Fixed Bed Sorption Studies On The Removal Of Uranium And Gadolinium Ions From Aqueous Solution Using Sonicated Emulsion Polymer

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Abstract

*Sorption isotherm studies were performed utilizing the batch technique **to get** equilibrium information for removal of Uranium and Gadolinium from aqueous solution using sonicated emulsion polymer synthesized by ultrasonic irradiation technique. Equilibrium sorption datum was analyzed using Langmuir and Freundlich models. The Langmuir model fit the obtained sorption data well as moderately indicated by the correlation coefficients R^2. Thermodynamic parameters of the studied sorption processes were calculated. The numerical value of ΔG^o decreases with an increase in temperature, indicating that the sorption reaction of each ion is more favorable at a higher temperature. The positive values of ΔH^o correspond to the endothermic nature of the sorption processes. The maximum capacity of Uranium ion was found to be higher than that Gadolinium ion.*

Different fixed bed variables were tested for the removal of each Uranium and Gadolinium utilizing sonicated emulsion polymer. The breakthrough characteristics of the resin were studied at various ions concentration (50, 100 and 150 mg/L), bed heights (7, 9 and 11 cm) and feed flow rates 2.3 and 6 mL/min for Uranium and Gadolinium ions. The Bed depth service time model has been used to describe the dynamic sorption of Uranium and Gadolinium and the critical bed depth have been calculated. The influence of the eluent type on the desorption of column has been investigated and exhibit that HNO_3 has a greater effect more than HCl for Uranium and Gadolinium ions with an elution efficiency of 98.0%. Results indicated that sonicated emulsion polymer can be used effectively as an ion exchange for the continuous removal of Uranium and Gadolinium ions from aqueous solutions in large-scale operations.

Keywords: Sonicated emulsion polymer, Uranium and Gadolinium, Fixed bed column, Thermodynamics.

1- INTRODUCTION

Fixed bed sorption has become a frequently used in several application and treatment processes. Various sonicated emulsion polymers have been studied for their applicability in the treatment of different types of effluents. With the increasing usage of lanthanides in various fields, studies to find efficient methods for their separation and elution are important. The use of sonicated emulsion polymers is one of the most common procedures for separation of lanthanides [1]. Studies on sorption and separation of lanthanides (III) indicate the possibility of ion exchange separation of these elements in a macro-macro component system. The most important criterion in the design of fixed bed system is the prediction of column breakthrough or the shape of the adsorption wave front, which determine the operational lifespan of the bed and regeneration times. Mathematical models facilitate the design and analysis of full-

scale systems by reducing the number of pilot-scale tests required to evaluate various operating condition and design parameters for sorption. The design of the adsorption process is based on the accurate prediction of breakthrough curves[2-3].

Sonicated emulsion polymers are widely studied for their ability of self-assembling into polymeric aggregates with different morphologies in aqueous solutions. Normally, the hydrophobic chains of the polymer tend to form the inner cores of the aggregates as a result of the hydrophobic interaction, with the hydrophilic chains forming the hydrated shells. Sonication is known to have the ability to affect the aggregation state of nanoparticles in solution [4-5].

This work is an extension of our previous work, where the sonicated emulsion polymer was successfully prepared using the high intensity ultrasound that is often unavailable by conventional methods and the influence of surfactant type, ultrasonic time and temperature on the particle morphology were systematically studied and tested for removal of trivalent lanthanides [6]. The main objective of this work is to investigate the behavior of the prepared sonicated emulsion polymer for sorption of Uranium and Gadolinium ions as an application in a fixed bed column and to examine the thermodynamic parameters and other parameters involved.

2- EXPERIMENTAL

2.1. Chemicals and Materials

In the present study, all chemicals and reagents are used with analytical grade and the experiments were performed using de-oxygenated double distilled water which bubbled using pure nitrogen gas at temperature 80°C.

2.2 Preparation of Emulsion polymer and characterization

The detailed description of preparation and characterization of sonicated emulsion polymer have been presented elsewhere [7]. The prepared polymer has several advantages such as deagglomeration and cavitations of the mixture component during homogenization and causes rupture of macromolecules and creation of free radicals which are attached as lateral branches making the polymer more grafted. The prepared polymer characterized by FTIR spectroscopy and scanning electron microscope SEM which demonstrated that the morphology showed cavitations and uniform pores. The use of sonication resulted in smaller particles than that in the absence of the sonication. As the sonication period increases, the formation of de-agglomerated particles appears, so the success of this method will likely depend on the nature of the molecule used.

2.3. Sorption Isotherms

Sorption isotherm studies were mainly performed using a batch technique to obtain equilibrium data and for these investigations, a series of 50-mL test tubes were employed. Each test tube was filled with 20 mL of the ions solution of varying concentration (50 to 500 mg/L) and 50 mg of sonicated emulsion polymer. The temperature of the system was maintained by a thermostat (303, 313 and 323 K) shaking water bath during the exchange process. The concentration of the studied in solution phase was determined using spectro photometric methods. Sodium hydroxide 1.0 M and 1.0 M HNO_3 solute were used to adjust the pH values. The amount adsorbed was determined by equation (1):-

$$q(mg/g) = \frac{(C_i - C_e)V}{m} \qquad \ldots\ldots\ldots\ldots (1)$$

Where (q) is the maximum capacity (mg/g), C_i and C_e are the initial and equilibrium concentration (mg/L) of ion respectively, m is the mass of the adsorbent used (g), V is the initial volume of the aqueous solution(L).

2.4. Fixed bed Column studies

Fixed-bed column experiments were carried out to evaluate the column performance for Uranium and Gadolinium ions onto the prepared sonicated emulsion polymer and conducted at room temperature using a vertical down flow

Pyrex glass column with an internal diameter of 1 cm and bed eight 15.0 Cm. Influent feed flow rate was supplied and maintained throughout the experiments by the use of a peristaltic pump. At the exit of the column, the flow rate was also controlled by the valve outlet to get steady-state condition the column. The sampling of effluent was done at predetermined time intervals in order to investigate the breakthrough point. The column was packed with a wet polymer in double distilled water to prevent the bubbles occurs. The required ion concentration was prepared individually from analytical grade. The initial pH was adjusted at optimum pH of 4.0 using a dilute solution of Nitric acid and sodium hydroxide to adjust pH. The effluent samples were analyzed for Uranium and Gadolinium. Effects of inlet feed flow rate (2.3 and 6.0 mL/min), polymer bed height (7.0, 9.0 and 11.0 cm) and initial Uranium and Gadolinium concentration (50, 100 and 150 mg/L) were investigated on the performance of the breakthrough curves for the sorption of each studied ion.

