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WM-3 The Use of Membranes Prepared by Radiation - Induced Grafting in Waste Water Treatment

M.B.El-Arnaouty – S.E.Abdel -Aal and A.M.DESSOUKI
National center for Radiation Research and Technology,
PO Box 29,Nasr City, Cairo, 11731, Egypt

ABSTRACT

Membranes were prepared by the radiation–induced grafting of N-vinylpyrrolidone onto low density polyethylene and the possibility for their practical use in the removal of two dyes: Acid Red 116 (Erionyl Red 2B) and Blue Reactive (Brilliant Bright Blue) was studied . The effect of the degree of grafting on the adsorption of these pollutants was investigated and showed maximum adsorption occurred at 394 % grafting. Radiation degradation of the dyes with a dose of ~ 5kGy was followed by adsorption of the residual concentration of the dyes by the membranes, which resulted in the complete removal of these pollutants as well as the radiolysis products present in the irradiated solutions. Also, characterization of the membranes before and after adsorption was carried out using thermogravimetric analysis and scanning electron microscopy.

Key Words: *Membranes / Radiation / Grafting / Dye / Removal*

INTRODUCTION

As a result of the 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, chlorine – containing dyes, pesticides, detergent and other chemicals, as wall as fertilizers in modern agriculture, contributes to contamination of ground water [1-10]. A rather heavy pollution of the global environment is occurring .The consequences of the environmental pollution are manifold: Health hazard for the population, respiratory diseases, cancer, allergies as well as polluted soil, drinking water, agriculture products and hence animal diseases, pollution of rivers and oceans resulting in plankton killing and reduction of fishes etc. Also, the CO_2 greenhouse effect is resulting in global warming and acid rains as well. Many technologies are being developed to overcome these huge problems all over the world [11-16]. In previous studies, copolymers were used in the removal of pesticides, heavy metals and dyes from waste waters.

In the present study radiation induced copolymers of low density polyethylene grafted by N-vinylpyrrolidone will be used to remove some toxic dyes from aqueous solutions . Factors affecting this process such as concentration, pH, degree of grafting … etc. will be studied. Also, some physical properties of the prepared membranes such as thermal, mechanical, scanning electron microscopy …etc . Will be studied.

EXPERIMENTAL

Materials:

Low-density polyethylene (LDPE) films of thickness 60 μ m were supplied by EL-Nasr Chemical Company - Egypt. N-vinyl - 2- pyrrolidone , (NVP) Merck-Schuchardt purity > 99%, were used without further purification.The two dyes used in the present work , namely Erionyl red 2B (Acid Red 116) and reactive dye Blue Brilliant Remazol (Bright Blue) .

Apparatus and Methods:

A. Gamma Radiation Source:

The Samples were irradiated with cobalt-60 gamma rays at a dose rate 0.61 Gy/ sec. Gamma chamber 4000 A, India. The graft copolymers were prepared by the direct radiation grafting of N-vinyl. Pyrrolidone (NVP) monomer onto LDPE films using cobalt-60 gamma rays at a dose rate 0.61 Gy / sec - Details of this technique are described in a previous study (17).

B. Dyes:

1 - Acid Red 116 (Erionyl Red 2B) IB , $C_{22}H_{15}O_4S_4$ Na (Molecular Weight 454) .

2 - Remazol Blue Reactive Dye (Brilliant Bright Blue) IIA, C_{22} H_{16} O_{11} N2 S_3 Na_2 (Molecular weight 626).

C. Thermogravimetric analysis (TGA):

A model (Shimadzu – 50) was used for the measurements of TGA. In the present study nitrogen flow must be kept at constant rate of about 60 ml / min to prevent oxidation of the polymer sample, the heating rate 10 C / min up to 600 C .

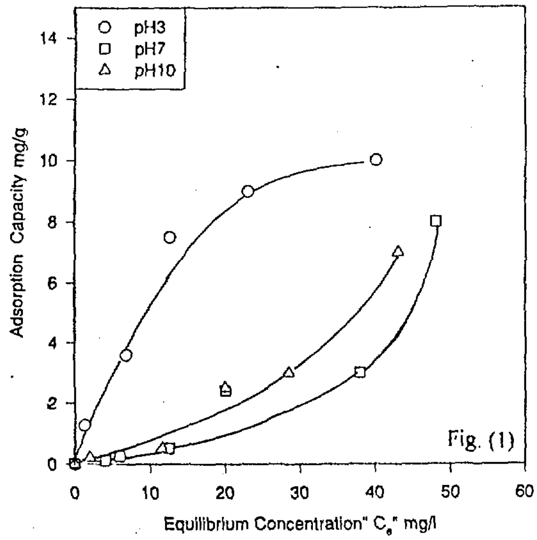
D. Scanning electron microscopy (SEM):

