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Separation and Extraction of Some Heavy and Toxic Metal Ions from Their Wastes by Ionic Membranes

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Synopsis

Preparation and characterisation of a series of ion-exchange membranes for the purpose of separation and extraction of some heavy and toxic metal ions from their wastes have been studied. Such ion exchange membranes prepared by γ- radiation grafting of acrylonitrile (AN) and vinyl acetate (VAc) in a binary monomers mixture onto low density polyethylene (LDPE) using direct technique of grafting. The reaction conditions at which grafting process proceeds successfully have been determined. Many modification treatments have been attempted for the prepared membranes to improve their ion-exchange properties. The possibility of their practical use in waste water treatment from some heavy and toxic metal ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Sr^{2+} and Li^{+} have been investigated. These grafted membranes showed great promise for its use in the field of extraction and removal of some heavy and toxic metals from their wastes.

Key words: *Gamma - Irradiation - Grafting - Membranes - Metal Separation.*

INTRODUCTION

Ion exchange membranes play an important role in modern technology, especially in separation and purification of materials. The search for improved membrane composition using almost every available polymeric materials has been subjected to extensive research because of the great practical importance of such composition[1]. Grafting of polymers with mixture of monomers is important since different types of chains containing various functional groups can be introduced in the polymer structure[2] . The properties of such ion-exchange membranes are determined by two parameters, the base polymer and the chemical structure and concentration of the fixed ionic moieties[3]. Radiation grafting is wonderful technique because of its large penetration in polymer matrix, rapid and uniformity of active sits for initiating grafting throughout the matrix[4]. Also, it can be effective and conveniently carried out at room temperature and various side reactions are minimal[5].

Preparation of graft copolymers by direct radiation grafting of acrylonitrile [AN] and vinyl acetate [VAc] in a binary monomer mixture onto low density polyethylene (LDPE) was studied. The effect of grafting conditions, such as type of solvents and total radiation dose on the grafting process, was determined. Many modification treatments have been attempted on these graft copolymers to improve their ion exchange property.

In this study, the main part is to investigate the physical and chemical properties of the resultant grafted membranes and possibility of their applications in various fields, such as waste water treatment. Some properties of these ion-exchange membranes have been studied as a function of grafting degree such as, water uptake, and mechanical characteristics. Some factors that influence the ion-exchange property of the prepared ion exchange membranes toward some selected ions have also been investigated.

EXPERIMENTAL

Low-density polyethylene (LDPE) films of thickness 80 μm were provided by El-Nasr Co. for Medical Supplies, Egypt. Reagent grade acrylonitrile (AN) of purity 99.3 % (Merck) and reagent grade vinyl acetate (VAc) of purity 99 % (Merck) were used as monomers. Other chemicals, such as solvents, inorganic salts, acids and other reagents were reagent grade of BDH type.

The direct radiation method was used as a grafting technique. The irradiation was carried out using Co-60 gamma rays at a dose rate ranging from 0.27-1.1 Gy/s, in nitrogen atmosphere. After irradiation the grafted films were removed and washed by Sohxlet-apparatus using acetone as a solvent to extract the embedded homopolymer. These films were then dried at 40 - 50 °C in oven for 24 hrs. to constant weight. The degree of grafting was calculated by using the following equation:

$$\text{Degree of Grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

Where W_o and W_g are the weights of blank and grafted films, respectively.

Chemical treatment process or hydrolysis of the functional groups in the prepared graft copolymers was carried out using different mediums. The first medium was 5% aqueous KOH solution and the second was 1: 1 alcoholic solution of methyl alcohol containing 5 % hydroxylamine, then boiling the solution and the samples in a reflux for 16 hrs. After treatment, the films immersed in bi-distilled water, for 24 hrs. to remove excess reagents, then rinsed with bi-distilled water, and dried at 40 -50 °C in oven for 24 hrs.

Water uptake measurements were carried out by the same method used in the previous study[6].

Metal uptake property was measured by immersing about one gram of dry treated film in 100 ml of metal ions solution (Cu, Co, Li, Fe, Pb, Sr and Cd) of definite concentration in 250 Cm^3 conical flask with reflux containing a magnet for stirring. Merck atomic absorption standard solutions of these metals were used for the calibration process. The pH of the solution was adjusted before adding the graft copolymer films by using HCI solution and/or NaOH solution. The temperature of the system was adjusted at desired value before adding the film, by using a thermostat oil bath. After the experiment the metal ions solution was analysed by atomic absorption technique using atomic absorption (Perkin Elmer model 2380) to determine the quantity of adsorbed metal ions. The effect of pH, temperature, time of adsorption.