2.5. Elution studies

Two different mobile phases (Nitric acid and Hydrochloric acid) were investigated with different concentrations; the effluent flow rate was set at 1.0 ml/min and constant pH isocratically to eluted a lanthanides elements and uranium. About 0.8 g (1.0 Cm height) of the strongly sonicated emulsion polymer was weighted in a beaker. The volume of distilled water was added to the beaker and shacked with resin until settling. Finally, the column is packed by poured the resin carefully in the form of a slurry into a vertical down flow Pyrex glass column[8].

Appropriate quantities of the different eluents were prepared individually at different concentration (0.1, 0.05 and 0.001) M. All solute were adjusted to the desired pH using high purity NaOH solutions. Firstly, the washed resin (stationary phase) was equilibrated by passing the prepared eluent through the column. Secondly, the prepared sample solute was added to the top of the resin column. The adsorbed sample in the upper part of the resin was eluted using different eluents(mobile phases) and then the convenient volume of fraction 20 mL was collected manually and measured using U.V spectrophotometer.

## 3- RESULTS AND DISCUSSION

3.1. Effect of pH

The pH of the solution is the significant factor for controlling the sorption process [9]. Figure (1) illustrates a typical dependence of the uptake on the solution pH. It was found that as the pH value increased from 1.0 to 5.0, the sorption capacity of resin increased and reached 39.2 and 39.2 mg.g^{-1} at pH 5.0 for the studied Uranium and Gadolinium respectively, this can be explained by the presence of a large number of carboxyl (–COOH) groups in the structure of the resin from NTA and acrylic acid groups, which, can dissociate to form carboxylate ion (COO−) at higher pH. However, at pH values higher than 5.0, the metal hydrolysis will take place [9]. On the other hand, at low pH values, the competitive sorption of H$^+$ and on the same active sorption site causes a decrease in metal uptake. The significant change in selectivity of polymer contain NTA toward U^{6+} and Gd^{3+} rather than light rare earth elements was observed as a function of increasing pH Hence, a significant selectivity of the prepared NTA-polymer toward U^{6+} and Gd^{3+} was obtained at pH 5.0.
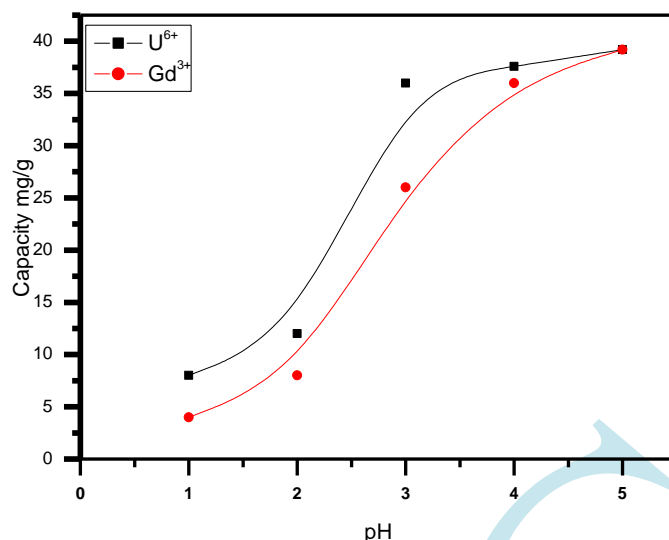
Figure. (1): Effect of pH on the sorption of resin (0.05 g resin, 10 ml and time= 2 hr's at 37°C).

The species of Uranium and Gadolinium ions on emulsion polymer surface are not only dominated by the properties of adsorbent, but also affected by the structure of ionized species at various pH values. As shown in figure (2a), the aqueous uranium speciation diagram, it was found that the uranyl ion (UO_2^{2+}) is the dominated species at pH < 4. Knowing that the free uranyl ion in acidic solution has five water molecules in its first hydration shell $([UO_2(H_2O)_5]^{2+})$. Under this condition, uranium typically occurs in the heptavalent or form as the mobile aqueous uranyl ion (UO_2^{2+}) [9]. On the other hand, Gd^{3+} hydrolysis started at pH 6.0 as given in figure (2b).
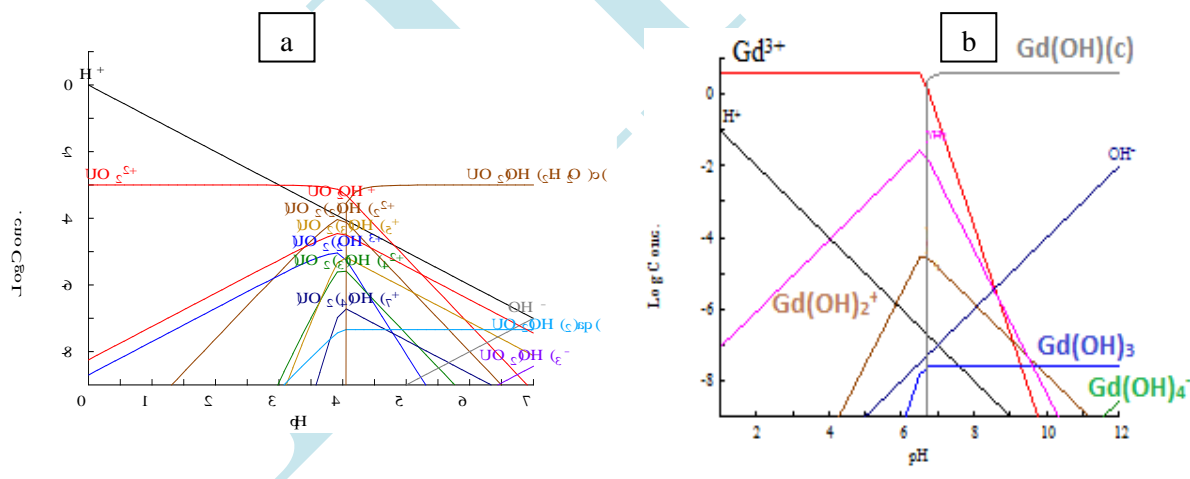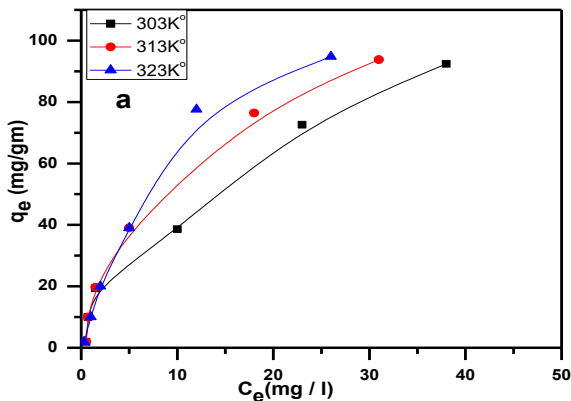