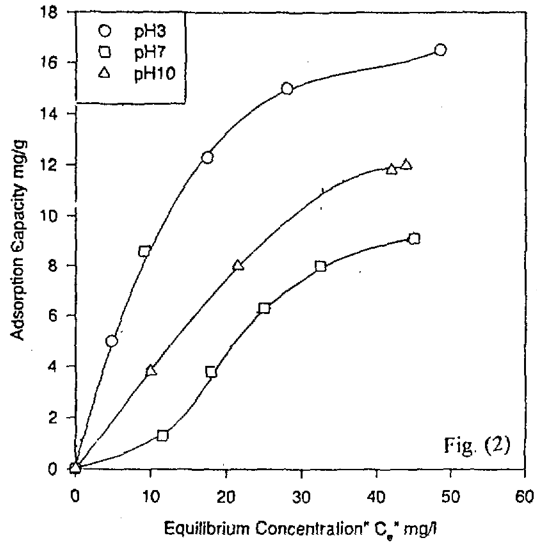
The surface topography of the grafted and adsorbed dye films was studied using a JEOL I SM – 5400 scanning microscope (JEOL , Japan).

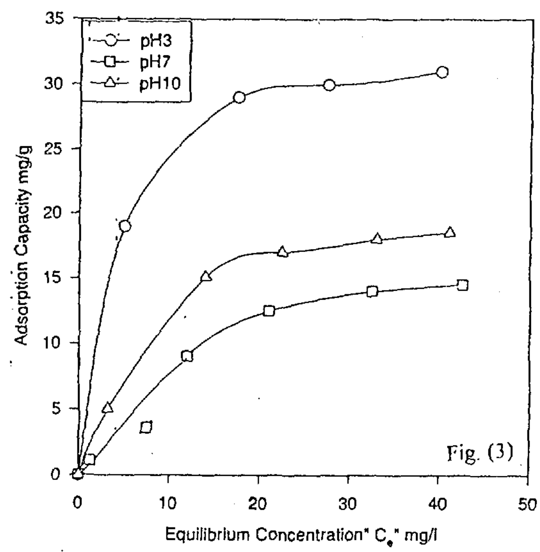
RESULTS AND DISCUSSION

Removal of toxic dyes: -

The direct radiation – induced grafting of N-vinyl-2 – Pyrrrolidone onto low-density polyethylene films was carried out to prepare membranes to be used in the removal of two toxic dyes from waste effluents [17]. These dyes are Remazol Blue Reactive dye (Brilliant Bright Blue IIA) and (Erionyl Red 2B) IB and acid dye. The effect of degree of grafting of the membrane on it's adsorption capacity of the two dyes was studied at various pH values (3,7 and 10). The results of this study are shown in Figs. (1-12) which show the adsorption capacity (mg/g) against equilibrium concentration (mg/l) for the blank polymer and for the grafted polymer (membrane) with various degrees of grafting ranging form 4% to 394%. It can be seen from the figures that relatively small amounts of the dyes was removed by the trunk polymer, while the grafted membranes showed appreciable adsorption capacity which increased with the increase in the degree of grafting between 4% up to 287%. However, a drop in the adsorption capacity was observed at 394% grafting, which may be due to saturation of the active sites (functional groups). Increasing the degree of grafting i .e increasing the



