



Preparation and application of acrylic acid grafted polytetrafluoroethylene fiber as a weak acid cation exchanger for adsorption of Er(III)

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ABSTRACT

In this work, a weakly acidic ion exchange fiber (PTFE-g-AA) has been prepared by ^{60}Co irradiation grafting with acrylic acid (AA) onto the polytetrafluoroethylene (PTFE) fiber. The grafted fiber was characterized by FTIR, SEM and TGA technique. The exchange capacity of the PTFE-g-AA fiber is 3.87 mmol/g. The adsorbent material was employed for Er(III) uptaking by batch and column experiments. Kinetics studies showed that the adsorption process obeyed pseudo-second-order kinetics. The adsorption isotherms followed both the Freundlich model and Langmuir model. The maximum adsorption capacity of the PTFE-g-AA fiber for Er(III) was evaluated to be 142.0 mg/g for the Langmuir model. It was found that 0.75 M HCl–0.25 M NaCl solution provided effectiveness of the desorption of Er(III) from the PTFE-g-AA fiber. Various thermodynamic parameters such as standard enthalpy (ΔH^0), standard entropy (ΔS^0) and standard free energy (ΔG^0) were evaluated. The adsorption of Er(III) on the PTFE-g-AA fiber was found to be endothermic in nature. The Thomas model was successfully applied to experimental data to predict the breakthrough curves and to determine the characteristics parameters of the column useful for process design.

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1. Introduction

During the past decades, rare earth elements (REEs) have been widely used in functional materials, catalysts and other products in industry, diagnosis reagents of magnetic resonance imaging in medicine and some fertilizers in agriculture (especially in China) [1]. The rising use of the REEs increases the possibility of their release into the environment, resulting in a potential risk to the environment. Extraction and preconcentration of these valuable metal ions from wastes are extremely important not only from the point of view of their limited resource availability, but also to reduce their quantum for disposal as radioactive wastes. Different techniques have been proposed for group separation and preconcentration of REEs, including off-line techniques like batch experiments, solid phase extraction (SPE) and counter current chromatography (CCC), as well as on-line methods using SPE chromatographic units, cloud-point and liquid/liquid extraction. For these techniques various agents have been employed, e.g. iminodiacetates, 8-hydroxyquinoline, cation-exchange resins [2], and organophosphates [3]. However, these techniques have certain disadvantages such as low speed of adsorption process, poor thermal stability and regeneration ability. Comparing with these materials, ion exchange fiber (IEF) has a larger effective specific surface

area, higher speeds of adsorption and elution process. Besides, IEF also has particular textile structure that is more convenient to be used in practice [4]. Many organic fibers or modified fibers, such as polyacrylonitrile and polypropylene, have been used as the precursor fiber for the preparation of IEF [5,6]. But for some special application, they are limited by their poor thermal stability and low content of surface oxygen-containing groups. Polytetrafluoroethylene (PTFE) has outstanding thermal and chemical stability. In recent years, the functional PTFE membrane prepared by radiation grafting has received more and more attention [7–10]. However, little attention has been paid to PTFE matrix based IEF and its adsorption property for the removal of the REEs.

The aim of this work is to prepare an IEF by radiation-induced grafting of AA onto PTFE fiber and apply it as a cation IEF to the adsorption of Er(III). The influence of experimental conditions such as metal ion concentration, pH value and temperature was discussed as to determine the optimum parameters for removal of Er(III) from aqueous solution by the new prepared fiber.

2. Materials and methods

2.1. Materials

The polytetrafluoroethylene (PTFE) fiber was purchased from Tongchuang Co., Beijing, China ($\phi = 20 \mu\text{m}$). The fiber was washed by acetone and distilled water and dried at 323 K before use. 1.0 mg/ml stock solution of Er(III) was prepared by dissolving

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1.1436 g analytical grade Er_2O_3 in appropriate amount of concentrated hydrochloric acid and then diluted with double distilled water in a 1000 ml volumetric flask. The required lower concentrations were prepared by dilution of the stock solution, which was prepared freshly for each experiment. Buffer solution of pH 3.00–7.00 was prepared from HAC–NaAc. Other reagents used were of analytical reagent grade.

2.2. Apparatus

Infrared spectra were obtained with FTS6000 Spectrometer (Bio-Rad), equipped with a continuum microscope and an ATR objective; SEM micrographs were obtained with SS-550 scanning electron microscope (Shimadzu); thermo-gravimetric analysis was performed on a TGA instrument (Mettler Toledo). A Shimadzu UV-2550 UV–vis spectrophotometer was used for quantitative determination of the concentration of Er(III); Mettler toledo delta 320 pH meter was used for pH measurement. The sample was shaken in the DSHZ-300A temperature constant shaking machines.

2.3. Preparation of the PTFE-g-AA fiber

The PTFE fibers were sequentially washed with DDW, 1 mol/l HCl, DDW, 1 mol/l NaOH, DDW and acetone, and then dried in a vacuum oven at 323 K for 48 h. Fifteen grams of the above treated PTFE fiber was immersed into a certain amount of AAC and deionized water in a 500 ml flask, and 2.8% Mohr's salt was also added as to minimize the homopolymerization of AA during the grafting process. The flask was sealed after the solution was degassed by bubbling with a high purity nitrogen flow for 20 min to remove oxygen and then directly subjected to ^{60}Co irradiation at a dose rate of 0.5 kGy/h for a given time [11]. After irradiation, the grafted PTFE fibers were filtered and repeatedly washed with 1 mol/l NaOH, DDW, 1 mol/l HCl, DDW for three times to remove absorbed iron ions and the residual monomer and homopolymers. Finally, the grafted fibers were washed with copious amount of acetone and dried in a vacuum oven at 323 K for 48 h and then weighed. The degree of grafting was obtained using the following formula:

$$G (\%) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o and W_g are the weights of the original and grafted fibers, respectively.