The metal uptake (E) was calculated as follows:

$$E\ (\text{m mole/ g}) = \frac{C_I - C_f}{W_g \times A \times 10} \qquad (2)$$

Where C_I and C_f are the initial and final concentration of metal ions in mg/L (ppm), Wg is the weight of the grafted film and A is the atomic weight of metal ion.

Results and Discussion

1.Effect of Solvent Type

In this study, different solvents were used for the grafting of binary mixture of acrylonitrile and vinyl acetate onto low density polyethylene to find the suitable solvent which enhances diffusion of the reaction mixtures to the interior part of the film and also enhances the grafting process. The effect of the selected solvents on the grafting process is shown in Table 1.

Table 1: Effect of some selected solvents on the grafting of AN/VAC binary monomers onto LDPE .

Solvent	DMF	Acetone/DMF (1:1 wt.%)	Acetone	DMF/MeOH (1:1 wt.%)	MeOH	Dioxane
Grafting (%)	19.2	18.8	12.8	19.5	14.3	13.2

It was observed that, no homopolymer was formed and homogenous grafting was obtained in the presence of DMF, acetone, and in a mixture of both together. The other solvents lead to high homopolymer formation and the samples were difficult to extract. The presence of DMF, acetone, and mixture of them as solvents may reduce the G-value of the monomers by chain transfer. This resulted in proceeding the graft polymerization and retarding the homopolymerization process. It was also observed that these solvents; DMF, acetone and mixture of them are vary in their ability to influence graft copolymerization and the following reactivity order was observed: DMF > acetone / DMF > acetone. The aforementioned results showed that the grafting of AN/VAc onto LDPE films were enhanced in the presence of DMF. This leads one to believe that the diffusibility of AN/VAc into the polymer matrix is enhanced in the presence of DMF.These results consequently suggested that DMF is the most suitable solvent for this grafting system.

2. Effect of Irradiation Dose

The effect of irradiation dose on the degree of grafting of (AN/VAc) at comonomer composition (70/30) and comonomer concentration (60 wt.%) onto LDPE films is shown in Fig. (1). It is found that, the degree of grafting increases with increasing irradiation dose and it tends to level off at higher doses.

Increasing the grafting yield with irradiation dose can be attributed to the increase of active sites. The acceleration occurs at total dose ranging from 10 - 20 kGy may be due to "gel-effect". At higher radiation doses > 20 kGy the grafting yield tends to level off due to the increase in number of active sites on the polymer and monomer pair and recombination of these active sites without initiating new sites for grafting. At the same time and at this high-absorbed dose high homopolymer is formed and the diffusion of the comonomer to the active sites is restricted[7].

3. Swelling Behaviour

Water content is very important for the practical application especially in the ion-exchangers. The membrane should exhibit suitable hydrophilicity as well as mechanical properties. So that, further chemical treatment was made for the graft copolymers to improve the hydrophilic properties of the membranes via introduction of hydrophilic groups by such chemical treatments. Swelling of the membranes in water was measured and the results are presented in Fig. (2) as a function of degree of grafting for the alkali-untreated and alkali-treated LDPE films grafted with PAN and PVAC. It can be seen that, water uptake percent increases linearly with degree of grafting for both the alkali-untreated and alkali-treated grafted films. However, the alkali-treated graft copolymers possess much higher water uptake.

Upon grafting of AN and VAc onto LDPE, no significant increase in their water uptake with increasing the grafting yield is observed. These results are attributed to the introduction of hydrophobic groups; nitrile from AN and acetate from (VAc). In Fig. (2) the modified membranes had a higher water uptake than the unmodified ones at a given degree of grafting. It means that, the alkali-treated graft copolymers should have a better hydrophilicity than the untreated ones. Moreover, the water uptake increases with increasing grafting yield because of the increase in hydrophilic properties of such treated graft copolymers by increasing the amount of hydrophilic groups introduced in the graft copolymer[8]. Figure.(2) shows also that for untreated LDPE membrane having 150% grafting, the swelling percent is 3.5%, while, it reaches to 35 % for the NH_2OH-treated graft copolymer having the same degree of grafting i.e. ten times more than the untreated one. For the KOH-treated membrane that having the same degree of grafting films, the water uptake percent reaches to 46 %. It can be seen that, the alkaline treatment resulted in hydrolysing the poly (vinyl acetate) to poly (vinyl alcohol). Hydroxyl groups are hydrophilic and they form strong hydrogen bonds. On the other hand, the alkaline treatment of the poly (acrylonitrile) with KOH and NH_20H convert the nitrile groups to carboxylic and amidoxime groups, respectively. It must be noted that, the swelling character for KOH-treated graft copolymers is higher than those treated with NH_20H, due to influence of carboxylic acid units on the properties of the graft copolymer. The hydrophilic character is direct consequence of the ability of a carboxylic acid unit to become highly solvated in water. From the above results, it is expected that, the KOH hydrolysed membranes have a stronger affinity to water than the NH_2OH-treated ones. These results indicated that, the swelling behaviour depends mainly on the amount and form of functional reactive groups introduced into the polymer substrate by grafting.