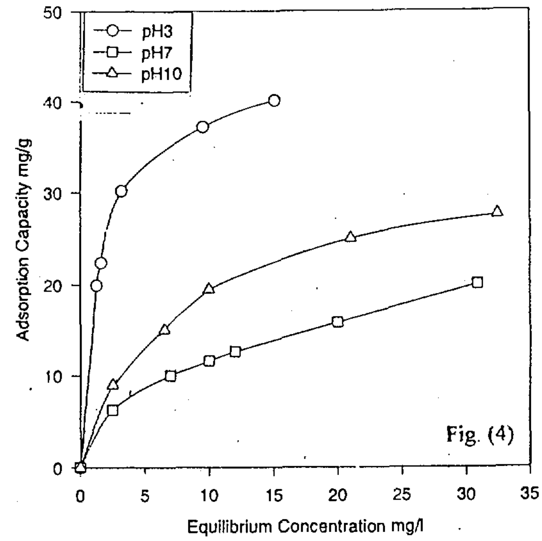


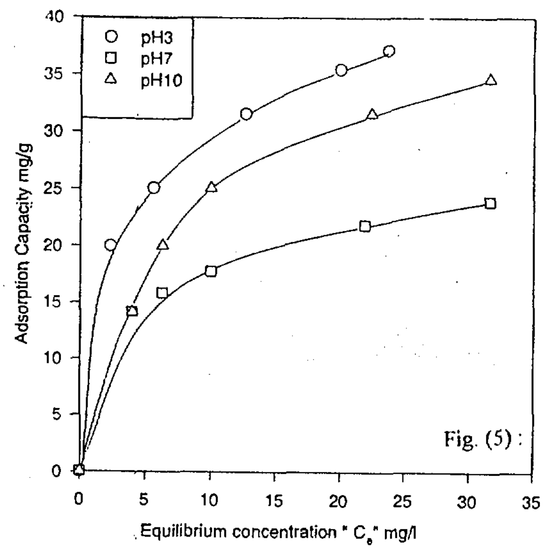


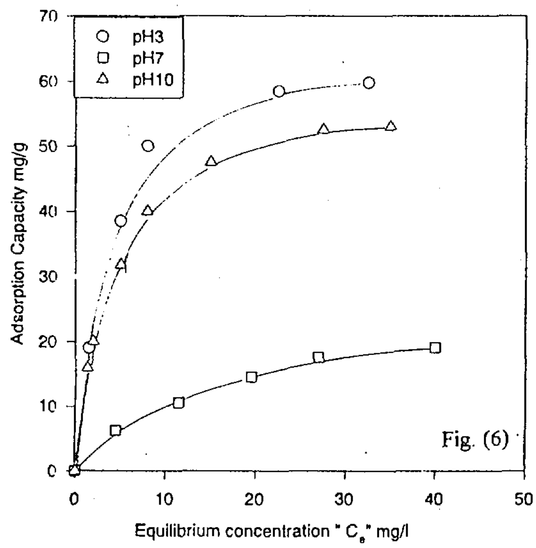
Relationship between the adsorption capacity of LDPE-g- NVP copolymer (mg/g) and the equilibrium concentration Ce of blue reactive dye at different PH values .

Fig. (1) : ungrafted LDPE . Fig. (2) : 4% grafting

Fig. (3) : 41% grafting .





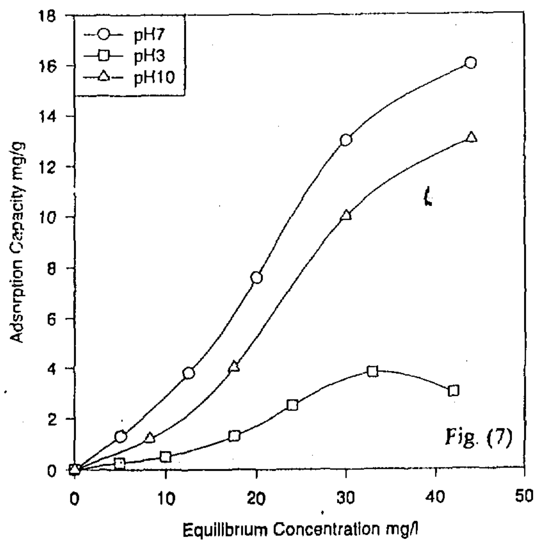


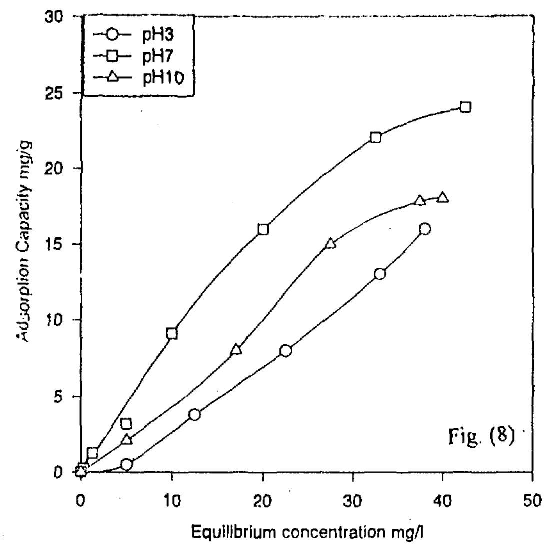
Relationship between the adsorption capacity of LDPE-g- NVP copolymer (mg/g) and the equilibrium concentration Ce of blue reactive dye at different PH values .

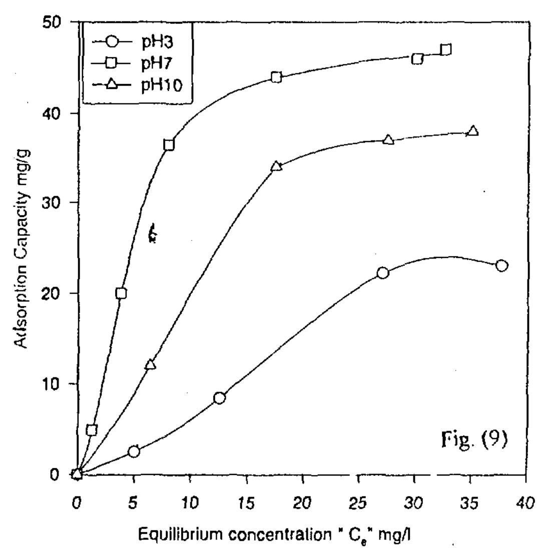
Fig. (4) : 84.3% grafting .

Fig. (5) : 287.4% grafting

Fig. (6) : 394% grafting .