2.4. Materials characterization

Infrared spectra were obtained with FTS6000 Spectrometer (Bio-Rad Co. Ltd.). FTIR-ATR measurements were carried out in a range of 4000–500 cm^{-1} , equipped with a continuum microscope and an ATR objective; SEM micrographs were obtained with SS-550 scanning electron microscope (Shimadzu); thermo-gravimetric analysis was performed in a range of 25–700 °C by 10 °C min^{-1} under nitrogen protection on a TGA instrument (Mettler Toledo, Switzerland). The adsorption properties of PTFE-g-AA fiber were evaluated by the adsorption of Er(III) from aqueous solution at different pH values, temperature, initial metal ion concentrations, contact time and adsorbent dosages.

2.5. Adsorption experiments

2.5.1. Batch studies

A desired amount of treated PTFE-g-AA fiber was weighed and added into a conical flask, in which a known volume of $\text{N}(\text{C}_2\text{H}_4\text{OH})_3\text{-HNO}_3$ buffer solution with pH 7.2 was added. After 24 h, a required amount of stock solution of Er(III) was put. The flask

was stirred at 100 rpm in a DSHZ-300A temperature constant shaking machine at the constant temperature. Aliquot samples were taken from the flask at appropriate time intervals as necessary. The residual concentration of the Er(III) ions in the aqueous phases was measured at 580 nm by a Shimadzu UV-2550 UV–vis spectrophotometer after the complexation of Er(III) ions with arsenazo I. The adsorption capacity (q_e) and distribution coefficient (D) were calculated with the following formulas, respectively:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$$D = \frac{q_e}{C_e} \quad (3)$$

where C_0 and C_e are the initial and equilibrium concentrations of Er(III) ions in solution, V is the total volume of solution and m is the mass of the fiber.

2.5.2. Desorption studies

Desorption of Er(III) ions was performed by mixing PTFE-g-AA–Er(III) complexes and HCl–NaCl eluent solution of different concentrations, and stirred at 100 rpm for 24 h at 298 K. The final Er(III) ion concentrations in the aqueous phase were similarly analyzed as described above. The desorption ratio (E) was calculated as follows:

$$E (\%) = \frac{(C_d V_d)}{(C_0 - C_e) V} \times 100 \quad (4)$$

where E is the desorption ratio; C_d is the concentration of the solutes in the desorption solutions; V_d is the volume of the desorption solution; and C_0 , C_e and V are the same as defined above.

2.5.3. Column studies

The fixed-bed experiments were carried out at in a water-jacketed glass column with an inner diameter of 6.0 mm and a full length of 200 mm. An aliquot of the fresh PTFE-g-AA fiber (150 mg) was put into the bed. The aqueous solution with known concentrations of Er(III) ions was then fed to the top of the bed at a desired flow rate until the breakthrough curve was completed. The samples in the outlet were taken at the preset time intervals and the concentrations of Er(III) ions were similarly determined as above. In addition, dynamic desorption procedures were also carried out. With respect to the stripping of Er(III) from the grafted fiber, eluent of 0.75 M HCl–0.25 M NaCl solution was employed.

2.6. Theoretical basis

2.6.1. Adsorption isotherms

Freundlich [12] and Langmuir [13] equations are the widely used equilibrium-based isotherm models. Their linear forms are expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (5)$$

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (6)$$

where q_e is the amount of sorption, C_e is the equilibrium concentration, q_m is the maximum adsorption capacity of Langmuir, b is Langmuir constant, n is a constant indicating the Freundlich isotherm curvature, and K_f is the Freundlich sorption coefficients.

The linear Langmuir and Freundlich plots may be obtained by plotting C_e/q_e versus C_e and $\lg q_e$ versus $\lg C_e$, respectively, from which the adsorption coefficients may be evaluated.

2.6.2. Adsorption kinetics

The adsorption kinetics was tested with the following well-known models:

Table 1
Effect of monomer concentration on grafting degree.

Concentration of AA ((v/v)%)	12.5	25.0	37.5	50.0	62.5
Grafting degree (%)	10.12	25.30	38.60	38.91	39.12

The reaction conditions: irradiation dose, 24 kGy; content of Mohr's salt, 2.8% (v/v).

(1) Lagergren model

The pseudo-first-order kinetics model was proposed by Lagergren [14]. The integral form of the model generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

where q_e and q_t are the amounts of Er(III) ions per unit mass of adsorbent adsorbed on the adsorbent at equilibrium and at various times t , and k_1 is the pseudo-first-order adsorption rate constant. The value of k_1 can be obtained from the slope of the linear plot of $\log(q_e - q_t)$ versus t .

(2) Pseudo-second-order model

The kinetics of adsorption process may also be described by the pseudo-second-order rate equation [15]. The linearized form of equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e^2} t \quad (8)$$

where k_2 is the pseudo-second-order adsorption rate constant. The $k_2 q_e^2$ can be regarded as the initial adsorption rate as $t \rightarrow 0$. The plot of t/q_t versus t gives a straight line, which allows computation of q_e and k_2 .

