Adsorption of Ce(III) from Aqueous Solution using Acrylic Acid Grafted Low Density Polyethylene Films

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Abstract: In this study, grafted and chemically treated low density polyethylene films (LDPE) has been used to remove cerium ions (CeIII) from liquid radioactive wastes to level permitting their discharge into the environment. Batch equilibrium techniques have been performed. The amount adsorbed of Ce(III) ions has been studied as a function of initial pH of solution, agitation time, adsorbate concentration and temperature to find that the amount adsorbed of Ce(III) increases with increasing initial Ce(III) concentration. Maximum adsorption of Ce (III) was found at pH 4 in an equilibrium time of 120 min. The maximum adsorption capacity of untreated and KOH-treated LDPE-g-P(AAc) films was found to be 34 and 37.1 mg/g, respectively. The kinetic sorption of Ce(III) onto grafted and chemically treated LDPE films were studied using Lagergren equation and the equilibrium rate constant for sorption (k_{ads}) was calculated. The results obtained revealed that sorption obeyed the first order rate expression according to Legergren. The value of k_{ads} at 30, 40, and 50 ^{0}C for both the untreated and KOH-treated films was calculated and shows that the process is endothermic. Arrhenius Equation was used to determine adsorption type of Ce(III) onto grafted-untreated and grafted-treated films. Activation energy values for the adsorption process were calculated to find that chemical force govern the adsorption of Ce(III) onto grafted-untreated and physical forces govern the adsorption onto grafted-treated films. The results obtained in this study illustrate that KOH-treated LDPE-g-P(AAc) films is expected to be an effective and economically valuable adsorbent for Ce(III) from aqueous system.

1. Introduction:

The environmental pollution has become one of the most essential problems that attracted the attention of many scientists at the present time. With increasing the peaceful applications of nuclear activities in Egypt, the relevant radioactive wastes have been increased[1]. The base of long term radioactive contamination of such wastes consist of long-lived radionuclides including mostly such fission products as Cs-137, Sr-90, Zr-93, 95, Ru-106, Ce-144, Sm-151, Eu-154, transuranium isotopes (Np-237, Pu-238, 239, 240, Am-241, 243, Cm-244) and radioactive isotopes induced by neutron radiation (Mn-54 and Co-60)[2]. Many methods have been used to remove the pollutants, namely, membrane filtration, coagulation, adsorption, oxidation, ion exchange, precipitation [3-8] etc. Radiation-induced copolymerization of monomers onto different polymers have been widely studied to produce membranes for various purposes, such as in separation processes and electrochemical applications[9-13]. Many studies concerning grafted membrane used to remove heavy metals such as Pb(II), Ag(I), Co(II), Mn(II) and Ni(II) from aqueous solution have been reported[14-16].

The aim of this study is to investigate the removal of Ce(III) from aqueous media and to elucidate the sorption mechanism operated in the sorption process. The study reports the results of the sorption of Ce (III) from aqueous solutions on grafted and chemically treated LDPE films. Also, interpret the kinetics of sorption of Ce(III) using the two types of sorbents.

2. 2. Experimental
2.1. Preparation

LDPE-g-PAAc was prepared as mentioned in previous study[17].

A stock solution of 1000 mg/l of the standardized Ce(III) was prepared by dissolving appropriate quantity of AR grade $Ce(NO_3).6H_2O$ (Merck) in 1000 ml of bidistilled water. The stock solution was further diluted with deionized water to desired concentration for obtaining the test solutions. The initial metal ion concentrations ranged from 50-100 ppm.

2.2. Characterization of the grafted films

Fourier transform infrared (FTIR) spectrophotometer analysis of the grafted treated films and those loaded with Ce(II) were recorded on

a FTIR-1000 spectrophotometer (Mattson, UK) in the range of 500-4000 cm^{-1}.