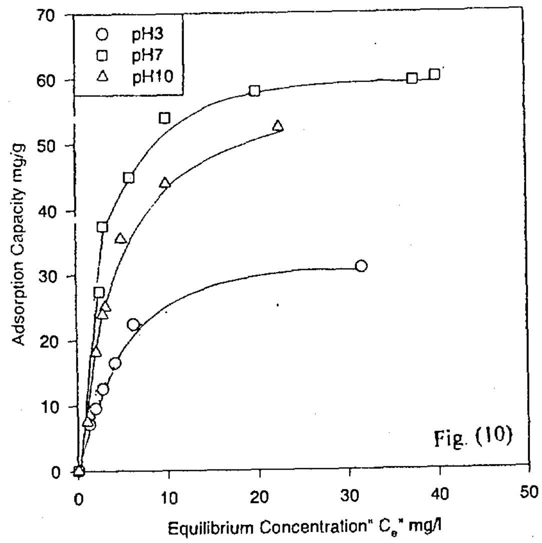


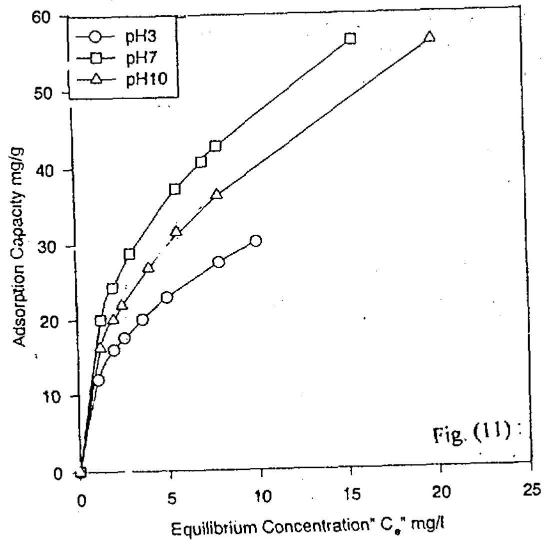
Relationship between the adsorption capacity of LDPE-g- NVP copolymer (mg/g) and the equilibrium concentration Ce of acid red dye at different PH values .

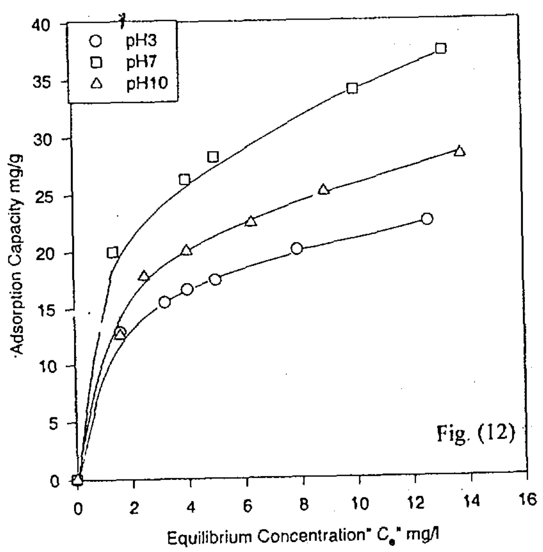
Fig. (7) : ungrafted LDPE .

Fig. (8) : 4% grafting

Fig. (9) : 41% grafting .







Relationship between the adsorption capacity of LDPE-g- NVP copolymer (mg/g) and the equilibrium concentration Ce of acid red dye at different PH values :

Fig. (10) : 84.3% grafting . Fig. (11) : 287.4% grafting

Fig. (12) : 394% grafting .

NVP groups resulted in more adsorption of the toxic dye. Membranes show generally good affinity for adsorption of different pollutants such as heavy metals [17], pesticides and dyes [1-16]. Physical properties of the membranes are also an important factor in the adsorption process as well as the physico-chemical characteristics (for example molecular size, molecular weight ...etc) of the adsorbent. The diffusion of the dye molecules through the porous ionic membrane which is dependent on the polarity, ionic radius , electronic structure and most important it's reaction with the functional groups of the grafted membrane.

Effect of solution pH:

The adsorption of reactive blue dye is best at pH 3 followed by the alkaline and neutral media, while the highest adsorption of acid red dye occurred at pH 7. Hwang and chen [18] reported that this phenomenon from an economic and practical stand point, a fluid should always be evaluated at the ambient pH. In other words, the pH of a solution of significance 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 and can directly affect the solution pH and therefore the solubility and the adsorption capacity. The acid dyes are so called because they are applied in a bath containing mineral or organic acid, and therefore pH is a very important factor. A wide range of dye pH was investigated. Figures (1-12) illustrate the influence of pH on the adsorption of acid red 116 and remazol blue reactive dye. The results show two different effects. The adsorption of the blue reactive dye increase with [H^+] as figures (1-6) show. This phenomenon is possibly caused by the electrostatic potential between the dye molecules and the membrane surfaces adsorbed hydrogen ion at low pH solution. This electrostatic potential can improve the adsorption affinity between dye and membrane. Figures (7-12) show that the adsorption effect between pH 6.0-7.0 was for acid red dye. This is possibly because of the good adsorption affinity between membrane and the anionic ion at low [H^+]. According to these results, most of the acid dyes can be adsorbed onto membranes at a very weak pH level (pH 6-7).