Figure. (2): Speciation of (a) Uranium and (b) Gadolinium ions.
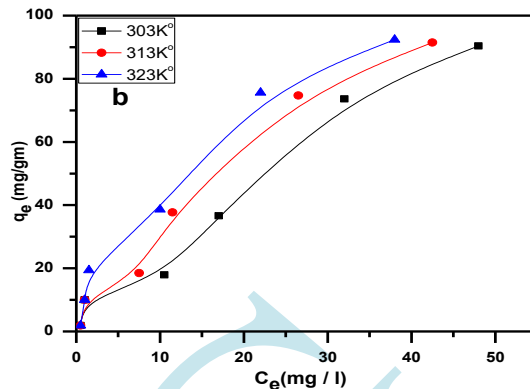
3.2. Sorption isotherms

Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the polymer, at a fixed temperature and pH. An adsorption isotherm describes the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [10]. In this concern, the sorption isotherms for the removal of U^{6+} and Gd^{3+} onto sonicated emulsion polymer at three different temperatures were determined. Figure (**3**) Illustrate the experimental data by Langmuir and Freundlich isotherm models at 303 K. The

isotherms are regular, confident, and concave to the concentration axis for both ions. The sorption data were analyzed to investigate whether the isotherm obeyed the Langmuir and Freundlich isotherm models equations.

Figure. (3). Sorption isotherm of (a) U⁶⁺ and (b) Gd³⁺ ions onto sonicated emulsion polymer at different temperature (303, 313 and 323) °K.

The figure indicated that the amount sorbed on sonicated emulsion polymer was increased with an increase in temperature for all ions, and reflecting the endothermic nature of the process. Models that are often used to describe the experimental isotherm data were developed by namely Langmuir and Freundlich. The equation parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties. The accuracy of the fit of an isotherm model to experimental equilibrium data was typically assessed based on the magnitude of the correlation coefficient (R^2) for the linear regression, i.e., the isotherm giving an R^2 value closest to unity was deemed to provide the best fit.

3.2.1. Langmuir isotherm model

The Langmuir sorption isotherm model, based on the ideal monolayer coverage of the sorption surfaces, proved to be deceptive for most real sorption systems that include structurally high porous and energetically heterogeneous solids. The linearized form of the Langmuir equation is given by eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e \ldots\ldots\ldots (2)$$

Where Q^o, the monolayer capacity of the adsorbent (mg/g), b Langmuir constant (L/mg) and related to the free energy of sorption, q_e theoretical saturation capacity (mg/g). The graphic presentations of (C_e/q_e) versus C_e give straight lines studied of ions sorbed onto sonicated emulsion polymer. One of the essential characteristics of the Langmuir model could be expressed by a dimensionless constant called equilibrium parameters RL

$$R_L = \frac{1}{1 + bC_o} \ldots\ldots\ldots\ldots\ldots(3)$$

where C_0 is the highest initial ion concentration (mg/L). The value of RL indicates the type of isotherm to be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1), or unfavorable (RL > 1). All the RL values (**Table 1**) were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of ions.
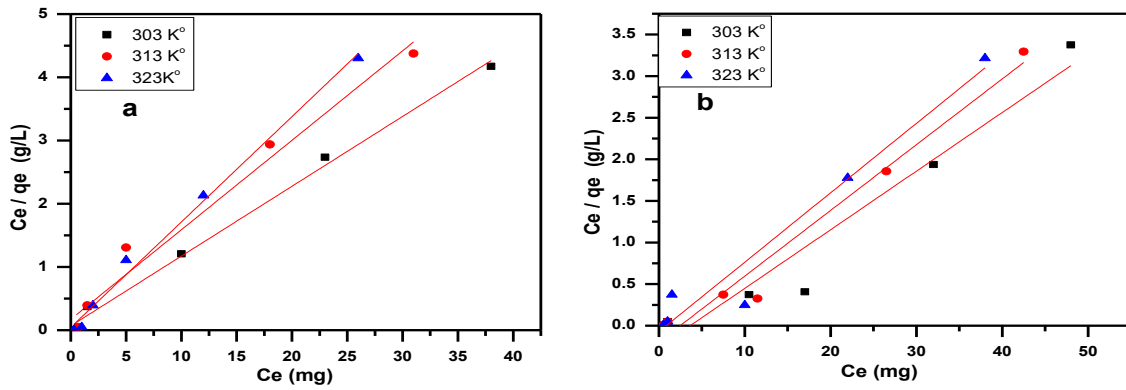
Figure(4):- Langmuir isotherm plots for the sorption of (a) U^{6+} and (b) Gd^{3+} ions sorbed onto sonicated emulsion polymer.
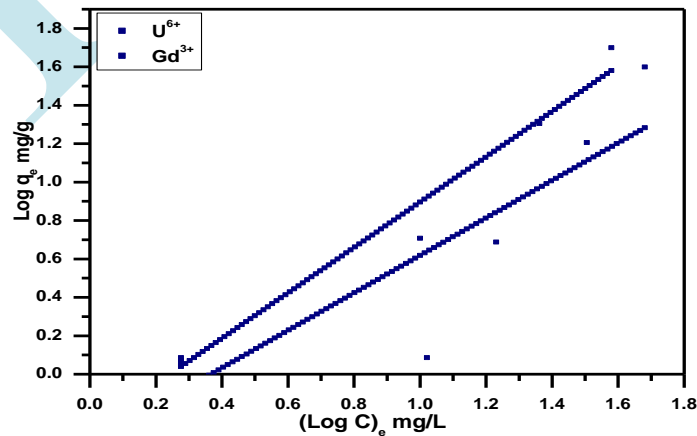
3.2.2. Freundlich isotherm model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces [12]. The logarithmic form of Freundlich equation may be written as:

$$\log q_e = \log K_f + (1/n)\log C_e \quad \ldots\ldots\ldots\ldots(4)$$

where K_f is constant indicative of the relative sorption capacity of polymer (mg/g) and 1/n is the constant indicative of the intensity of the sorption process[11]. The pictorial illustration of log q_e versus log Ce is shown in Figure (5), which suggests that the sorption of studied obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants 1/n and K_f are computed from the slope and the intercepts, using of a linear least square fitting method, and also given in **Table 1**. It can be seen from these data that the

Freundlich intensity constant (n) are greater than unity for both studied ions. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interaction between species and polymer In our case, n > 1 for all ions species, the polymeric materials show an increasing tendency for sorption with increasing solid phase concentration. This should be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the ions species such as Vander Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion (electrostatic force), and consequently, the manifest a stronger tendency to bind to the sonicated emulsion polymer[13].