2.3. Adsorption procedure

The adsorption of Ce(III) usinf grafted and chemically treated LDPE were studied by a batch technique including the effect of pH, contact time, initial metal ion concentration, and temperature. In the first set of experiments, adsorption percentage was studied at various pH values of (1-6) for the grafted and grafted treated LDPE of 0.05 g/20 ml. The initial Ce(III) concentration was 50 ppm and the predetermined time (180 min.) in a shaking bath (FIRSTEK model B601 D) at a speed of 100 rpm. The second set of experiments were conducted with various agitation time, various initial Ce(III) concentration (from 50 to 100 ppm) at constant adsorbent dosage (0.05g/20 ml) and at optimized pH 4. After completion of every set of experiments the supernatant was separated by fil tration using Whatman filter paper no. 42 and then collected and analyzed for Ce(III) ions concentration by atomic absorption spectrophotometer (Perkin-Elmer 2380) using lamps for Ce(III). Merck atomic absorption standard solutions of Ce(III) metal were used for calibration process. To estimate the percentage removal of Ce(III) from aqueous solution the following equation was used:

Adsorption capacity q (mg/g) = (A-A$_o$) V/m   (1)

Metal uptake (q_e) at equilibrium time was calculated by mass balance expression:

$$w (q_e - q_o) = v (C_{0-}C_e)   .... (2)$$

Where C_o and C_e are the initial and equilibrium metal ion concentration, respectively.

3. Result and Discussions
FTIR - spectrophotometer

The use of IR spectroscopy is a well-known method for the identification of groups and quantitative analysis. Peak around 1600 Cm^{-1} due to C=O group of COOH and a broad band of the O-H stretching appeared around 3500 Cm^{-1}, suggesting the presence of OH groups of carboxylic acid groups and water molecules within the film. Fig. 1 (curve 1) shows an FTIR spectrum of LDPE-g-P(AAc)/KOH-treated loaded with Ce(III). Weak bands due to the asymmetric and symmetric stretching of CH$_2$ were observed at 2938 and 2864 Cm^{-1} in the spectrum. Bands assigned to the asymmetric and symmetric stretching modes of COO$^-$ appeared at 1513 and 1468 Cm^{-1} in the spectrum. The triplet of peaks at 1640, 1513 and 1468 Cm^{-1} may be due to a compination of carbonyl groups with other substituents[18].

The absorption band at 1030 Cm^{-1} along with the triplet at 3699, 3653 and 3622 Cm^{-1} is indicative of Ce-carboxylate.
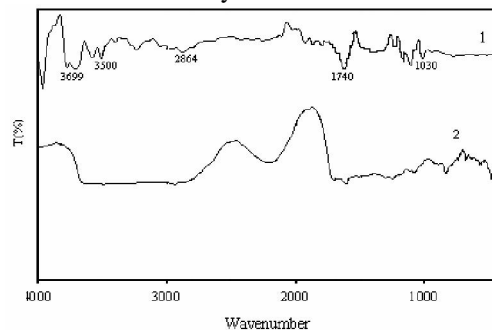

Fig.1. IR-spectra of (1) LDPE-g-(PAAc)-KOH treated and loaded with Ce(III) (2) LDPE-g-(PAAc)-KOH treated .

Thermal behavior

The thermal behavior of grafted-untreated, grafted-treated membranes containing 85 % degree of grafting and that at which Ce(III) ions is adsorbed with various concentrations was evaluated using thermogravimetric analysis (TGA). The TGA thermograms are presented in figure 2. The membranes showed a multi-step degradation pattern in the temperature range of 50-600 ^{o}C. The thermograms may be devided into three distinct steps (i.e. dehydration, grafted side chain degradiation and PE main chain decomposition). Unlike the grafted-untreated membrane, all samples show residue at the end of the thermograme. Since the membrane is hydrophilic in nature, the initial weight loss in the thermograme is due to the loss of water from the membrane matrix up to 160 ^{o}C. In the TGA thermograme, the initial decomposition temperature (IDT) is evaluated to be 232 ^{o}C for the grafted-untreated membrane and it increases with KOH-treatment to become 293 ^{o}C. the weight loss at 232 ^{o}C was due to dehydration of AAc-grafted chains[19].
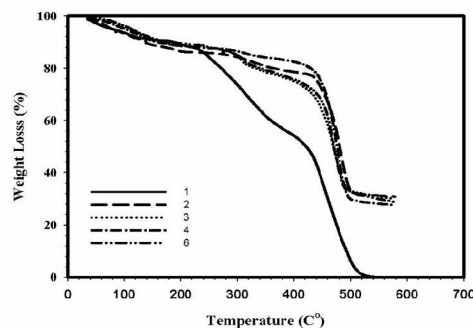