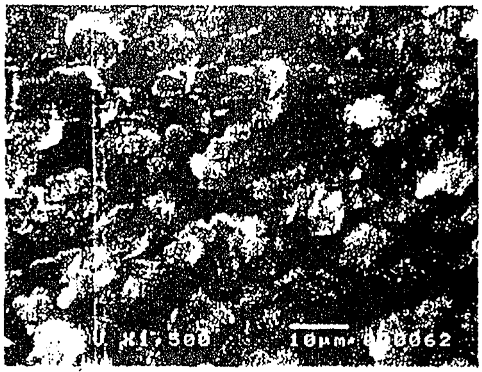
Hwang and Chen [18] reported that polyamide – epichlorohydrin – cellulose polymer (PAE – cell) was able to remove various acid dyes from aqueous solution and that these polymers exhibit better capacity for acid dye removal than some commercial activated carbons, this is in good agreement with our results.

SEM of adsorbent adsorbed dyes:

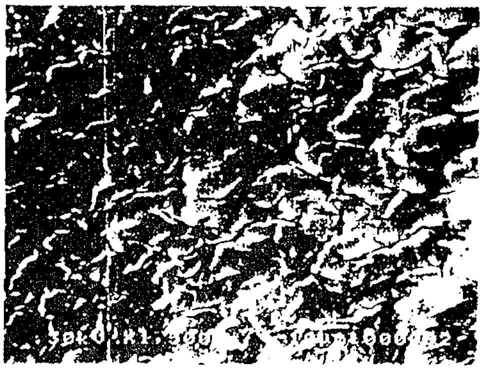
The surface of a macroreticular adsorbent was observed by scanning electron microscope (SEM). The SEM photo of grafted membrane shows the pore structure and fiber structure Fig.13 (a). After adsorbing a low initial concentration of blue reactive dye, the SEM photo showed particles of aggregates dye, but some pore and fiber structures also were observed in Fig.13 (b). In addition, the shadowing on the SEM photo clearly reveals that the visible particles are in the pore structure of the grafted membrane, and the largest particles were seen to be those nearest to the outer surface, as shown in Fig. 13 (c).

Desorption:

Figs. 14 and 15 show the desorption rate of the dye release concentration as a function of time (min.) for the reactive and acid dyes at various degrees of grafting, respectively (5 % HCL was used at room temp.). There was, however, a slight release of the dyes, which reached its maximum after 2 hours .It is obvious that membrane uptake of the dyes is strong and the release is not that much.



(a)



(b)

(c)

Fig. (13) : Scanning electron micrographs of the surface of grafted LDPE films at 394% grafting and adsorption dyes

(a) before adsorption (b) after adsorption of blue reactive dye .

(c) after adsorption of acid red dye .

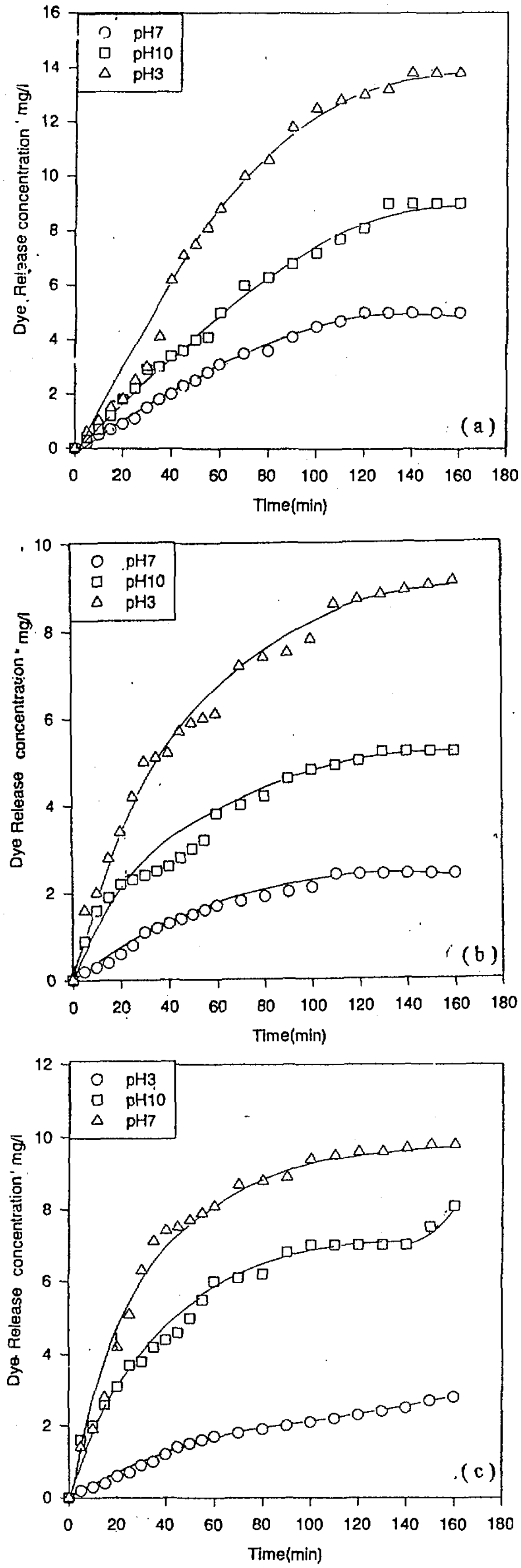


Fig. (14) : Effect of time on dye release concentration of blue reactive dye from grafted membrane at different PH values .