3. Results and discussion**3.1. Graft polymerization**

Effects of the monomer concentration and irradiation dose on the grafting degree are shown in Tables 1 and 2. The grafting degree increased with the increase of the monomer concentration within the range applied in this study due to a higher concentration of the monomer at the grafting sites. However, higher monomer concentration could also cause more homopolymers and lower grafting efficiency. Higher grafting degree was obtained with the increase of irradiation dose due to the increase of the grafting sites on the fiber. However, the grafting degree reached a limit value above which the increase of the dose has little effect. A large irradiation dose could also damage the mechanical properties of PTFE fibers. According to the results of this study, the optimal monomer concentration and irradiation dose were 37.5% and 24 kGy for a moderate grafting degree. The grafting degree and carboxylic content of the grafted fibers under the optimal conditions were evaluated to be 38.60% and 3.87 mmol/g, respectively.

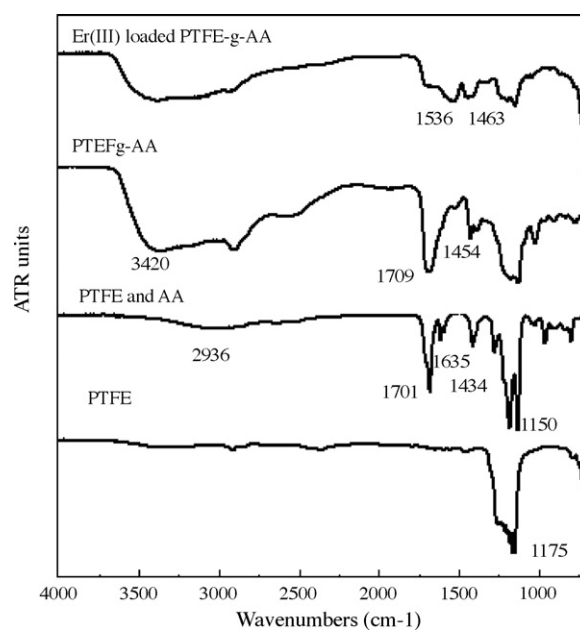
3.2. Materials characterization**3.2.1. IR spectra**

Fig. 1 shows the IR spectra of the original, acrylic acid grafted PTFE fibers and Er(III) loaded PTFE-g-AA fiber. There was a strong adsorption band at around 1175 cm^{-1} (C–F) for all of the above mentioned PTFE fibers. Compared to the spectrum of the original fiber,

Table 2
Effect of irradiation dose on grafting degree.

Irradiation dose (kGy)	8	16	24	36	48
Grafting degree (%)	16.7	32.3	38.60	38.76	38.91

The reaction conditions: monomer concentration, 37.5%; content of Mohr's salt, 2.8% (v/v).

**Fig. 1.** IR spectra of PTFE, PTFE and AA, PTFE-g-AA and Er(III) loaded PTFE-g-AA (3) fibers.

the appearance of the new bands at 1709 and $3500\text{--}2900 \text{ cm}^{-1}$ was due to the stretching vibrations of C=O and O–H, respectively, expressing the existence of carboxylic acid groups. The bands at $1470\text{--}1410 \text{ cm}^{-1}$ were corresponding to the bending vibration of O–H. In the spectrum of the mixture of PTFE and AA, a characteristic band for C=C stretching vibrations occurred at about 1635 cm^{-1} , which was not observed in the spectrum of PTFE-g-AA fiber, that may be due to the damage of C=C double-bond of AA during the irradiation. In addition, a band at around 2936 cm^{-1} corresponding to the stretching vibrations of O–H of AA was observed, which was different from that of the spectrum of the PTFE-g-AA fiber. These were the evidence for the acrylic acid had been grafted onto the PTFE fiber.

In the IR spectra of Er(III) adsorbed onto PTFE-g-AA fiber, the disappearance of the peak at 1709 cm^{-1} , the decreasing intensity at 1414 and 1454 cm^{-1} , and the appearance of a new peak around 1463 cm^{-1} were observed. Additionally, the changes in the IR spectra at $3500\text{--}2900 \text{ cm}^{-1}$ were identified. These findings may suggest that the hydrogen and oxygen atoms in the –OH and C=O groups were involved in Er(III) adsorption.

3.2.2. Scanning electron micrograph

Fig. 2(a) and (b) were the SEM analysis results. Comparing the surface of the original PTFE fiber with the grafted PTFE fiber, the smooth surface of the original PTFE fiber turned into rough. A rough grafting layer was formed on the surface of fiber after grafting, making the fiber thicker and coarser, which indicates that AA has been grafted onto the PTFE fiber after the irradiation.

3.2.3. TG analysis

The thermo-gravimetric analysis (TGA) curves for PTFE and PTFE-g-AA fibers are presented in Fig. 3. The PTFE shows an outstanding thermal stability since its starting weight loss temperature is at around 530°C . The grafting of AA has a big influence on PTFE thermal properties. Two more decomposition steps are observed in the curves of PTFE-g-AA than that of PTFE. The two decomposition steps are from 140 to 340°C and 340 to 530°C , respectively, corresponding to the damage of AA from PTFE-g-AA. In the curve of the mixture of PTFE and AA, there is a sharp weight loss up to 200°C , attributed to the loss of AA, and a similar decomposition step start-