Fig. 2. TGA Thermal digram for a series of (1) LDPE-g-P(AAc), (2) LDPE-g-P(AAc)-KOH treatedI), (3) LDPE-g-P(AAc)/KOH treated and loaded with 70 wt.% Ce(III), (4) LDPE-g-P(AAc)/KOH treated and loaded with 80 wt.% Ce(III), and (6) LDPE-g-P(AAc)/KOH treated and loaded with80 wt.% Ce(III).

The weight loss at different decomposition temperature for the grafted, grafted-treated, and that contain Ce(III) films are presented in table (1).

Table 1. Weight loss at different decomposition temperature for (1) LDPE-g-P(AAc), (2) LDPE-g-P(AAc)-KOH treatedI), (3) LDPE-g-P(AAc)/KOH treated and loaded with 70 wt.% Ce(III), (4) LDPE-g-P(AAc)/KOH treated and loaded with 80 wt.% Ce(III), and (6) LDPE-g-P(AAc)/KOH treated and loaded with80 wt.% Ce(III).

Sample No	Initial Temp	30 % Wt loss	50 % Wt loss	70 % Wt loss
		Temp	Temp	Temp
1	232	314.7	421.6	459.7
2	293	453.8	480.6	577.8
3	293	432.6	469.6	577.3
4	293	456.8	475.5	499
6	293	440.7	469.8	549.4

The alkaline treatment of the graft copolymer enhances its thermal stability as shown in table (1). Thus for the grafted treated with KOH event up to a temperature of 480.6 ^{o}C only about 50 % in weight loss of grafted-treated films takes place, however, the same weight loss was occurred at 421.6 ^{o}C for the grafted untreated films.

These results suggest that the thermal stability of the grafted membranes is enhanced by the introduction of Ce(III) ions.

3.2. Adsorption procedure
3.2.1. Effect of contact time

These experiments were carried out to establish the proper time for shaking until sorption of Ce(III) at various temperatures reaches equilibrium on both untreated and chemically treated LDPE-g-PAAc and the data obtained are shown in figures (3&4). It was observed that, at a given temperature, the chemically treated LDPE-g-PAAc has a higher initial adsorption rate for Ce(III) ions than chemically untreated ones and the adsorption equilibrium of both chemically treated and untreated ones for Ce(III) ions was attained after 120 min, and it reached to 19.5 mg/g, 15.5 mg/g by using KOH-treated and untreated LDPE-g-PAAc, respectively. It was found that the adsorption temperature has possessed no influence on equilibrium. It was also observed that at a given contact time, the adsorption amount of Ce(III) ions onto chemically treated grafted films is not affected to great extent with increasing adsorption temperature, but the adsorption amount increases with increasing adsorption temperature for chemically untreated ones. This indicating that the

adsorption process is endothermic and higher temperature is needed for adsorption of Ce(III) ions onto the untreated grafted films (H-form).
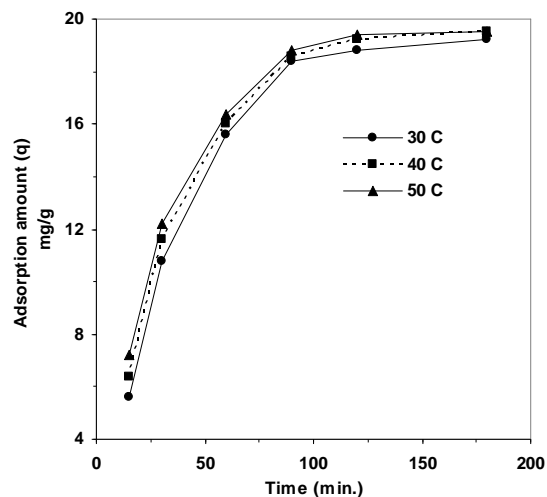