(a) 84.3% grafting .

(b) 287.4% grafting .

(c) 394% grafting .

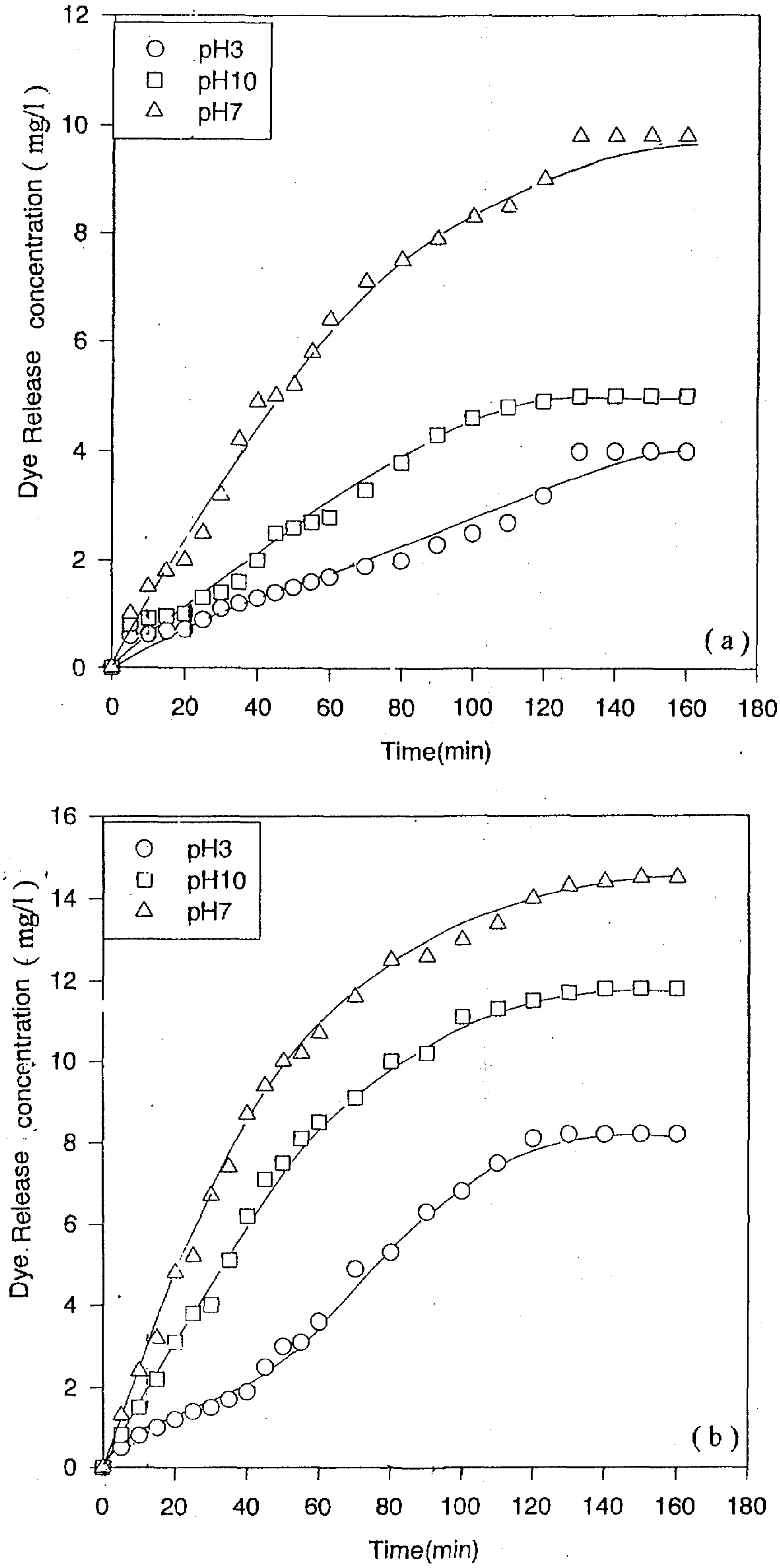


Fig. (15) : Effect of time on dye release concentration of acid dye from grafted membrane at different PH values .

(a) 84.3% grafting . (b) 394% grafting .