4. Mechanical Properties

One of the necessities for the membrane properties is to exhibit mechanical properties acceptable for the practical use. Figure (3,4) shows the changes of elongation percent (E_b) and tensile strength (T_b) at break point for the original, grafted and alkali-treated grafted LDPE membranes. It can be seen that, T_b increases with increasing the degree of grafting but E_b decreases. T_b of the graft Copolymer increases with increasing degree of grafting due to two reasons; the first one is the incorporation of the polar nitrile groups of PAN and their interactions. The second reason is the crosslinking formation due to grafting and irradiation, that leading to a restriction in chain mobility and consequently decrease in E_b was occurred. But at a lower degree of grafting, the crosslinking network structure is located close to the film surface.

The above figures shows that, the alkaline treatment of such grafted films either with KOH or NH_20H resulted in an increase in the T_b and decrease in E_b compared with the untreated graft copolymer. These results indicated that the conversion of acetate groups, which are non-polar to the polar hydroxyl groups and their interactions and the formation of amidoxime and carboxylic acid groups by the alkaline treatment of nitrile groups with NH_20H or KOH has an effect. It is also observed that, at a given graft percent, the T_b of the KOH- treated membranes is higher than that of NH_2OH-treated ones due to the carboxylic acid groups formed by such treatment. The formation of such -COOH groups, on one hand leads to polar-polar interaction and on the other hand causes some crosslink formation, such crosslinking structure may be formed by acrylic acid, which easily forms acrylic dimmer bridged by hydrogen bonds [(9)] . These two factors increase the T_b and decrease the E_b compared to NH_20H treated membrane in which this crosslink formation is lake.

APPLICATION OF GRAFTED MEMBRANES IN METAL UPTAKE

Separation of some selected metal ions, which are commonly existing in waste water, was investigated. The selectivity of the different prepared membranes towards Pb^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Sr^{2+} and Li^{+} is determined. Among the factors affecting the treatment process of such metal ions from their wastes using the prepared membranes is the following

1- pH of metal ion feed solution.
2- Operation time and temperature.

1. Effect of Treatment Time

From the economical point of view, the time of treatment is an important factor. Also, the efficiency of membrane in waste treatment can be determined from the time required to adsorb the maximum capacity of metal ions by celation or complexation with its fictional groups.

Figures. (5, 6) show the metal uptake as a function of time for different metals using grafted LDPE films treated either with KOH or NH_2OH. It can be seen that, the metal uptake increases with time to reach its maximum value (which is termed here as the maximum membrane capacity) at almost 8 hr. of treatment for different metal ions investigated. Increasing the treatment time higher than 8 hr. causes no significant increase in metal uptake even after 24 hr. It can be seen that, the maximum metal uptake is ordered in the sequence of, $Fe^{3+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Sr^{2+} > Pb^{2+} > LI^{+}$. The ionic size of the investigated metal ions has a great influence not only on its maximum uptake but also on its initial rate (Table.2).

Table 2. Atomic, ionic radii and electronic configuration for different metal Ions investigated[(10)].

Elements	Valence	Atomic radius	Ionic radius,	Ionic electr configuration
Fe	3+	1.24	0.67	$[Ar]^{18},3d^5$
Cu	2+	1.27	0.72	$[Ar]^{18},3d^9$
Li	1+	1.52	0.78	$[He]^2,2s^0$
Co	2+	1.25	0.82	$[Ar]^{18},3d^7$
Cd	2+	1.48	1.03	$[Kr]^{36},4d^{10}$
Sr	2+	2.15	1.27	$[Kr]^{36},5s^0$
Pb	2+	1.75	1.32	$[Xe]^{54},6s^2$

This is reasonably explained by considering the diffusion coefficient of these metals through the porous ionic membrane which is mainly dependent on their polarity, electronic configuration, ionic radii,.. etc., and also importantly on the nature of interaction with the functional groups of the membranes. Li^+ , wich is tested as a toxic metal ion , is not capable of chelation or complexation with the functional groups of membranes because of its electronic configuration and its uptake may be a type of adsorption.

It is also observed that, under the same reaction conditions, KOH -treated membranes show high tendency to metal chelation or complexation than the NH_2OH -treated ones, but the sequence order of metal uptake remains the same .