Fig.3. Effect of contact time on the adsorption amount of Ce(III) KOH-treated LDPE-g-P(Aac) at different temperatures. Ce(III) concen. 50 mg/l; m 0.05 g; vol; 20 ml; pH 4.
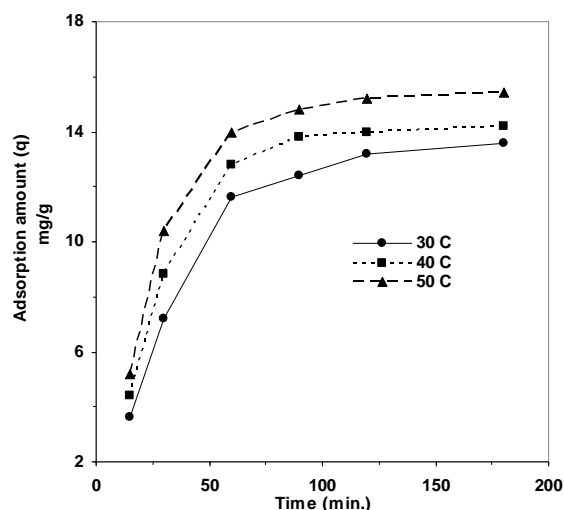

Fig.4. Effect of contact time on the adsorption amount of Ce(III) onto untreated LDPE-g-PAAc at different temperatures. pH 4; Ce(III) concen. 50 mg/l; m 0.05 g; vol. 20 ml.

3.2.2. Effect of pH

The aqueous solution pH is an important operational parameter in the adsorption process because of its effect on the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction[20]. The effect of the initial pH on adsorption amount was investigated at the pH ranges of 2.5-6 at room temperature and the results are shown in figure (5). It can be seen that the adsorption of Ce(III) ions on the

untreated and KOH-treated LDPE-g-PAAc is poor at pH which is lower than pH3. Thereafter, the adsorption increased significantly with the increase of pH value reaching a maximum value of 19.4 and 13.8 mg/g at pH 4 for the chemically treated and untreated LDPE-g-PAAc, respectively. The adsorbed amount of Ce(III) ions onto the chemically treated grafted films is much more than that of the untreated ones because more ionizable and have higher hydrophilicity. At low pH values, (<pH 3) the high concentration of hydrogen ion at the interface repels the positively charged metal ions electrostatically and prevent their approach to the adsorbent surface [21]. At higher pH value (> pH 4) the adsorption amount reached a plateau value.
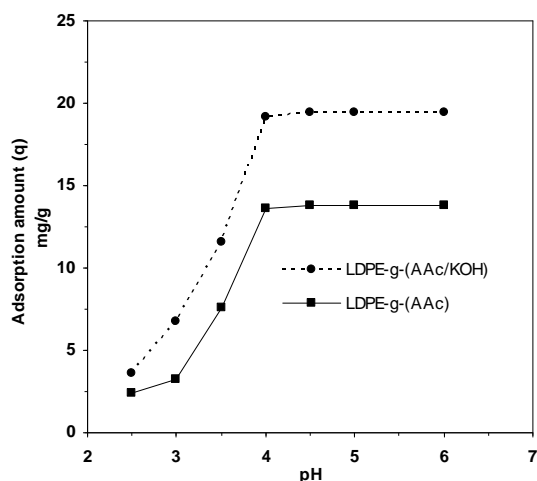

Fig.5. Effect of pH on the adsorption amount of Ce(III) by using grafted-untreated and chemically treated LDPE. Time 120 min.; Concen.; 50 mg/l; M 0.05g; Vol.; 20 ml.