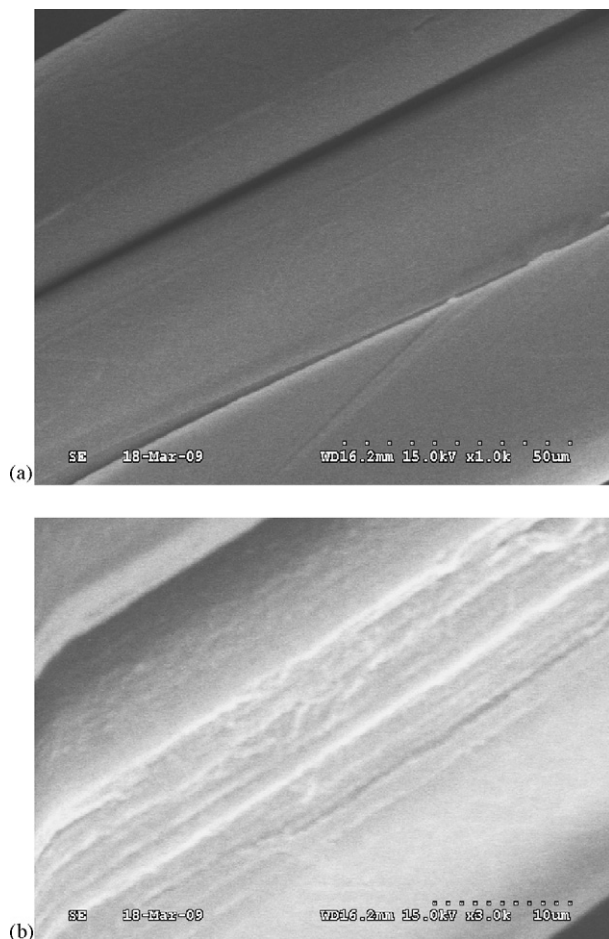


Fig. 2. SEM images of PTFE and PTFE-g-AA fibers. (a) PTFE and (b) PTFE-g-AA.

ing at about 530 °C is noted as that in the curves of the PTFE. These results mentioned above indicate that the AA has been successfully grafted onto the PTFE.

3.3. Batch studies

3.3.1. Effect of pH on distribution coefficient (*D*)

There are several factors that influence the uptake of Er(III) on the PTFE-g-AA fiber. Among these factors, the pH of the sample solution is the most important parameter for the effective uptake

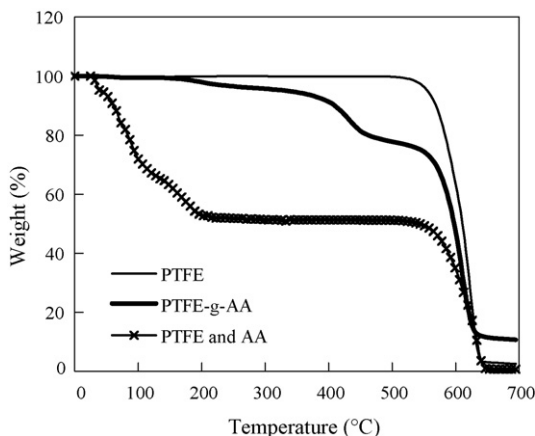


Fig. 3. TGA curves for PTFE fiber, PTFE-g-AA fiber and PTFE-AA mixture.

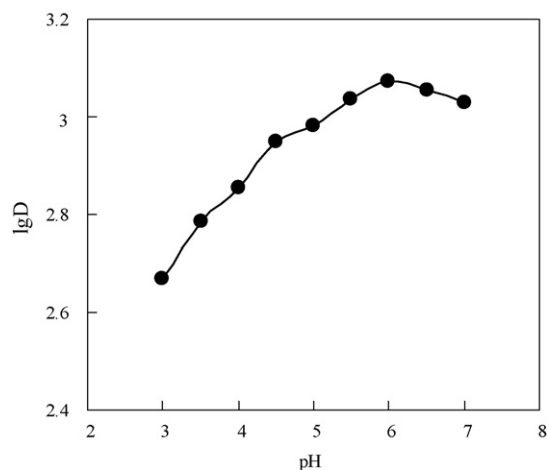


Fig. 4. Effect of pH on sorption distribution of Er(III). Initial Er(III) conc. (167 mg/l), adsorbent dose (15 mg), batch volume (30 ml), rpm (100), temperature 298 K.

of Er(III). The effect of the pH of the sample solution was evaluated in a pH range of 3.00–7.00. As shown in Fig. 4, the maximal distribution coefficient was obtained when pH is 6.00 with HAc–NaAc and it decreased by either raising or lowering the pH. The low distribution coefficient of the analyte at low pH may result from the low retention efficiency of the adsorbent due to the occupation of the active sites of the weak ion-exchanger by proton, whereas the hydrolysis of Er(III) at high pH probably account for the decrease of the absorbance of the analytes due to the diminution of free ions. Thus, all the following experiments were carried out at pH 6.00.

3.3.2. Effect of temperature

The effect of temperature on the adsorption of Er(III) by PTFE-g-AA fiber was studied over the range of temperature from 288 to 308 K. The result obviously indicates that it is favorable for the adsorption with the temperature going up, which implies that the adsorption process is an endothermic process [16]. The van't Hoff equation [17] given below, can be used to calculate the enthalpy changes associated with the adsorption process of the metal ions.

$$\lg D = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \quad (9)$$

where R is the universal gas constant, D is the distribution coefficient, T is the absolute temperature and C is a constant. The plot of $\lg D$ versus $1/T$ gives a straight line, from which ΔH^0 (the enthalpy variation) and ΔS^0 (the entropy variation) were deduced from the slope and intercept of the line, respectively. And the free energy variation, ΔG^0 was calculated from:

$$\Delta S^0 = \Delta H^0 - \Delta G^0 T \quad (10)$$

The thermodynamic parameters of the sorption of Er(III) were calculated and given in Table 3. The positive values of ΔH^0 indicate the endothermic character of the solid phase extraction and sorption process, but the negative value of ΔG^0 indicates the spontaneous nature of Er(III) sorption. The positive entropy change (ΔS^0) value corresponds to an increase in the degree of freedom of the adsorbed species.

