doses (2- 20 KG y) and the results are shown in fig (3). The results show that the degradation of dye solution by irradiation increases with increasing irradiation up to 20 KG y, where about 86% of dye solution was degraded. It is indicative of the role of hydroxyl radicals in decolouration of the aqueous dye solutions. The degree of decolouration of these solutions was found to increase in air-saturated solutions, which is accounted for by the addition of the HO_2 radicals in the degradation of the dye chromofore system[15].



Fig(3): Effect of irradiation dose on the degree of degradation of atrazine at different pH values.

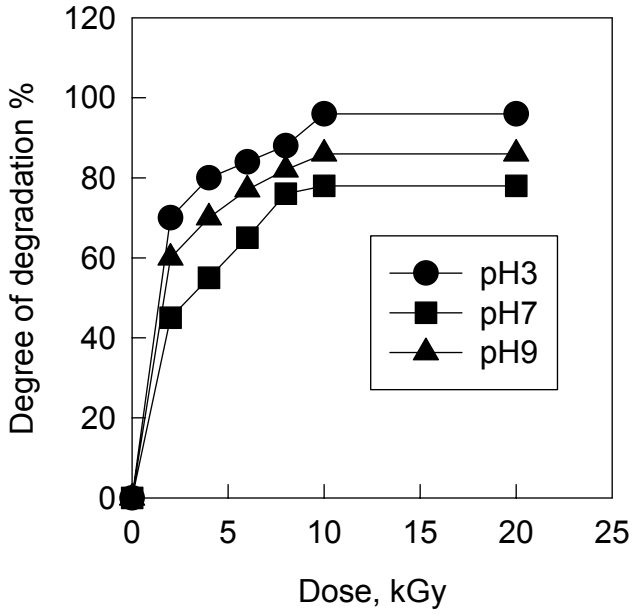
Effect of pH on the degradation of the dye:

Fig.(4) shows the effect of pH on the degree of degradation of aqueous dye solutions. 250 ppm of dye solution at different pH values (3,7,9) respectively was subjected to different radiation doses up to 20 KG y. The results showed that the radiation degradation of dye solution is higher in acidic medium than in alkaline medium, whereas the neutral medium showed the lowest degree of degradation[12].

Radiation degradation of bisolute solution:

Bisolute solution containing dye and pesticide of different concentrations (2,3,4 ppm) , (50,74, 100 ppm) of pesticide and dye solutions was subjected to radiation dose of 20 KG y. The remaining concentration of dye and pesticide solutions was illustrated in table (2). The results showed that the degree of degradation of pesticide

and dye in bisolute solution is lower than that, when irradiation was carried out in monosolute system. This may be attributed to the fact that, the radiolytic species produced from radiolysis of water and responsible for degradation of such pollutants is not enough sufficient for successive degradation of both (dye and pesticide), where strong interaction between their transients takes place[12].



Fif(4):Effect of irradiation dose (in air) on the degree of degradation of cresol red at different pH values.

Preparation of graft copolymer:

Graft copolymerization was carried out by preparation of 10 % soln of PVA and AAm. 6 % of AAm was mixed with 4 % by weight of PVA with vigorous stirring until homogenous system was obtained, then exposed to radiation dose 1.5 M.rad using electron beam accelerator[16].

FTIR Spectroscopy:-

Fig. (5) shows the infrared (FTIR) spectra of PVA, AAm and a representative AAm-g-PVA . The spectrum of the grafted PVA exhibits strong absorption bands at 1300, 1670 and 3440 cm^{-1} characteristics for C-O for alcohol, C = O of amide and alcoholic hydroxyl group respectively.