3.2.3. Effect of initial metal ion concentration

The effect of initial concentration of Ce(III) ions on the adsorption amount was investigated and the results are shown in figure 6 (a & b). It can be obvious that at a given contact time the adsorption amount of Ce(III) ions increased with increasing initial Ce(III) concentration for both the untreated and chemically treated grafted films and it reached to steady state for all metal ion concentration after 120 min. The adsorption amount of Ce(III) ions by the chemically treated grafted films is higher than that of the untreated ones which may be attributed to the presence of more ionizable groups (-COOK) in the chemically treated grafted films.
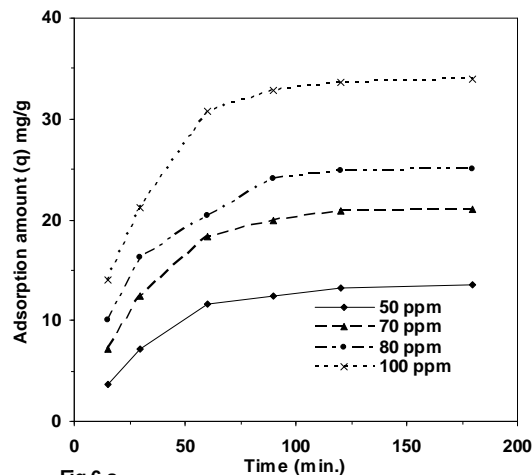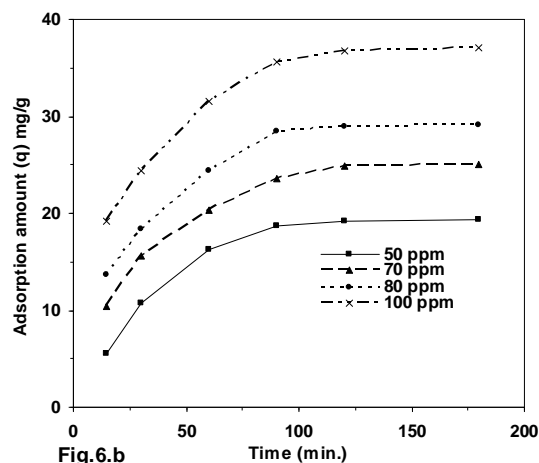

Fig 6.a

Fig.6.b

Fig. 6 (a & b) Rate of adsorption as a function of initial Ce(III) concentration for (a) LDPE-g-P(AAc) and (b) LDPE-g-P(AAc)/KOH-treated.
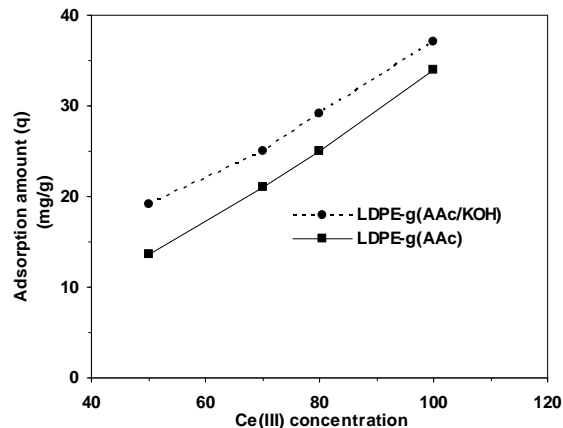

Fig. 7 Effect of initial concentration on the adsorption amount of Ce(III) by using grafted and chemically treated LDPE. Time 120 min.; Vol.; 20 ml; M 0.05 g; pH 4,Temp. 40 ℃.

3.2.4. Kinetic study

The kinetic sorption of Ce(III) onto grafted and chemically treated polyethylene films were studied using Lagergren equation[21]:

$$\ln(q_e-q) = \ln q_e - (K_{ads})\, t \quad …(3)$$

Where, q (mg/g) is the amount of sorbed Ce(III) ions at time t, q_e (mg/g) is the amount sorbed at equilibrium, and K_{ads} is the equilibrium rate constant for sorption.

Figures (8&9) show the plots of ln (q_e-q) versus time (t) at different temperatures for grafted and grafted-treated polyethylene films. The results obtained revealed that sorption obeyed the first order rate expression according to Legergren. The correlation coefficient values (R^2) for the first-order rate expression were found greater than 0.97 for all temperature studied. The value of K_{ads} at 30, 40, and 50 ^{0}C for both the untreated and KOH-treated were calculated from the slops of the straight lines and the data are shown in table (2). The increase in rate constants depending on temperature shows that the process is endothermic.