Table 3

Thermodynamic data calculated for adsorption of Er(III) on PTFE-g-AA fiber at different temperatures.

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
288	–16.2	21.4	130.8
298	–17.6		
308	–18.9		

Table 4
Langmuir and Freundlich adsorption isotherm constants for adsorption of Er(III) on PTFE-g-AA fiber.

Langmuir constants			Freundlich constants		
q_m (mg/g)	b (l/mg)	R^2	K_f ((mg/g)/(mg/l) ^{1/n})	n	R^2
142.0	0.06	0.9955	44.61	4.54	0.9963

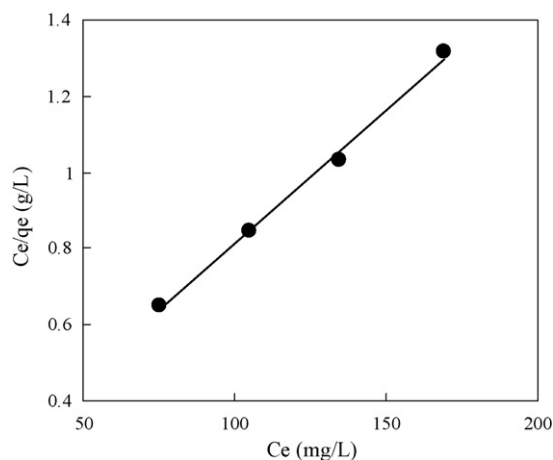


Fig. 5. Langmuir plot for the adsorption of Er(III) on PTFE-g-AA fiber. Adsorbent dose (15 mg), batch volume (30 ml), rpm (100), temperature 298 K.

3.3.3. Adsorption isotherm

An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent system or for varied conditions within any given systems. These parameters of equilibrium isotherms often provide some insight into both sorption mechanism and surface properties and affinity of the adsorbent. Therefore, it is important to establish the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems. There are many equations for analyzing experimental adsorption equilibrium data. In this work, the experimental results obtained for the adsorption of Er(III) on PTFE-g-AA fiber at constant temperature 298 K under the optimum pH 6.0 and oscillations frequency 100 rpm were tested by the Langmuir and Freundlich isotherm models. And the results are shown in Figs. 5 and 6. In general, both the Langmuir and the Freundlich models fitted the results well with the R^2 values greater than 0.98 (Table 4). This suggests that the adsorption of

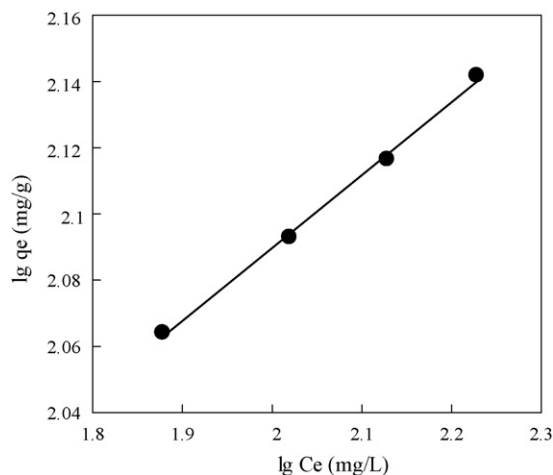


Fig. 6. Freundlich plot for the adsorption of Er(III) on PTFE-g-AA fiber. Initial Er(III) conc. (219 mg/l), batch volume (30 ml), rpm (100), temperature 298 K.

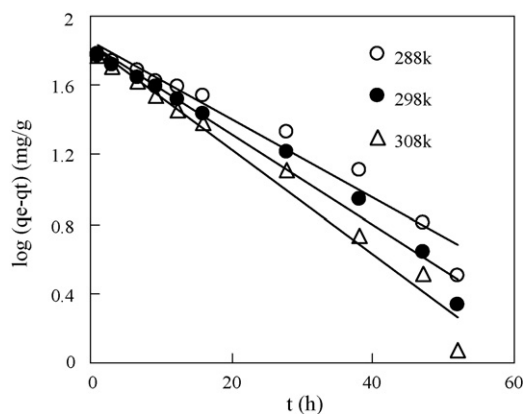


Fig. 7. Pseudo-first-order plot of Er(III) adsorption by PTFE-g-AA fiber. Initial Er(III) conc. (167 mg/l), adsorbent dose (30 mg), batch volume (60 ml), rpm (100).

Er(III) ions by the grafted fiber is monolayer-type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface. On the other hand, the equilibrium data was also well described with the Freundlich model, probably due to the real heterogeneous nature of the surface sites involved in the metal uptake [18]. The fact that both monolayer and heterogeneous surface conditions exist under the experimental condition used, implies that the adsorption of Er(III) ions on PTFE-g-AA fiber is thus complex, involving more than one mechanism.