Figure(5):- Freundlich isotherm plots for the sorption of U^{6+} and Gd^{3+} ions sorbed onto sonicated emulsion polymer.

Table (1):- Langmuir and Freundlich isotherm parameters for the sorption of Gd³⁺ and U⁶⁺ ions onto sonicated emulsion polymer.

| Ions | Temperature (K) | Langmuir model parameter | | | |
		Q^o (mg/g)	b (L/mg)	R^2	R_L
U⁶⁺	303	92.4	0.016	0.87	0.21
	313	93.5	0.019	0.87	0.21
	323	94.4	0.025	0.87	0.21
Gd³⁺	303	90.1	0.034	0.95	0.07
	313	91.3	0.042	0.94	0.06
	323	92.1	0.048	0.95	0.05

Thermodynamic parameters

Thermodynamic parameters were evaluated to confirm the sorption nature of prepared emulsion polymer. The experimental data obtained at different temperatures and different ions concentration were used to calculating the thermodynamic parameters; such as Gibbs free energy change ΔG^o, enthalpy change (ΔH^o), and entropy change (ΔS^o) were calculated using the relationships

$$ln\ K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \ldots\ldots\ldots\ldots\ldots(5)$$

where Kc is the sorption equilibrium constant. while T is the temperature in K

and R is the gas constant (8.314 J/mol K). q_e is the concentration of metal on polymer surfaces at equilibrium in mg/g and Ce is the equilibrium concentration of the ion in solution in mg/L.

The values of the thermodynamic equilibrium constant (Kc) at different studied temperatures were determined from the product of the Langmuir equation parameters Q^o and b [**14**]. The Gibbs free energy change ΔG^o is given by the following equation:

$$\Delta G^o = -RT \ln K_c \quad \ldots\ldots\ldots\ldots\ldots(6)$$

where R the gas constant and T is the absolute temperature (K).

Table (2):- Thermodynamic parameters and activation energy for sorption of lanthanide ions onto prepared emulsion polymer.

Ions	Temprature(K)	K_c	ΔG^o (kJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/moLK)
U⁶⁺	303	1.4	-27.7	33.6	10.4
	313	1.7	-41.4		
	323	2.3	-64.9		
Gd³⁺	303	3.1	-79.6	31.4	8.7
	313	3.9	-99.7		
	323	4.5	-113.2		

The thermodynamic parameters of U⁶⁺ and Gd³⁺ ions sorption removal at equilibrium; ΔH^o and ΔS^o studied at different temperature and determined by plotting ln Kc against 1/T. The values of ΔH^o and ΔS^o have been computed from the slope and intercept of the plot with ln Kc versus 1/T. The obtained value of the ΔG^o, ΔH^o, and ΔS^o of the sorption of Gd³⁺ and U⁶⁺ metal

are summarized in **Table 2**. It is clear from data that, the enthalpy values, ΔH^o are 336.03 and 314.24 for metal respectively. The values of ΔH^o are positive; this demonstrates that the sorption process is of endothermic nature in all cases. In other words, at a higher temperature, there is higher sorption removal of ions. The entropy values ΔS^o for metal 10.4 and 8.7

(J/mol K) for Gd^{3+} and U^{6+} ions respectively. The positive value of entropy change (ΔS^o) means, theoretically, that more disorder is associated with the sorption process and reflects good affinity of studied metal towards the sonicated emulsion polymer and increasing the randomness at the solid-solution interface during the sorption process. The Gibbs free energy, ΔG^o values decrease with the increase of temperature from 303 to 325 ^{o}K as shown in (Table 3), suggesting the more adsorbable of ion species with increasing temperature and confirm the feasibility and the spontaneous nature of Gd^{3+} and U^{6+} metal sorption removal using emulsion polymer[15].

3.3. Fixed bed sorption studies

The fixed bed column operation allows more efficient utilization of the sorptive capacity than the batch process due to, the isotherms are unable to give accurate data for scale-up since a flow in the column is not at equilibrium. The concept of fixed bed column is expressed graphically regarding the breakthrough curve and the shape of the breakthrough curve and the time for the

breakthrough appearance are the predominant factors for determining the operation and the dynamic response of the sorption column [16]. In this concern, the loading behavior of U^{6+} and Gd^{3+} ions sorbed onto prepared polymer in a fixed bed are shown by breakthrough curves that are expressed in terms of adsorbed metal concentration (Cad), inlet metal concentration (C$_o$), outlet metal concentration (C$_t$) or normalized concentration [ratio of outlet metal concentration to inlet metal concentration (C$_t$/C$_o$)] as a function of time or volume of solution for a pre-defined bed height [17]. The effects of process variables on the emulsion polymer column performance were studied, these include bed depth, flow rate, and initial ion concentrations [18]. The value of the total mass of metal adsorbed, q$_{total}$ (mg), for a given feed concentration (C_0, mg/L) and flow rate (Q, mL/min), can be found by calculating the area under the breakthrough curve obtained by integrating the sorbed ion concentration (C_{ads}, mg/L) versus time plot as shown in equation. (7):

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=total} C_{ad} dt \quad …………………………….. \textbf{(7)}$$

Where X is the dry weight of adsorbent in the column (g). The total amount of ion entering column (Xtotal) is calculated from the following equation (8)**:**

$$X = \frac{C_o V_{eff}}{1000} \quad …………………….. \textbf{(8)}$$

The total percent removal of metal can be calculated from the following equation (9):

$$R(\%) = \frac{q_{total}}{X} * 100 \quad …………………….\textbf{(9)}$$

Table (3): Fixed bed data of (U^{6+} and Gd^{3+}) metal sorbed onto the resin at different parameters and Wt 0.7 g.