In general, the grafted and treated membranes showed a good affinity towards the chelation and/or complexation with different heavy or toxic metal ions investigated here and the efficiency of such membranes is high and the maximum metal uptake reached after 8 hr.

2. Effect of pH of Feed Solution

The availability of grafted polymers under investigation for metal ion complexation is pH dependent. The sorption characteristics of grafted membranes treated either with KOH or NH_20H toward Fe^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+} ,Pb^{2+} and LI^{+} metal ions are investigated over pH that ranged from 1 - 6. The sorption affinity of the sorbents are plotted as a function of pH and shown in Figs. (7 , 8). It can be seen that, the amount of metal ions uptake by chelating polymer increases significantly as the pH increases and the maximum uptake reaches at pH=5. The uptake of Fe^{3+} ions reaches its maximum at pH=3 then it decreases due to the formation of its hydroxide. On the other hand, the metal ion uptake under high acidic conditions is sharply decreased for almost every chelating exchanger due to competition from hydrogen ions.

The above results indicated that, each metal ion has its optimum pH at which it can be easily extracted by these membranes, i.e. the metal uptake is very dependent on pH of its feed solution.

3. Effect of Temperature

The temperature is another important factor which affect the chelation or complexation of metal ions with the functional groups, i.e. affecting the amount of metal uptake by the tested membranes. Figures. (9, 10) show the relation between the amount of metal ions uptake expressed in (m mole/g) and temperature for grafted LDPE membranes that treated with either KOH or NH_20H. It can be seen that, the amount of metal ions uptake increases with increasing temperature for all kinds of membranes investigated. This is attributed to the increase in' kinetic energy of the metal ions with temperature and the flexibility of the polymer graft chains increases as well. Consequently, the diffusion of the metal ion solution in the membrane increases with temperature and the amount of metal ion uptake increase as well. It was observed that, the maximum metal ions uptake obtained at the boiling point at which the highest diffusion is occurred.

Conclusion

It can be concluded that, the prepared graft copolymer possessed good mechanical, electrical and hydrophilic properties. The grafted films, thus obtained, containing both nitrile and carboxylic groups which were then hydrolysed with KOH or NH_20H to confer ionic character of easily ionizable groups may be of interest in some practical uses as in the field of waste water treatment. These synthetic grafted membranes can be used for removal of some toxic and heavy metals such as Fe^{3+}, Cu^{2+} ,Co^{2+}, Cd^{2+}, Sr^{2+} ,Pb^{2+} , and Li^{+}... etc.

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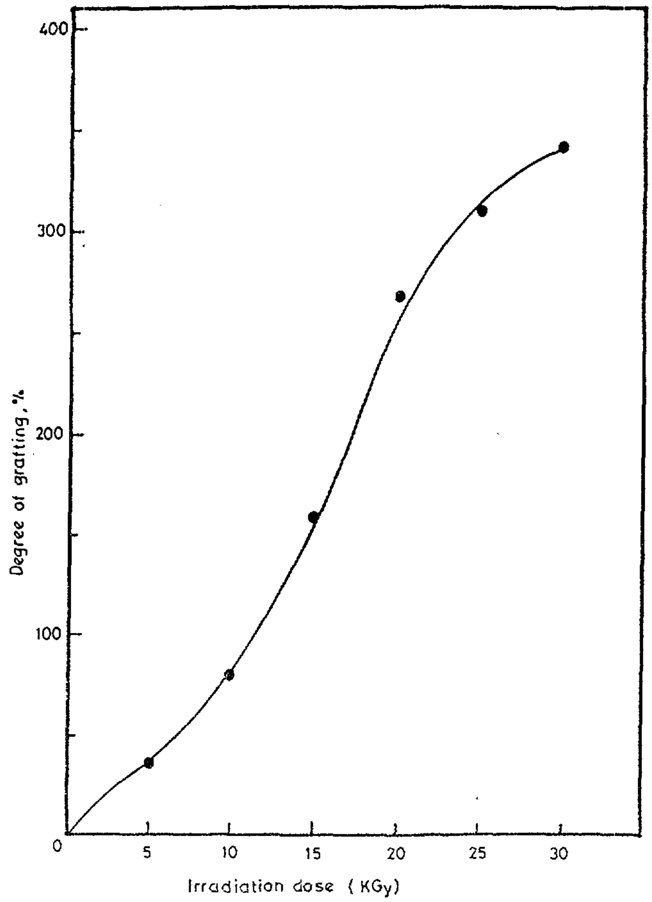

Fig. 1 : Effect of Irradiation Dose on The Grafting Yield of AN/Vac 70/30 (wt.%) onto LDPE in DMF Where Comonomer Concentration is 60(wt.%).