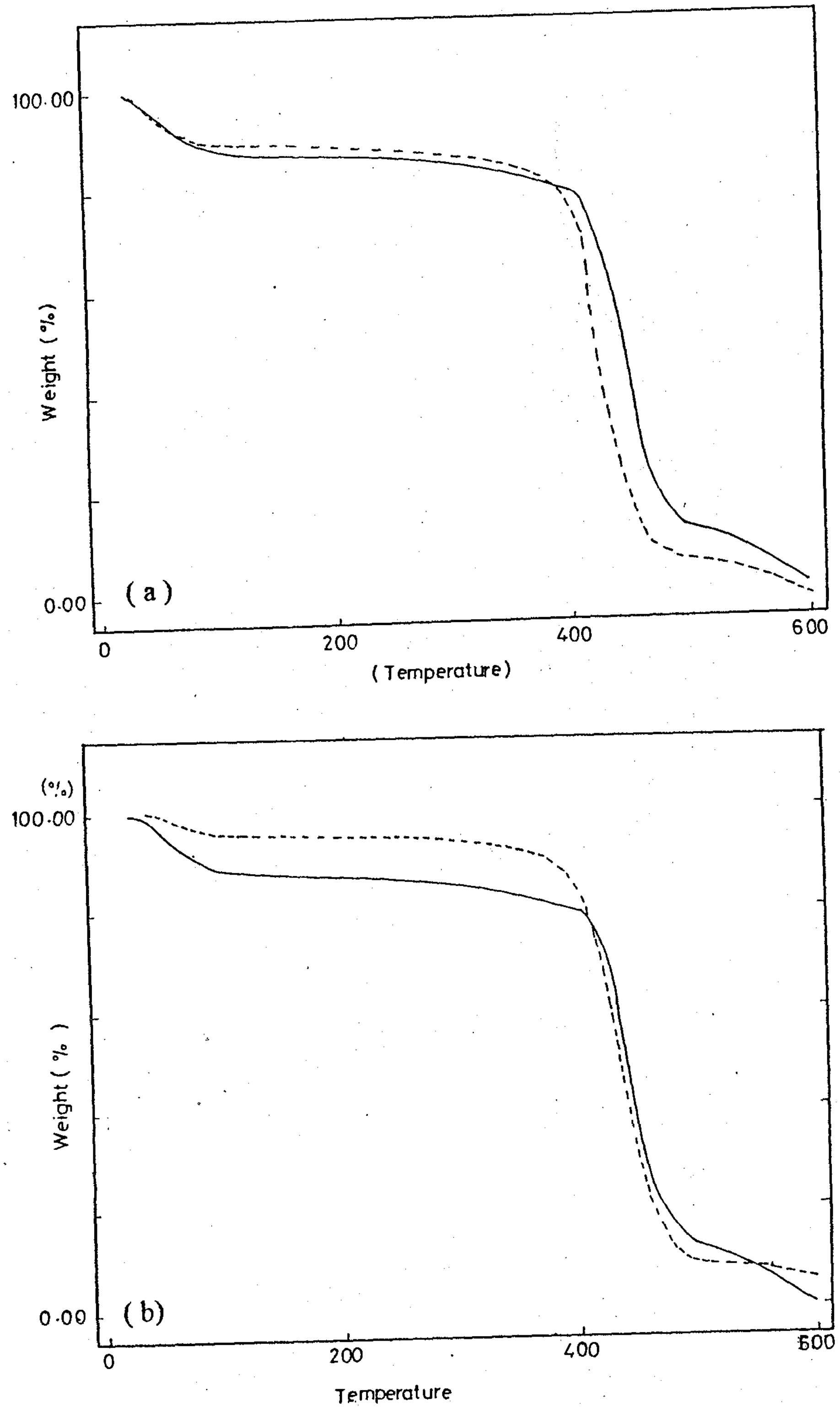


Fig. (16) : Thermogravimetric curves for the grafted LDPE films at 394% grafting (dotted line , solid line) after and before adsorption dye respectively.

(a) blue reactive dye .   (b) acid red dye.