| Ions	C_o (mg/L)	Q (mL/min)	Z (cm)	X (mg)	Q_{total} (mg)	Column Performance (%)	Bed Capacity (mg/g)
U^{6+}	50	2.3	7.0	22	12.5	55.6	17.8
			7.0	45	23.2	23.0	33.2
	100	2.3	9.0	55	27.5	27.5	29.8
			11.0	65	33.0	33.0	28.1
	150	2.3	7.0	52	24.0	45.7	34.3
Gd^{3+}	50	2.3	7.0	20	11.3	56.8	16.2
			7.0	40	21.9	21.9	31.3
	100	2.3	9.0	52	26.5	26.5	28.0
			11.0	40	30.0	30.0	25.0
	150	2.3	7.0	45	21.9	48.8	31.3

3.3.1. Effect of effluent concentration (Effect of initial ion concentration)

The breakthrough curves for sorption of U^{6+} and Gd^{3+} curves at different bed depths of emulsion polymer are shown in Figure (6), at the following parameters:- (C_0 = 50, 100 and 150 mg/L), column $\emptyset$=1cm, H = 7cm, flow rate (Q) = 2.3 mL/min, pH = 5.0.

The exhaust occurred after 195, 173 min for 50 mg/L while the breakthrough occurred at 195 and 173 concentrations, 141 and 130 min for 100 and 150 mg/L initial Uranium and Gadolinium respectively. When the effluent concentration of metal was increased, sharper breakthrough curves were obtained

and a steep breakthrough curve was obtained at 150 mg/L.

The total sorbed U^{6+} and Gd^{3+} quantities, treated volume at breakthrough times and removal percent with respect to the U^{6+} and/or Gd^{3+} concentration were evaluated from the sorption data are also presented in Tables (5) and illustrated that, with the rise of U^{6+} and Gd^{3+} concentration, the volume of solution treated before breakthrough reduces considerably. This is because a high ion concentration easily saturates the column bed, thereby decreasing the breakthrough time [19]. The main driving force for the sorption process is the concentration difference between the ions in the solution and the sorbent.
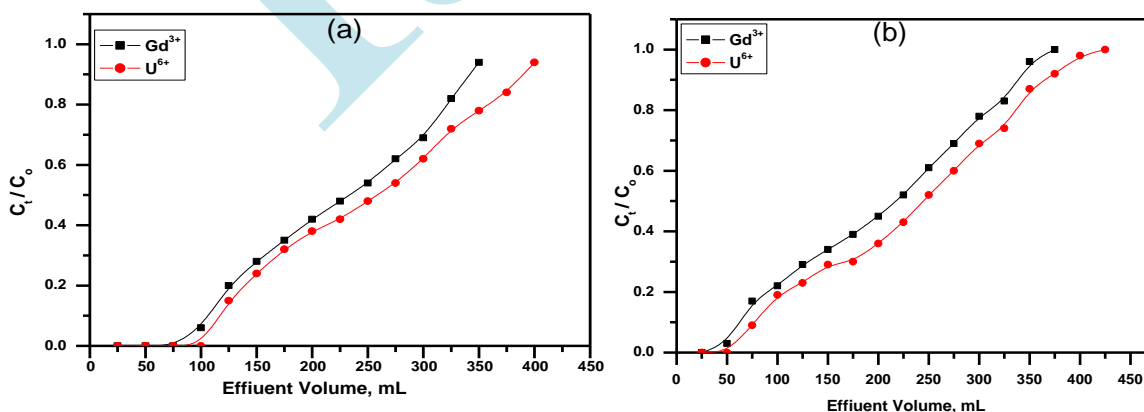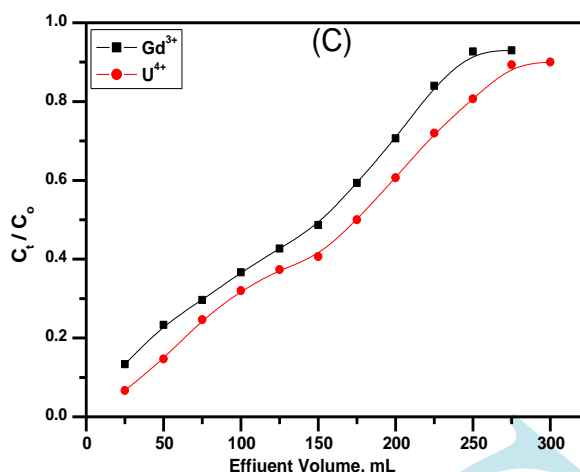
Figure (6)(a, b and c):- Effect of effluent concentration (a)50 mg/L (b) 100 mg/L(c) 150 mg/L on the breakthrough curve, bed depth 7.0 cm; flow rate 2.3 ml/min and pH 5.0.

3.3.2. Effect of different bed depths on breakthrough curve

Effect of bed height on a breakthrough curve was studied by operating the column at three different heights (Z = 7, 9 and 11 Cm) by charging 0.8, 1.1 and 1.5 g of sonicated emulsion polymer, respectively. The experimental condition controlled at flow rate (*Q*) 2. 3 mL/min, initial U^{6+} and Gd^{3+} concentration 100 mg/L at pH = 5.0 and expressed in figure (7), make a relation between (C_t/C_0) and effluent volume.