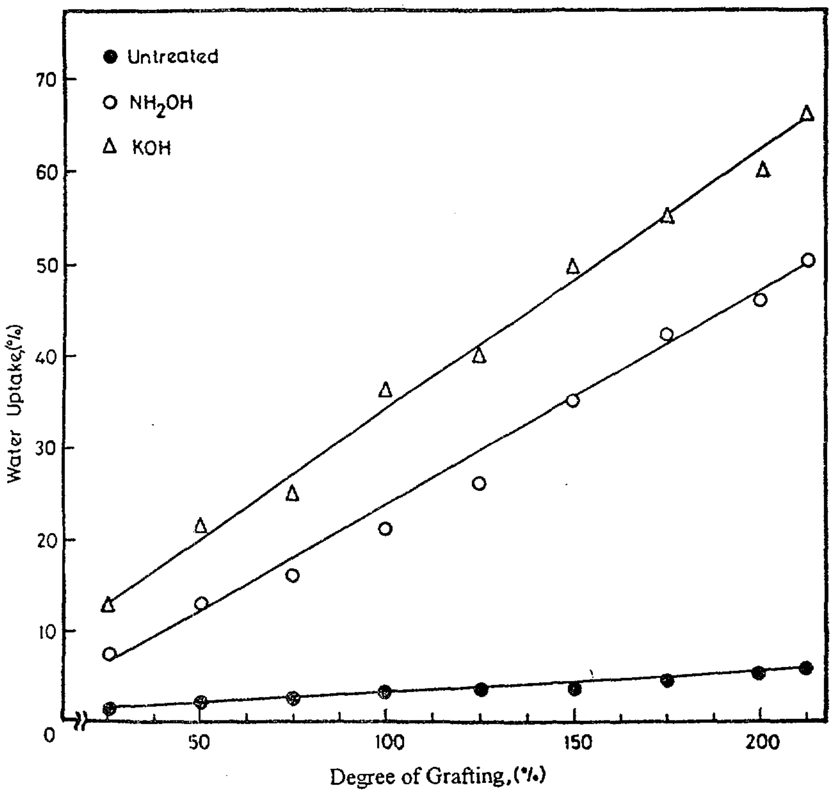

Fig. 2 : Water Uptake as a Function of Grafting Yield of AN/Vac 70/30 (wt.%) onto LDPE films.

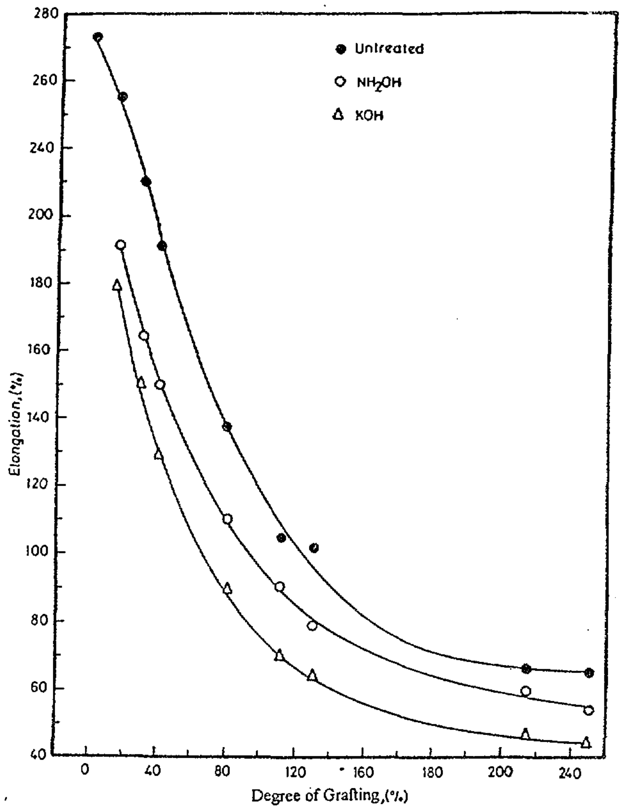

Fig. 3 : Change in Elongation percent for Untreated and Treated LDPE with Degree of Grafting.