Table 2. K_{ads} values of Ce(III) at different temperatures by using KOH-grafted treated LDPE films and untreated LDPE-g-P(AAc).

Temperature (^{o}C)	30	40	50
K_{ad} (treated)	-0.015	-0.0162	-0.0194
(untreated)	-0.013	-0.0157	-0.0169

Fig.9. Lagergren plot for the sorption of Ce(III) ions using LDPE-g-(PAAc)-KOH treated

In order to determine adsorption type of Ce(III) onto grafted-untreated and grafted-treated LDPE films, Arrhenius Equation was used. For this purpose ln K_{ads} values were plotted versus 1/T and activation energy values were calculated from the slop of the line obtained (Fig. 10). Activation energy values for the adsorption process were calculated to be 11 and 7 Kj/g mole for the grafted-untreated and grafted-treated LDPE, respectively. These values suggest that chemical force govern the adsorption of Ce(III) onto grafted-untreated and physical forces govern the adsorption onto grafted-treated films.
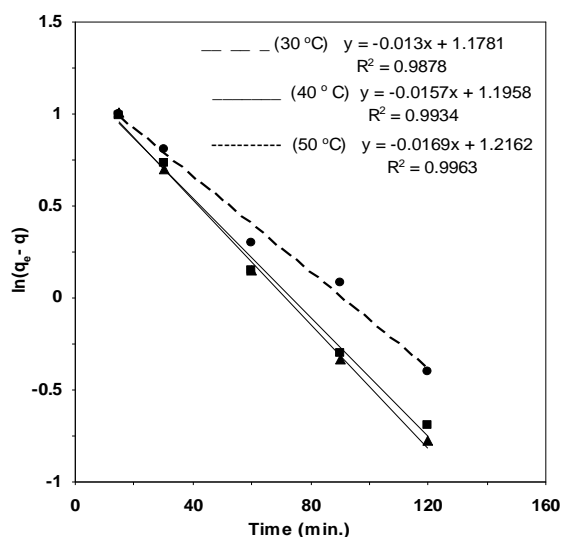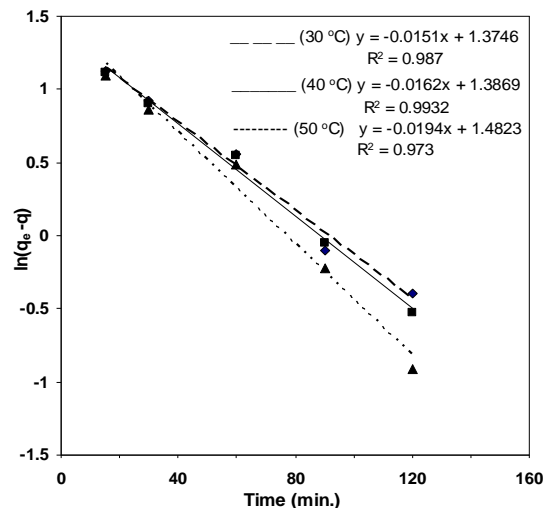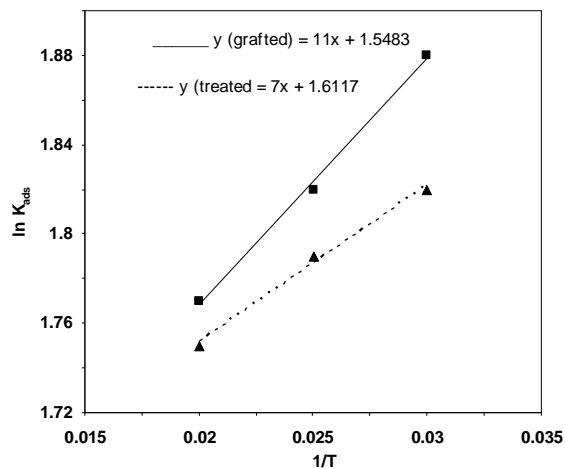

Fig.8. Lagergren plot for the sorption of Ce(III) ions using LDPE-g(PAAc)- untreated.