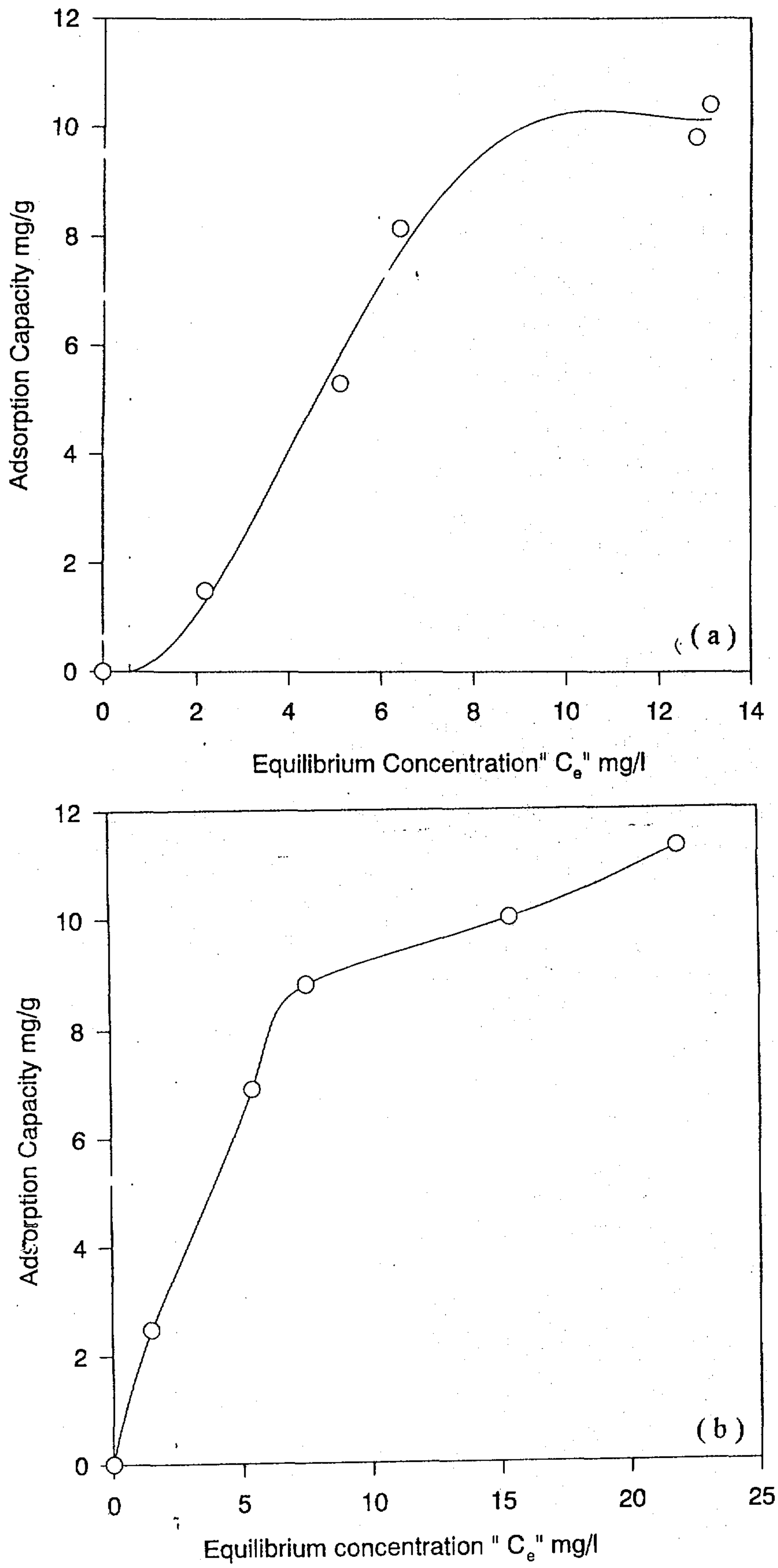


Fig. (17,) : relationship between the adsorption capacity (mg / g) of 287.4 % grafting LDPE-g-NVP and the equilibrium concentration of (γ) irradiation solution for two dyes
(a) blue reactive dye at pH_3 (5 KGy) .(b)acid dye at pH_7 (4 KGy).

Thermal stability of prepared membranes:

The thermal resistance is an indicator of the chemical stability of the polymeric membrane at high temperatures in vacuum, air or an inert atmosphere. It is a very important factor for the durability of these membranes during practical use. Fig.16 shows the percentage weight loss at elevated temperature during the dynamic TGA for LDPE-g- NVP copolymer and for the copolymer saturated with the acid and the reactive dye. It can be seen that the grafted membrane and the grafted one plus the adsorbed dye show a slight difference, (the membrane with the dye is less by 10 ^{0}C than the grafted one) i.e. a good thermal stability for both . It is known that the stabilization is governed by the strength of binding of the dye with the copolymer i.e. the complexation and / or exchange, chelation with the groups of the membrane. Also, the thermal stability of the copolymers can be explained according to ligand field stabilizing energy and ionic radii. It may be concluded that the LDPE / NVP membrane showed good removal of the two toxic dyes studied as well as good stability which makes it suitable for practical uses.

Radiation – adsorption purification:

This method combines the radiation treatment of the two organic dyes coupled with the conventional adsorption by the polymeric membranes. The reactive and acid dyes were subjected to γ – irradiation dose of 5 (pH 3 and 100 mg / L concentration) and 4 KGy by (pH 7 and 100 mg / L concentration) for the two dyes , respectively.
After irradiation the dyes suffered (25 %) for the reactive dyes, while the acid dye suffered (18 %). After which, the residual dye concentration was got in contact with the grafted membranes (287 % grafting) for a period of 8 days, Fig. (17) shows the adsorption capacity (mg/g) of the membranes for both dyes as a function of equilibrium concentration (Ce). It can be seen from the figure that both dyes were adsorbed by the membranes to almost the same extent, Also, it was observed that not all the residual dye concentration was removed .The removal percent reached (86 %) and\ (78 %). However, this removal percent is with the maximum permissible concentration (MPC) according to the FAO regulations. The radiation adsorption method proved to be more efficient than either method alone.

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