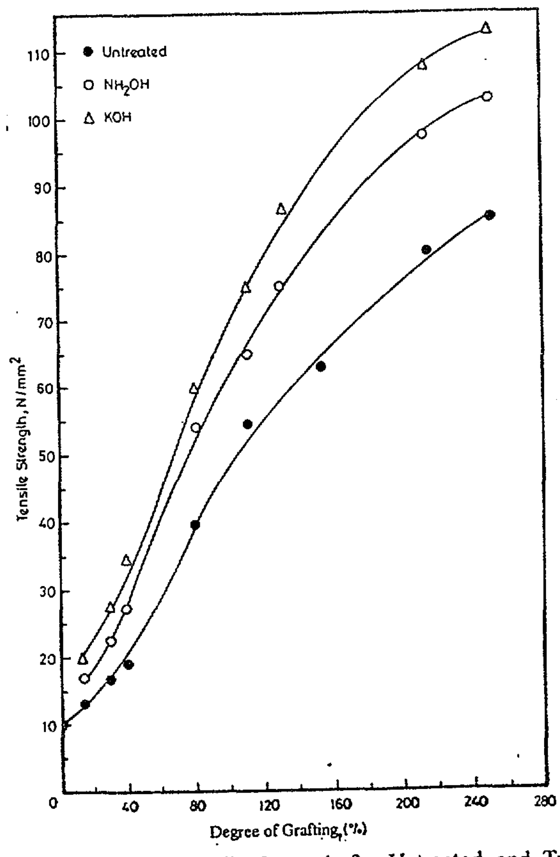

Fig. 4 : Change in Tensile Strength for Untreated and Treated LDPE with Degree of Grafting.

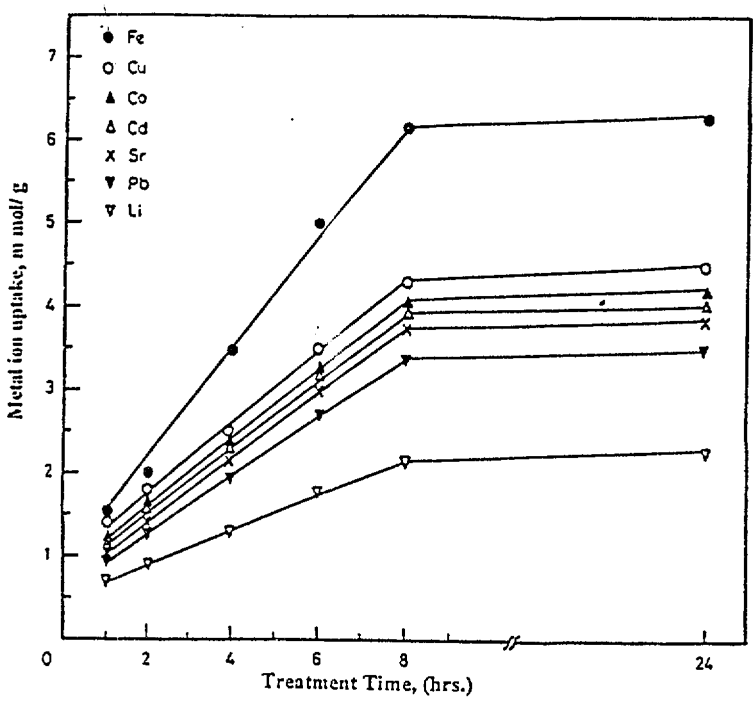

Fig.5 : Effect of Treatment Time on Metal Uptake For Treated Grafted LDPE by KOH having Degree of Grafting 200%; Initial Feed Conc.= 1000 ppm; pH (Fe=3; Cu, pb and Sr= 5 and Li, Cd and Co= 6) and Temp.= 100 °C.

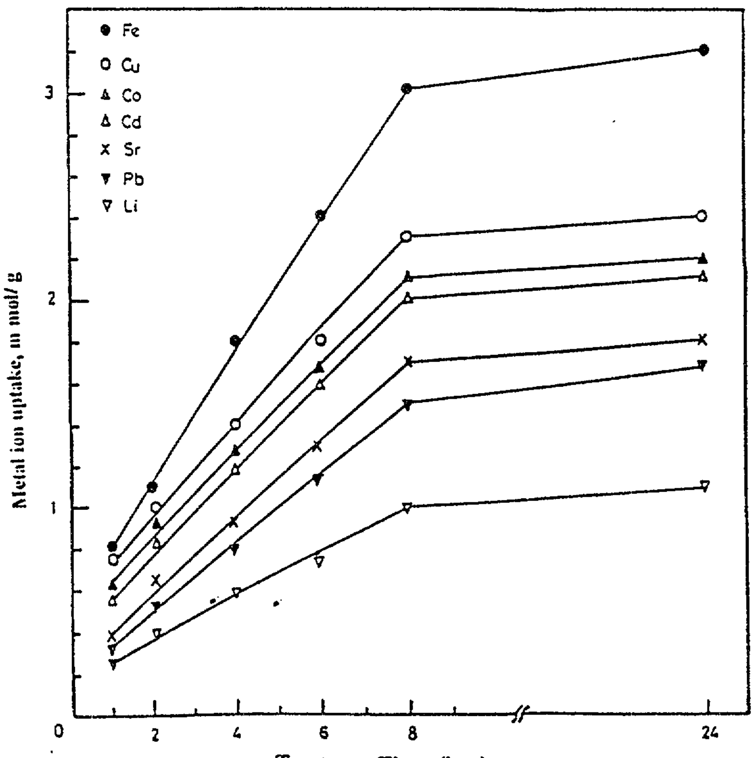

Fig. 6 : Effect of Treatment Time on Metal Uptake For Treated Grafted LDPE by NH_2OH having Degree of Grafting 200%; Initial Feed Conc.= 1000 ppm; pH (Fe=3; Cu, pb and Sr=5 and Li, Cd and Co= 6) and Temp.= 100 °C.