The results revealed that the volume of solution treated increased with the increase in bed depth, due to the higher availability of exchange functional groups. The exhaust time grew at 450, 550 and 650 mL. It is clear that as the bed depth increased, both the exhaustion time and effluent volume (V_{eff}) increased might be due to the more contact time. when the bed height was increased from 7, 9 and 11 Cm, respectively. An increase in column length (the other parameters being kept constant) improves both the breakthrough and the overall capacity[20]. There is a greater quantity of emulsion polymer in the column consequently, availability of ion exchange sites increases linearly with the height of the column.
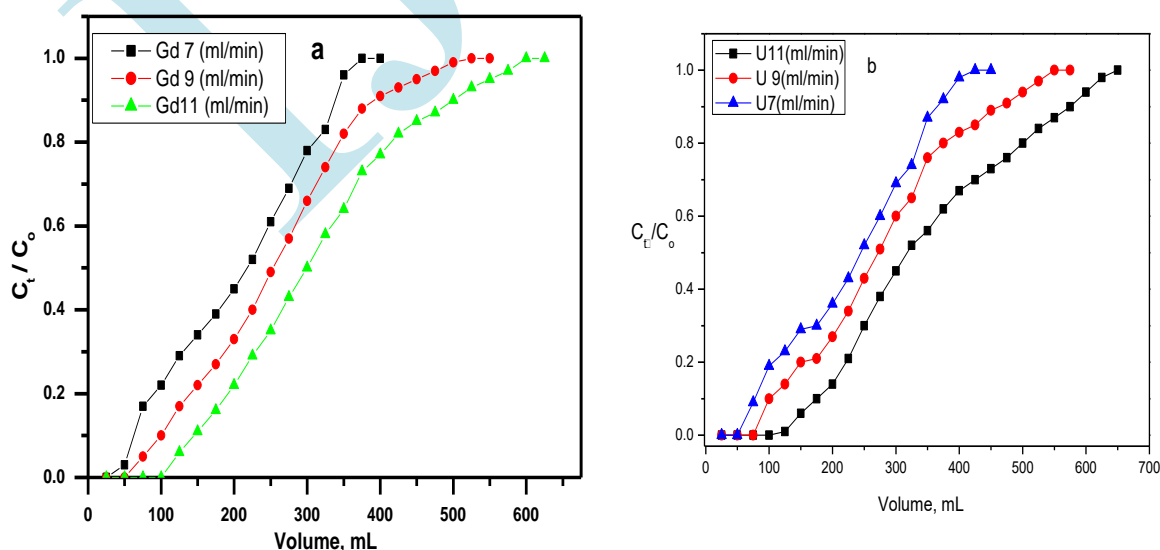

Figure (7): Effect of various bed depths on the breakthrough curve of (a) Gd^{3+} and (b) U^{6+} ions.

3.3.3. Effect of feed flow rate on breakthrough Curve

To study the effect of flow rate, columns were charged at flow rates of 2.3 and 6 mL/min with initial concentration maintained at 100 mg/L and: column, Ø=10 mm, H = 7.0 Cm and X = 1.4g , initial metal concentration 100 mg/L, pH = 5. Since the flow rate is varying, breakthrough curves are shown in Fig. (8). When the flow rate is increased from 2.3 to 6.0 mL/min the exhaust time decreased from 380 to 500 min for Gd^{3+} and from 405 to 520 min for U^{6+} and earlier breakthrough and exhaustion were observed with increase in flow rate. This reduction is due to insufficient contact time in the bed [21]. At higher flow rates, the slope of the curve decreased showing a high volume of an unsaturated zone as a result of insufficient contact and gives the lower removal efficiency.
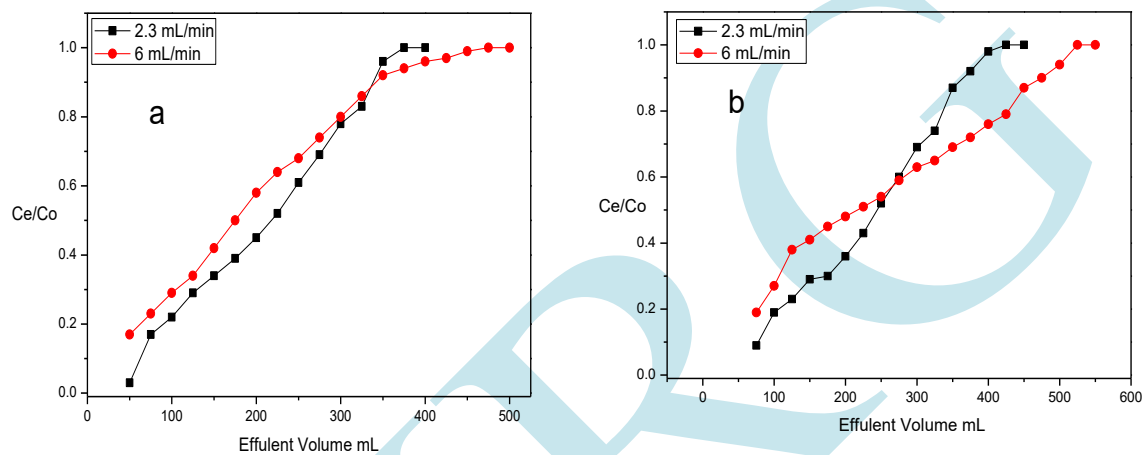
Figure (8): Effect of various flow rates on the breakthrough curve of (a) $Gd^{3+}$and (b) U^{6+} ions.

3.4. Breakthrough Curve Modeling

The most critical stander in the design of fixed bed sorption systems is the prediction of fixed bed column breakthrough which, determines the operational lifespan of the bed it is. In this research studying the dynamics of the sorption process was achieved by using (**BDST**) Bed depth service time method.

3.4.1. The Bed depth service time (BDST) Model.

The BDST model is a simple model was applied to the present experimental data to study the breakthrough behavior of U^{6+} and Gd^{3+} metal onto sonicated emulsion polymer and predicting the relationship between bed depth, Z, and service time, t, in terms of process concentration and adsorption parameters, which revealed to estimate the characteristic parameters, K and N_0 from the slope and intercept of the linear plot as illustrated in **table (2)**. The origin of (BDST) is a model proposed by Bohart and Adams. The BDST model is based on the assumption that the rate of adsorption is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent [22]. The values of breakthrough time obtained for various bed depth used in this study were introduced into the BDST model. A linear relationship between bed depth and service time is given by **Eq. (10)**:

$$t = \frac{N_O Z}{C_O U_o} - \frac{1}{KC_o} ln\left(\frac{C_O}{C_t} - 1\right) \ldots\ldots\ldots(10)$$

where C_t is the effluent concentration of each ion (mg/L), C_o the initial ion concentration (mg/L), t the breakthrough service time, N_o the volumetric adsorption capacity (mg/L), Z the bed depth of the column (cm), U_o the linear flow velocity of feed to bed (cm/min) and K is the sorption rate

constant (L/mg min). The equation of a straight line on the BDST curve is expressed as in the form of:

$$t = m\,Z + b \quad\ldots\ldots\ldots\ldots\ldots(11)$$

where m is the slope, and b is the ordinate intercept represented by[12]:

$$m = \frac{N_o}{C_o U_o} \quad \text{and}$$

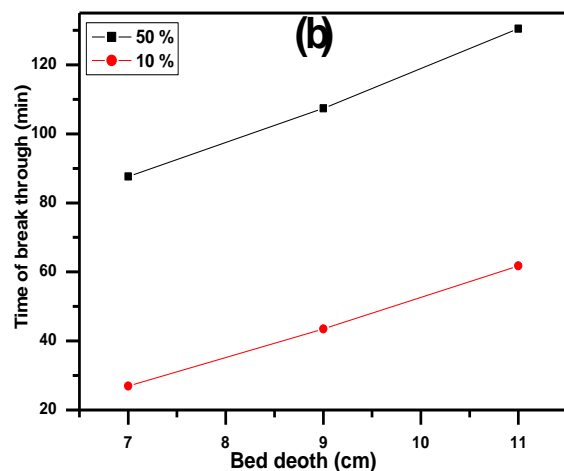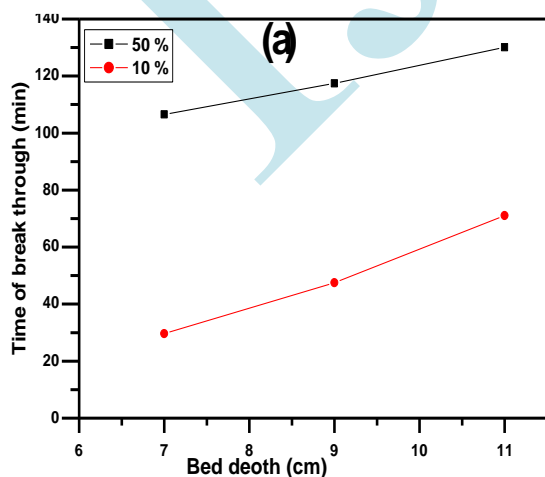$$b = -\frac{1}{KC_o} ln\left(\frac{C_O}{C_t} - 1\right) \quad\ldots\ldots\ldots(12)$$

The critical bed depth (Z_o), which represent the theoretical depth of sonicated polymer which sufficient to prevent the U^{6+} and Gd^{3+} concentration from exceeding

C_b at t = 0, was estimated from Eq. (9). The critical bed depth (Z_o) is obtained for t = 0 and for a fixed outlet concentration C_t = C_b, where C_b is the breakthrough concentration defined as a limit concentration or a fixed percent of initial concentration [23] given by Eq. (12). The critical bed depth (Z_o) represents the theoretical depth of sorbent, necessary to prevent the sorbate concentration to exceed the limit concentration C_b, are illustrated in **table (4).**

$$Z_O = \frac{U_o}{KN_o} ln\left(\frac{C_O}{C_b} - 1\right) \quad\ldots\ldots\ldots\ldots(13)$$

Table(4):- BDST model parameters of U^{6+} and Gd^{3+} metal sorbed on polymer at different bed depths.

Ions	Q (mL/min)	Z(cm)	Time to 10% breakthrough (min)	N_o Mg/mL	$K*10^4$ (L/mg min)	Z_o (Cm)
		7	29.6		0.0005	2.5
	2.3	9	47.4			
		11	71.1	3.03		
U^{6+}		7	20.52		0.0003	3.2
		9	41.3			
	6.0	11	59.1	1.72		
		7	26.9	3.13	0.0006	2.3
		9	43.4			
	2.3	11	61.7			
Gd^{3+}		7	21.6	2.54	0.0002	2.9
	6.0	9	38.3			
		11	57.4			

Figure (9):- BDST plots at 50 % and 10 % breakthrough for sorption of (a) U^{6+} and (b) Gd^{3+} ions.

The data present in Table (4), revealed that the maximum sorption capacity (N_o) decreased with the increase in flow rate and the values of the sorption rate constant (K) were influenced by flow rate and increased. The external mass transfer commanded the overall system in the initial section of the sorption in the column which increased with the increase of flow rate. The obtained values of critical bed depth (Z_o) (2.5 and 3.2) for the removal of U^{6+} metal were higher than(2.3 and 2.9) Gd^{3+} metal and these values increased with the increase in flow rate.

3.4.2. Elution curve

Efficient elution of adsorbed solute from the polymer in a column was essential to ensure the fixed concentration of samples were loaded and eluted individually with different concentration using (0.1, 0.05 and 0.001) M of HCl and 0.5, 0.1 and 0.05) M of HNO_3 as shown in figure (10 and 11).