Fig. 10. Arrhenius plot for adsorption of Ce(III) on grafted and chemically treated LDPE.

3.2.5. Effect of temperature

The effect of temperature on the adsorption amount of Ce(III) ions onto grafted and grafted-KOH-treated was studied within range 30-50 ^{o}C and the results are shown in figure (11 a). With increasing

adsorption temperature the adsorption amount of Ce(III) on the KOH – treated films is not affected to great extent because they possess high hydrophilicity and ionisability properties. Figure (11 b) was deduced from figure 10 and the activation energies of adsorption were calculated from the slop of fig. 11 b as 1.3 and 6 Kj/mol for the grafted-treated and grafted-untreated films, respectively, which indicates that adsorption of Ce(III) on the grafted – treated was easier than on grafted – untreated ones.
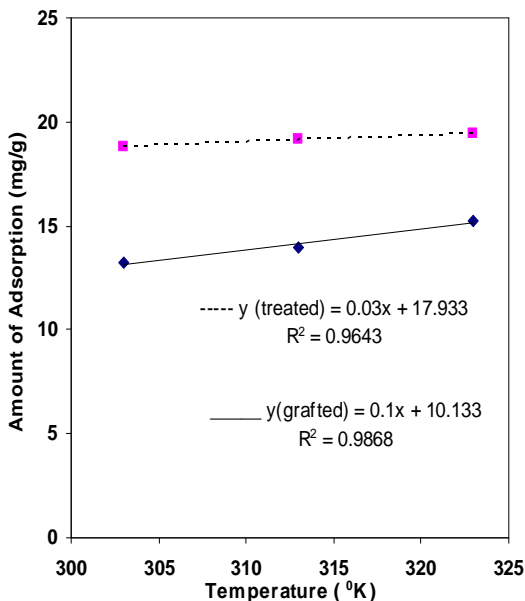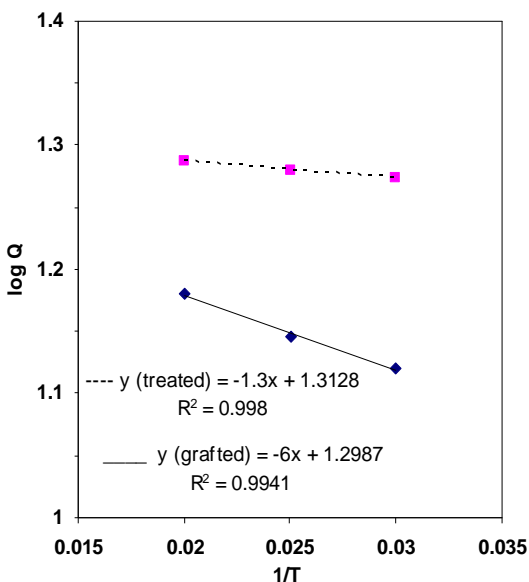
Fig.11(a)

Fig.11(b)

Fig.11(a&b) Effect of temperature on the adsorption amount of Ce(III) using grafted and chemically treated LDPE.

4. Conclusion:

Grafted and chemically treated low density polyethylene has been used to remove cerium from liquid radioactive wastes to level permitting their discharge into the environment. Maximum cerium (III) removal was found at pH 4.0 in an equilibrium time 120 min and temperature 50 °C. The adsorption capacity for LDPE-g-P(AAc)/KOH-treated films was found to be 37.1 mg/g when the initial Ce(III) concentration was 100 ppm. The kinetic sorption of Ce(III) onto grafted and chemically treated polyethylene films revealed that sorption obeyed the first order rate expression according to Legergren equation. The value of K_{ads} at 30, 40 and 50 °C for both the untreated and KOH-treated were calculated to find that the rate constant depends on temperature and the process is endothermic. The activation energy values for the adsorption process suggest that chemical force govern the adsorption of Ce(III) onto grafted-untreated and physical force govern the adsorption onto grafted-treated films. The results obtained in this study illustrate that the grafted and chemically treated LDPE films is expected to be an effective and economically valuable adsorbent for Ce(III) from aqueous system.

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