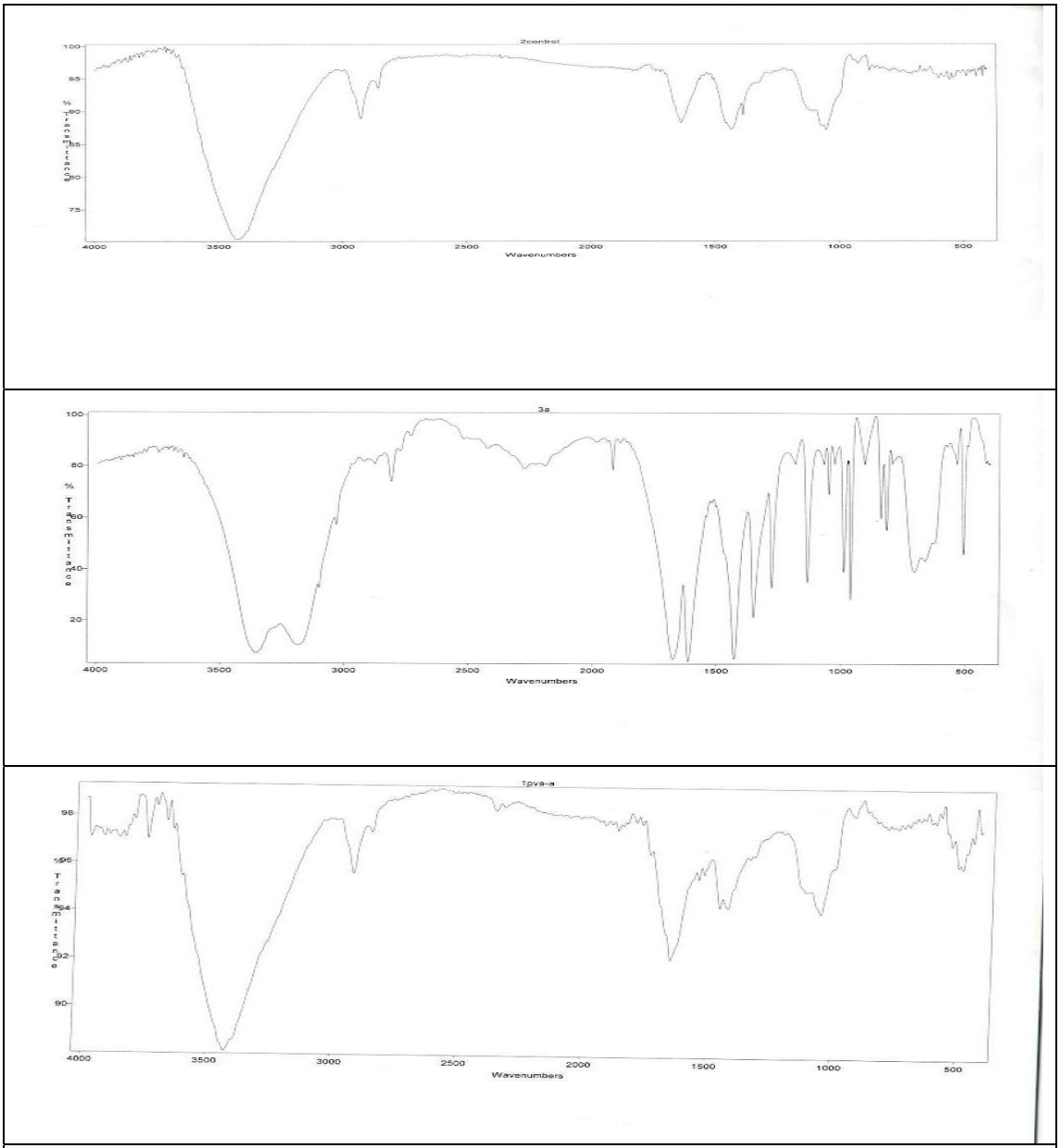


Fig.(5): IR spectra of PVA (a), AAM (b) and AAM grafted onto PVA (c)

Adsorption purification of undegraded pollutants:

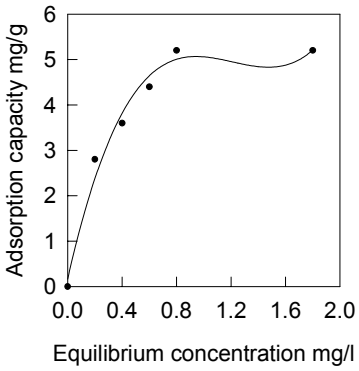
The results mentioned above showed that , no complete degradation occurs of dye and pesticide alone or in their mixture. Therefore adsorption purification was carried out alone and in combination with radiation using GAC and copolymer of AAm-g-PVA to improve the process of purification. Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatment. Adsorption treatment was carried out for single and bisolute before and after radiation treatment. Freundlich isotherm was applied for adsorption of dye and pesticide solution onto GAC and graft copolymer. This isotherm takes the following form for single solute adsorption:

$$Q = K\,C^{1/n} \quad \text{..} \quad (7)$$

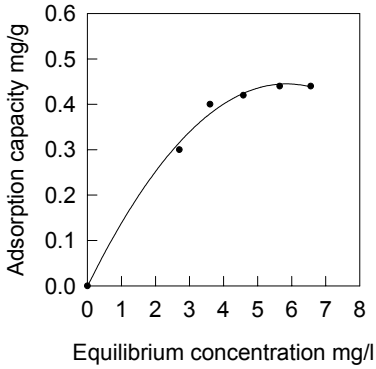
Where K and 1/n are the Freundlich constants related to the sorption capacity and intensity for the sorbent , respectively (17). Figs. (6-9) show the relationship between equilibrium concentration (mg/l) of pesticide and dye solutions, respectively and the adsorption capacity (mg/g) for GAC and AAm-g-PVA.The results show that the affinity of dye adsorption onto GAC is higher than that of atrazine pesticide, this may be attributed to the difference in their structure, solubilities and physicochemical characteristics. Also, it can be seen that, the removal percent of both dye and pesticide is higher in case of GAC than that of AAm-g-PVA, which is due to the very high surface area of GAC (1100 m^2 g^{-1}) . The values of 1/n and K for Gac and AAm-g-Pva

are shown in table (3).these values show the high affinity of dye and pesticide solutions towards GAC in comparison with that obtained for a graft copolymer.