3.3.4. Adsorption kinetics

In order to investigate the rate-controlling step of the Er(III) adsorption process, the pseudo-first-order and pseudo-second-order models were tested to fit the kinetics sorption data. The kinetics data are plotted as the linear form of the models (Figs. 7 and 8), and the comparison made between the experimental adsorption capacity and the theoretical values estimated from the second-order equation is presented in Table 5. The second-order equation fitted well with the experimental data. The theoretical q_e

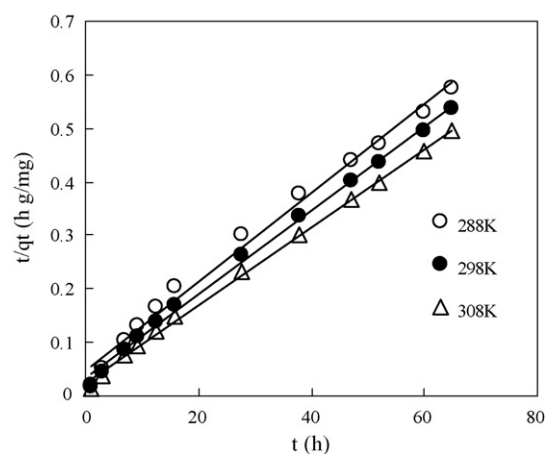


Fig. 8. Pseudo-second-order plot of Er(III) adsorption by PTFE-g-AA fiber. Initial Er(III) conc. (167 mg/l), adsorbent dose (30 mg), batch volume (60 ml), rpm (100).

Table 5
The first-order and second-order kinetics constants for adsorption of Er(III) on PTFE-g-AA fiber.

T (K)	q_e (exp) (mg/g)	First-order kinetics			Second-order kinetics		
		k_1 (h^{-1})	q_e (mg/g)	R^2	k_2 (g/mg h)	q_e (mg/g)	R^2
288	102.5	5.20×10^2	71.5	0.9619	1.45×10^{-3}	120.5	0.9905
298	123.9	6.01×10^2	68.7	0.9799	1.86×10^{-3}	128.2	0.9962
308	147.5	7.09×10^2	69.5	0.9782	2.31×10^{-3}	137.0	0.9982

values for the adsorbent were very close to the experimental ones in the case of second-order kinetics. On the other hand, the theoretical q_e values estimated from the first-order kinetics model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be slightly lower. These results showed that the second-order kinetics better described the data than the first-order kinetics model.

The pseudo-second-order model is based on the assumption that the rate-limiting step is a chemical sorption involving valance force through sharing or exchange of electrons between adsorbent and adsorbate [19]. Thus, successful fitting of this model suggests that chemisorption is the rate-controlling step [20].

3.4. Desorption studies

Adsorption of metal ions on any sorbent can be by physical, chemical bonding, ion exchange or combination of all. If adsorption is by physical bonding then the loosely bound metal ions can be easily desorbed with distilled water. However, if the adsorption process is by chemical bonding or ion exchange or combination of both, then desorption can be affected by stronger eluents like acid or alkali solution. Thus, desorption study can give a clear idea about the mechanism of adsorption and is useful in recycling of the adsorbent and recovery of metals. In this work, desorption of Er(III) ions with various concentrations of eluent solution was carried out. The results presented in Table 6 show that the elution ratio is different when the concentration of eluent changes. Maximum recovery of Er(III), at 100%, was achieved with a 0.75 M HCl–0.25 M NaCl eluent solution under the experimental condition. The results show that the Er(III) adsorbed by the PTFE-g-AA fiber can easily be desorbed, which indicates that the fiber can be employed repeatedly in Er(III) adsorption.

3.5. Column studies

3.5.1. Dynamic adsorption curve

The fixed-bed column operation is more effective for cyclic adsorption/desorption than the batch process. Total sorption capacity of Er(III) (q_0) in the column for a given feed concentration and flow rate is calculated from [21]:

$$q_0 = \int_0^{V_e} \frac{(C_0 - C_e)}{m} dV \quad (11)$$

where C_0 and C_e are metal ion concentrations in the influent and effluent, respectively, m is the total mass of the sorbent loaded in

Table 6
Desorption of Er(III) ions by different eluent solutions in varying concentrations.

Eluents	Concentration (mol/l)	Elution percentage (%)
HCl	3.00	88.3
	2.00	91.8
	1.00	100.0
	0.50	93.5
HCl and NaCl	0.85 + 0.15	100.0
	0.75 + 0.25	100.0
NaCl	0.65 + 0.35	96.5
	0.55 + 0.45	94.2

the column and V_e is the volume of metal solution passed through the column. The maximum sorption capacity value q_0 was obtained by graphical integration as 125.1 mg/g.

Successful design of a column sorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum sorption capacity of a sorbent is also needed in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form [21]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[K_T(q_0 m - C_0 V_e)/\theta]} \quad (12)$$

where K_T is the Thomas rate constant and θ is the volumetric flow rate. The linearized form of the Thomas model is as follows:

$$\ln \left(\frac{C_0}{C_e} - 1 \right) = \frac{K_T q_0 m}{\theta} - \frac{K_T C_0}{\theta} V_e \quad (13)$$

The kinetics coefficient K_T and the sorption capacity of the bed q_0 can be determined from a plot of $\ln[(C_0/C_e) - 1]$ against t at a given flow rate (Fig. 9). The Thomas equation coefficients for Er(III) sorption were $K_T = 5.50 \times 10^{-2}$ ml/(min mg) and $q_0 = 129.3$ mg/g. The theoretical predictions based on the model parameters are compared with the observed data in Fig. 10.

The Thomas model was found in a relatively good fitness with breakthrough curves for sorption of Er(III) on PTFE-g-AA fiber with the high R^2 value (0.9875), and the theoretical q_0 value was very close to the experimental one. Therefore, it can be concluded that the experimental data fitted well to the Thomas model, which indicates that the external and internal diffusion will not be the limiting step.