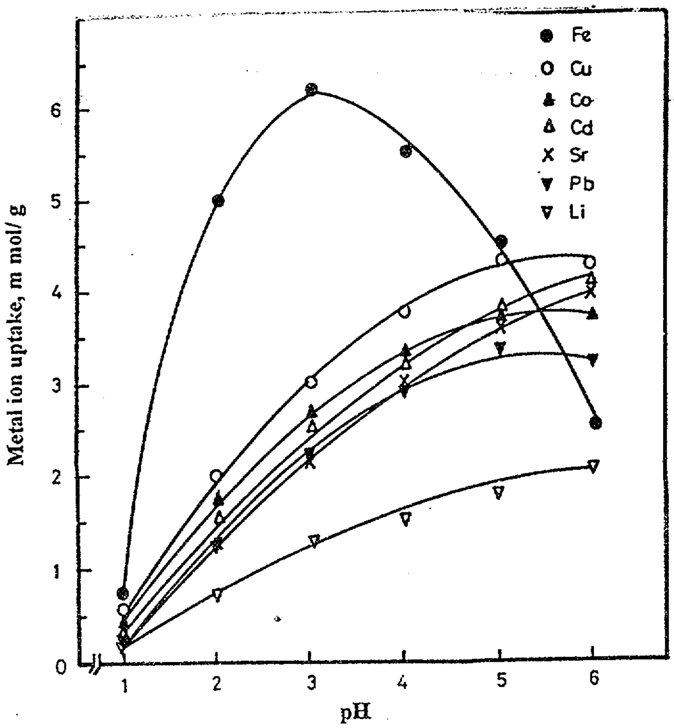

Fig. 7 : Effect of pH on Metal Uptake For Treated Grafted LDPE by KOH having Degree of Grafting 200%; Initial Feed Conc.= 1000 ppm; Time= 8 hr. and Temp.=100 °C.

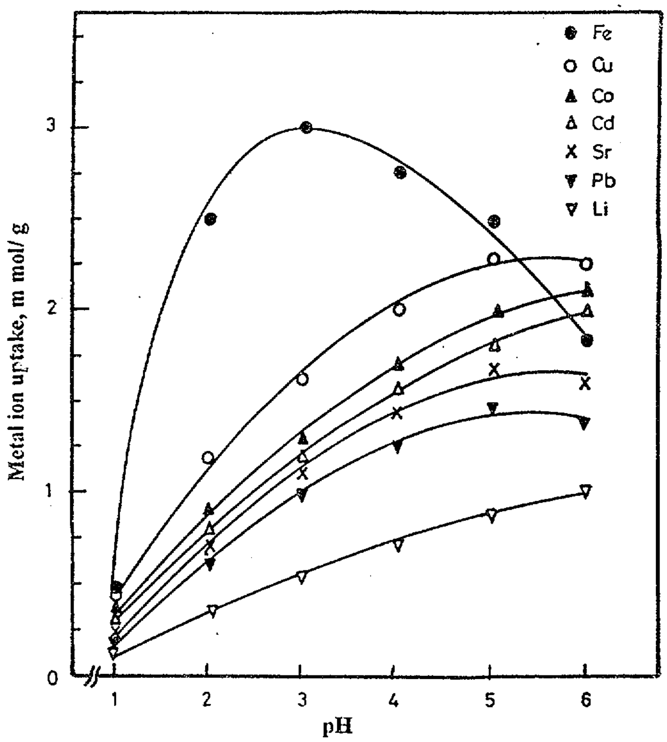

Fig. 8 : Effect of pH on Metal Uptake For Treated Grafted LDPE by NH_2OH having Degree of Grafting 200%; Initial Feed Conc.= 1000ppm; Time = 8hr. and Temp.= 100 °C.