The desorption of U^{6+} and Gd^{3+} on the column have been optimized systematically and the effluent was collected in 10 ml vials and measured using U.V and the affinity of elution for each concentration was frequently represented at the following figure. Desorption curve was plotted as the effluent concentration (Ce) vs. elution volume from the column at a specific flow rate. It can be seen from Figure (10) that the desorption flow rate was low so that the volume of elution was small which helped in easy handling and high in concentration for economical removal of Gd^{3+}. It was observed that the total volume of eluent was 200 mL and the time of desorption process took depended on flow rate. Therefore, the 0.5mol/L HCl and 0.1 mol/L HNO_3 eluent could help in easy handling and removal of studied ions.
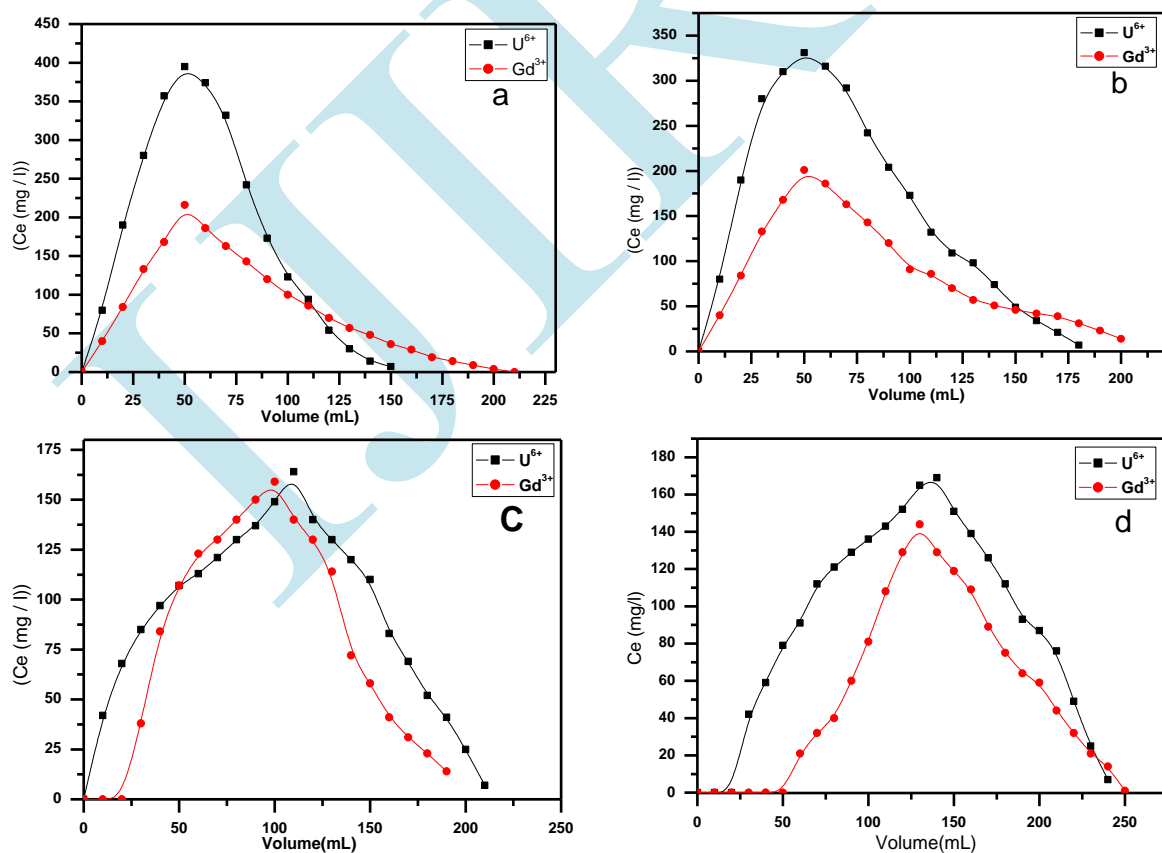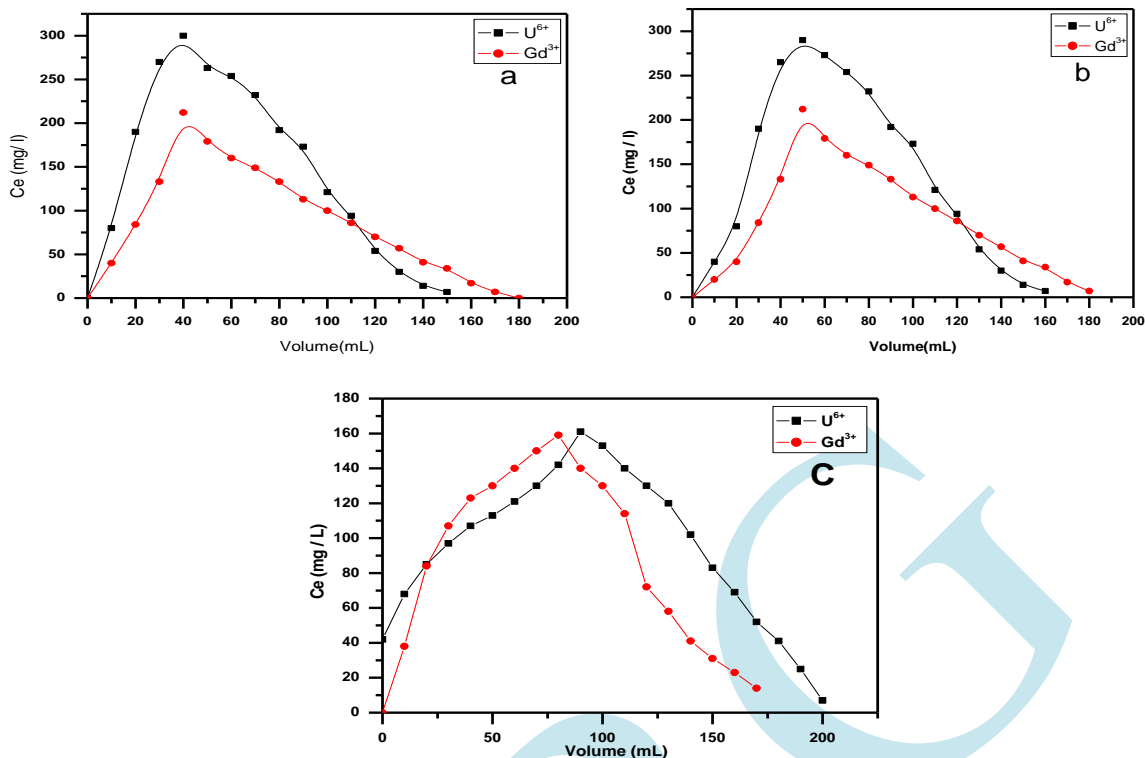

Figure (10): Dynamic desorption curve (a) 0.5 M (b) 0.1 M (C) 0.05 M(d) 0.001 M Hcl resin 1.0g , flow rate=2.3 mL/min, T=298K.

Figure (11): Elution curve (a, b and c) (0.5, 0.1 and 0.01) M HNO₃ Resin 1.0 g, flow rate=2.3 mL/min, T=298K.

4- CONCLUSION

The synthetic sonicated emulsion polymer was tested as organic ion exchange material for the removal of Uranium and gadolinium metal from aqueous solution. The kinetics of both metals was experimentally studied and the obtained rate data were analyzed using simple kinetic models. Results explained that the pseudo-second-order sorption mechanism is predominant and the overall rate constant of each sorption process appears to be controlled by chemical sorption process. Equilibrium isotherms have been determined and tested for different isotherm express and the sorption data were successfully modeled using Langmuir and Freundlich approaches and illustrated that the maximum sorption capacity and the mean free energy of the studied have been determined. The sorption of each ion is an endothermic process and spontaneous.

Sorption of Uranium (IV) and Gadolinium (III) onto sonicated emulsion polymer was investigated using fixed-bed column. The effect of operation condition the adsorption of fixed bed column has been investigated and systematically and the results show that the adsorption capacity increased with increasing effluent concentration but decreased with increasing bed depth and flow rate Consequently a lower flow rate gives a higher sorption capacity at a fixed U^{6+} and Gd^{3+} .

The Bed depth service time model has been used to describe the dynamic sorption of U^{6+} and Gd^{3+} through the packed column. The effect of the eluent type on the desorption of the column has been investigated and optimized systematically. The results show that HNO₃ has a more significant effect more than HCl for U^{6+} and Gd^{3+} ions with an elution efficiency of 98.0% and found to be suitable for reuse in successive adsorption-desorption cycles even times without significant loss in adsorption capacity.

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