3.5.2. Dynamic desorption curve

Once the column reached exhaustion, efficient elution of adsorbed solute from PTFE-g-AA fiber in column is essential to ensure the recovery of metal ions as well as the reuse of fiber for repeated adsorption/desorption cycles. In this work, 0.75 M HCl–0.25 M NaCl has been used to elute Er(III). Desorption curve

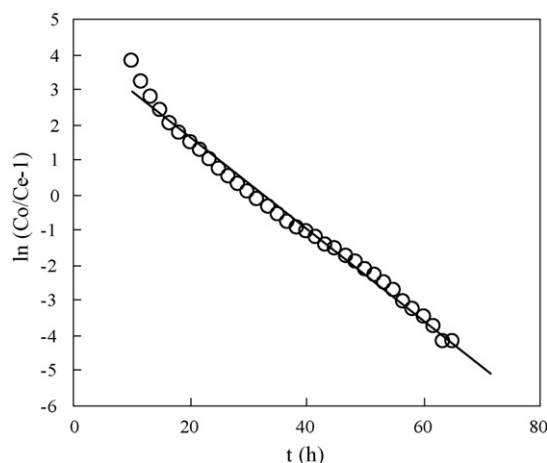


Fig. 9. Linear plots of $\ln(C_0/C_e - 1)$ versus t by application of Thomas model. Initial Er(III) conc. (40 mg/l), adsorbent dose (150 mg), flow rate (0.015 l/h), temperature 298 K.

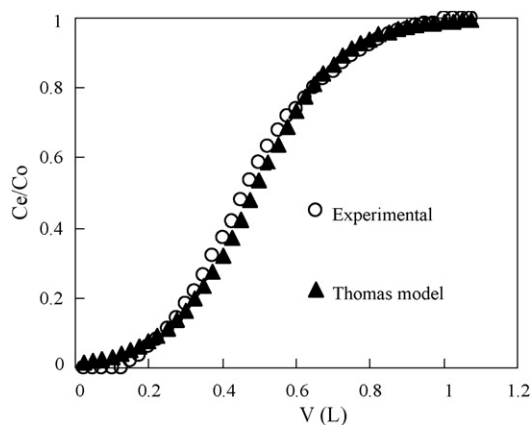


Fig. 10. The experimental and predicted breakthrough curves using the Thomas model for Er(III) adsorption by PTFE-g-AA fiber.

(Fig. 11) was obtained by plotting the effluent concentration (C_e) versus elution volume from the column at a flow rate of 0.15 ml/min, less than the sorption flow rate so that volume of elution is less which helps in easy handling and high in concentration so that economical metal recovery is possible.

It was observed that the total volume of eluent was 50 ml and the desorption process took 2.8 h, after which further desorption was negligible. Therefore, 0.75 M HCl–0.25 M NaCl could help in easy handling and recovering of Er(III).

3.6. Proposed Er(III) adsorption mechanism with PTFE-g-AA fiber

The IR studies performed on PTFE-g-AA fiber previously loaded with Er(III) indicated that the complexing main sites are the carboxyl functional groups, and the adsorption mechanism might be partly a result of the ion exchange or complexation between the Er(III) ions and carboxyl groups of PTFE-g-AA fiber. Thus, the Er(III) ions/PTFE-g-AA fibers reaction may be represented in two ways as shown in Fig. 12 [22].

Since the oxygen of the carboxyl has a pair of electrons that can add themselves to a proton or a metal ion to form a complex through a coordinated covalent bond, it takes us to propose that the complexes between metal ions (Er(III)) and PTFE-g-AA fiber are formed according to the mechanism illustrated in Fig. 12(a). In this mechanism, the metal ions (Er(III)) with empty orbitals function as a Lewis acid capable of accepting electron pairs. In contrast, the carboxyl groups that have non-shared electron pairs function as Lewis bases donating their electrons pair. This behavior depends on the solution

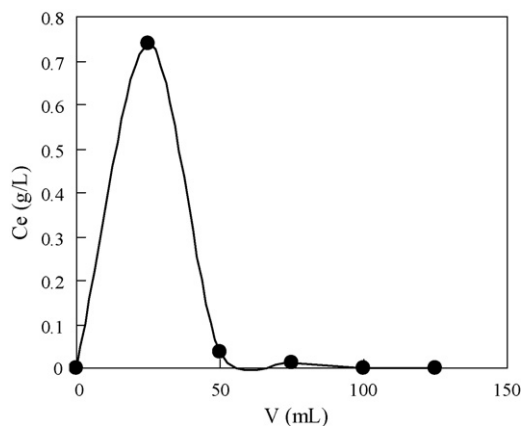


Fig. 11. Desorption curve of PTFE-g-AA fiber for Er(III). Flow rate (0.009 l/h), temperature 298 K.

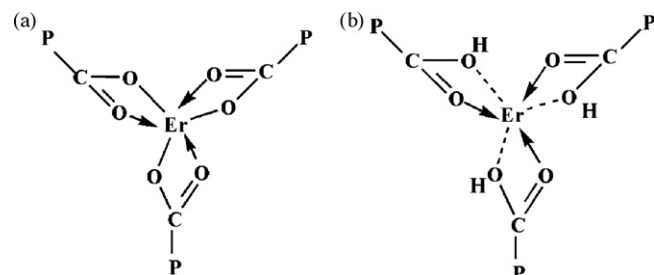


Fig. 12. Proposed Er(III) adsorption mechanism with PTFE-g-AA fiber (a) complexation and ion exchange and (b) complexation.

pH. That is, if the adsorption system is in a neutral or slightly acid pH, the mechanism shown in Fig. 12(a) will predominate.