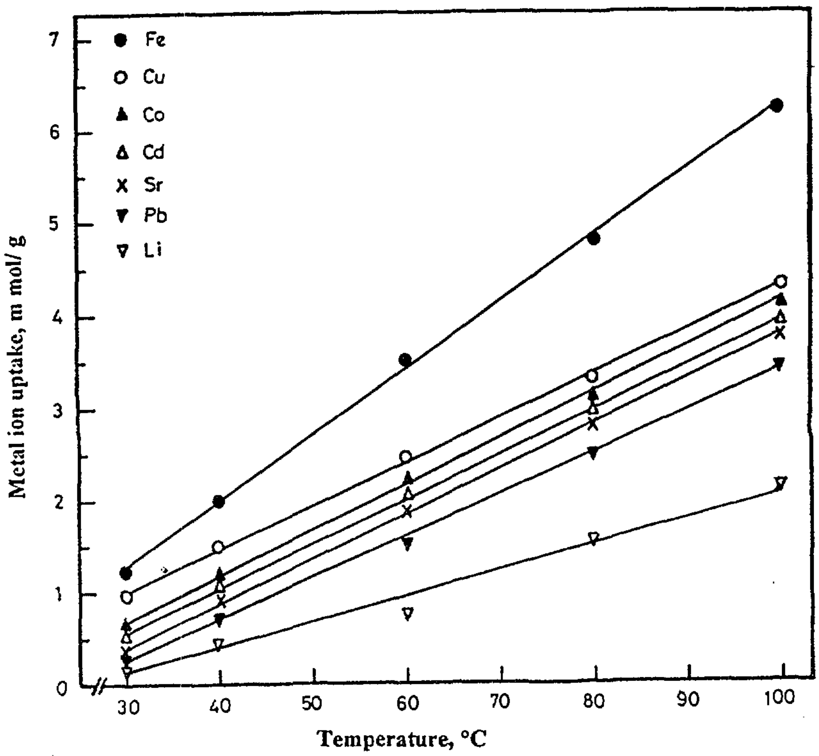

Fig. 9: Effect of Temp. on The Metal Uptake For Treated GraftedLDPE by KOH having degreeof Grafting 200%; Initial Feed Conc. =1000 ppm; Time= 8 hr.and pH (Fe=3; Cu, pb and Sr= 5 and Li, Cd and Co= 6)

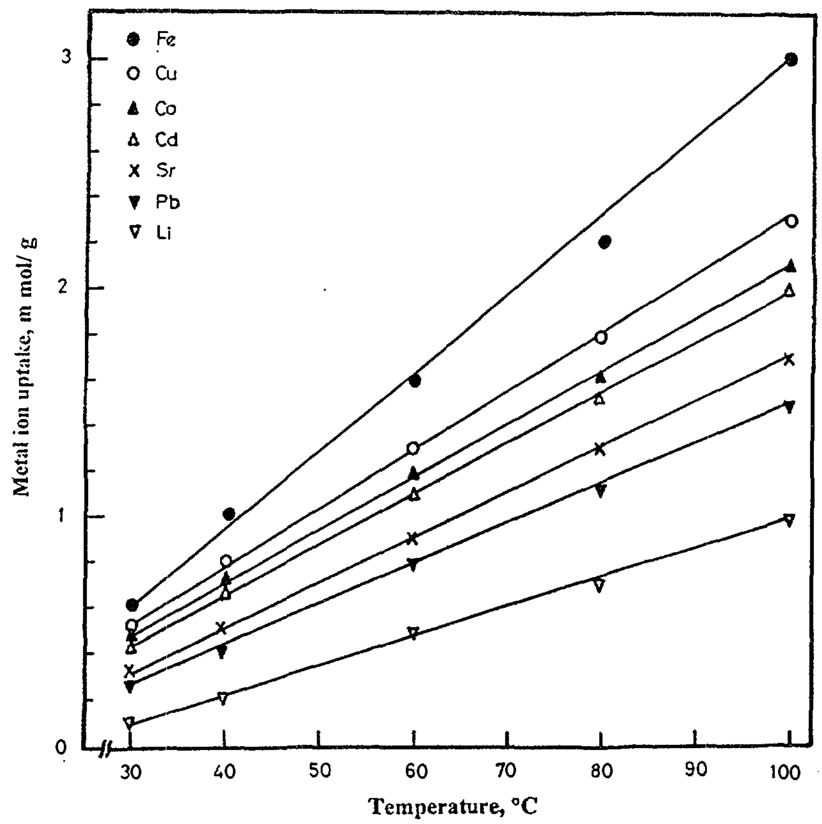

Fig. 10 : Effect of Temp. on The Metal Uptake For Treated Grafted LDPE by NH_2OH having Degree of Grafting 200%; Initial Feed Conc.=1000ppm;Time=8hr.and pH (Fe=3; Cu, pb and Sr= 5 and Li, Cd and Co= 6) .