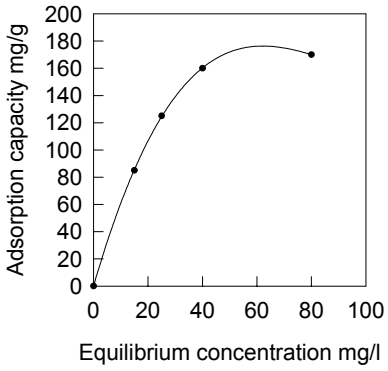
For pesticide and dye, no complete destruction was achieved by radiation alone in both single and bisolute systems as well as no complete removal of these pollutants occurs by adsorption Figs (6-9). Therefore radiation-adsorption process is carried out



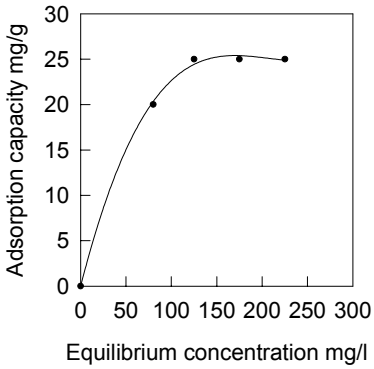
Fig(6): Relationship between equilibrium concentration (mg/l) of atrazine solutions and adsorption capacity of GAC (mg/g)at pH 7.



fig(7): Relationship between equilibrium concentration(mg/l) of atrazine solutions and adsorption capacity of PVA-g-AAm (mg/g) at pH 7.



Fig(8): Relationship between equilibrium concentration(mg/l) of cresol red solutions and the adsorption capcity (mg/g) of GAC at pH 7.



Fig(9): Relationship between equilibrium concentration (mg/l) of cresol red solutions and the adsorption capacity (mg/g) of PVA-g-AAm at pH 7.

to improve the process of purification . Table (4) shows the removal percent of bisolute (dye and pesticide) after radiation- adsorption purification. The results show that GAC showed the higher degree of removal %, where 99% of both pollutants was removed by using GAC, whereas only about 15 % removal of both pollutants was observed in case of graft copplymer. This my indicate the selective behavior of the graft copolymer towards the removal of different pollutants, whereas many different products of different functional groups may be obtained during the degradation process and the possibility for their removal by using a graft copolymer seems to be more difficult.

Pesticide concentration mg/l	Remaining concentration mg/l
3 mg/l	1.7
4 mg/l	2.3
5 mg/l	2.8
6 mg/l	3.3
7 mg/l	3.8

Table (1): Effect of irradiation dose (20 k,Gy) on various pesticide concentrations at pH 7.

Table (2): Effect of irradiation dose (20 k,Gy) on various dye concentrations at pH 7.

dye concentration mg/l	Remaining concentration mg/l
100 mg/l	0.001
150 mg/l	0.05
200 mg/l	0.093
250mg/l	2

Table (3): Remaining concentration of dye and pesticide solutions At irradiation dose (20 k,Gy) and at pH 7.

Dye concentration mg/l	Pesticide concentration mg/l	Remaining concentration of dye mg/l	Remaining concentration of pesticide mg/l
50 mg/l	2 mg/l	5 mg/l	1.1 mg/l
75 mg/l	3 mg/l	7 mg/l	1.9 mg/l
100 mg/l	4 mg/l	9 mg/l	2.9 mg/l

Table (4): Remaining concentration of dye and pesticide in their mixture After adsorption by GAC and PVA-g-AAm.

Dye conccentration mg/l	Pesticide conccentration mg/l	Remaining concentration of dye after adsorption by GAC	Remaining concentration of dye after adsorption by PVA-g-AAm	Remaining concentration of pesticide after adsorption by GAC	Remaining concentration of pesticide after adsorption by PVA-g-AAm
50	2	10	38	0.4	1.6
75	3	15	69	0.8	2.8
100	4	25	88	1.2	3.8

Table (5): Remaining concentration of dye and pesticide in their mixture
After radiation- adsorption by GAC and PVA-g-AAm.

Dye conccentration mg/l	Pesticide conccentration mg/l	Remaining concentration of dye after adsorption by GAC	Remaining concentration of dye after adsorption by PVA-g-AAm	Remaining concentration of pesticide after adsorption by GAC	Remaining concentration of pesticide after adsorption by PVA-g-AAm
50	2	0.001	2.4	0.001	0.9
75	3	0.003	3.4	0.001	1.7
100	4	25	4.7	0.001	2.6

Conclusion

Radiation purification of wastewater seems to be the most promising technique. The use of gamma radiation in the treatment of atrazine and cresol red either separately or in their mixtures is not enough sufficient for their complete removal from their solutions. A combined treatment with a conventional method (adsorption) seems to be more effective for such removal.GAC is the most powerful adsorbent material for the removal of both pollutants from their solutions.AAm-g-PVA show only a low removal percent in all cases.

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