Nevertheless, under acidic environment, the metal adsorption capacity diminishes as the solution pH decreases. This may be a result of the decrease of the retention efficiency of the adsorbent due to the occupation of the active sites of the weak ion-exchanger by protons. The proposed mechanism is illustrated in Fig. 12(b).

4. Conclusion

In this work, a polymeric adsorbent PTFE-g-AA fiber has been prepared and successfully employed as a new adsorbent material for uptaking of Er(III). The adsorption characteristics have been investigated at different pH values, temperature and initial metal ion concentrations by batch and column experiments. The obtained results showed that Er(III) adsorption is highly dependent on pH. In addition, initial Er(III) concentration are influential on the adsorption process. Kinetics studies showed that the adsorption process obeyed pseudo-second-order kinetics, and the adsorption behavior could be modeled using both the Langmuir isotherm and Freundlich isotherm. The maximum adsorption capacity of the PTFE-g-AA fiber for Er(III) for the Langmuir model was evaluated to be 142.0 mg/g. The adsorption of Er(III) on the PTFE-g-AA fiber was found to be endothermic in nature. TGA results indicated that the new prepared fiber has outstanding thermal stability, and elution study proves the excellent regeneration property of the fiber. Column experiments showed that it was possible to remove the Er(III) ions from aqueous medium dynamically. In conclusion, the PTFE-g-AA fiber can be used for removal of Er(III) very effectively and it has a potential for the treatment of REEs containing industrial effluents.

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References

- [1] P. Liang, Y. Liu, L. Guo, Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes, *Spectrochim. Acta Part B* 60 (2005) 125–129.
- [2] C.H. Xiong, C.P. Yao, Y.J. Wang, Sorption behaviour and mechanism of ytterbium(III) on imino-diacetic acid resin, *Hydrometallurgy* 82 (2006) 190–194.
- [3] K. Hennebrüder, R. Wennrich, J. Mattusch, H.J. Stärk, W. Engewald, Determination of gadolinium in river water by SPE preconcentration and ICP-MS, *Talanta* 63 (2004) 309–316.
- [4] V.S. Soldatov, A.A. Shunkevich, I.S. Elinson, J. Johann, H. Iraushbek, Chemically active textile materials as efficient means for water purification, *Desalination* 124 (1999) 181–192.
- [5] K. Saeed, S. Haider, T.-J. Oh, S.-Y. Park, Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption, *J. Membr. Sci.* 322 (2008) 400–405.

- [6] Q.K. Zhang, S.J. Zhang, S.X. Chen, P.Y. Li, T.Y. Qin, S.G. Yuan, Preparation and characterization of a strong basic anion exchanger by radiation-induced grafting of styrene onto poly(tetrafluoroethylene) fiber, *J. Colloid Interface Sci.* 322 (2008) 421–428.
- [7] N.M. Al El-Sawy, F. Sagheer, Radiation-induced graft polymerization of acrylic acid onto poly(tetrafluoroethylene-perfluorovinyl ether) copolymer films: complexation with some transition metals and biological activity, *Eur. Polym. J.* 37 (2001) 161–166.
- [8] N.M. Al El-Sawy, F. Sagheer, Physicochemical investigation of radiation-grafted poly(acrylic acid)-graft-poly(tetrafluoroethylene-ethylene) copolymer membranes and their use in metal recovery from aqueous solution, *J. Appl. Polym. Sci.* 85 (2002) 2692–2698.
- [9] M.M. Nasef, H. Saidi, M.M. Senna, Hydrolysis of sucrose by radiation grafted sulfonic acid membranes, *Chem. Eng. J.* 108 (2005) 13–17.
- [10] M.M. Nasef, H. Saidi, A.M. Dessouki, E.M. El-Nesr, Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films. I. Effect of grafting conditions and properties of the grafted films, *Polym. Int.* 49 (2000) 399–406.
- [11] A. Oshima, T. Seguchi, Y. Tabata, ESR study on free radicals trapped in crosslinked polytetrafluoroethylene (PTFE)-II radical formation and reactivity, *Radiat. Phys. Chem.* 55 (1999) 61–71.
- [12] I. Langmuir, Adsorption of gases on plain surface of glass mica platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [13] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [14] O. Keskinan, M.Z.L. Goksu, M. Basibuyuk, C.F. Forster, Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*), *Bioresour. Technol.* 92 (2004) 197–200.
- [15] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of lead (II) from effluents by sorption on peat using second-order kinetics, *Sep. Sci. Technol.* 36 (2001) 241–261.
- [16] C.H. Xiong, C.P. Yao, X.M. Wu, Adsorption of rhenium(VII) on 4-amino-1,2,4-triazole resin, *Hydrometallurgy* 90 (2008) 221–226.
- [17] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, S.B. Lyubchik, Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes, *Colloids Surf. A: Physicochem. Eng. Aspects* 242 (2004) 151–158.
- [18] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Enhancement of basic dye adsorption uptake from aqueous solutions using chemically modified oil palm shell activated carbon, *Colloids Surf. A: Physicochem. Eng. Aspects* 318 (2008) 88–96.
- [19] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl₂ activation, *Bioresour. Technol.* 99 (2008) 492–501.
- [20] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.
- [21] M. Tabakci, M. Yilmaz, Sorption characteristics of Cu(II) ions onto silica gel-immobilized calix[4]arene polymer in aqueous solutions: batch and column studies, *J. Hazard. Mater.* 151 (2008) 331–338.
- [22] I. Ayhan Sengil, M. Ozacar, Biosorption of Cu(II) from aqueous solutions by mimosa tannin gel, *J. Hazard. Mater.* 157 (2008) 277–285.