Preparation of new modified silica gel terminated with phenylphosphonic acid-amide moieties for adsorption of uranium(VI) from aqueous solutions

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Abstract
PAMAM dendrimers modified silica gel terminated phenylphosphonic acid-amide moieties (Si-6G PAMAM-PPAAM) was prepared for uranium(VI) adsorption from aqueous solutions by batch and fixed-bed column methods. The experimental results showed that the maximum capacity was 434.78 mg g⁻¹. Equilibrium isotherm data obeyed Langmuir isotherm model. Kinetic adsorption followed pseudo-second order model and thermodynamic parameters implied the adsorption was spontaneous, endothermic. The adsorption performance of the new adsorbent toward uranium using fixed-bed column method was also investigated. The investigated adsorbent (Si-6G PAMAM-PPAAM) was successfully used to extract uranium from leach liquor of granitic rock sample.

Keywords PAMAM dendrimer · Phenylphosphonic acid-amide · Uranium · Silica gel · Batch technique and column method

Introduction
Adjusting the energy structure and reducing carbon emissions need rapid development of nuclear power industry, but nuclear fuel pretreatment cause environmental problems. Uranium mining and hydrometallurgy processes produce a large number of uranium wastewater (production wastewater, tailings wastewater, mine water, contaminated groundwater by in situ leaching uranium mining, etc.), which cause a serious threat to the ecological environment and waste resources [1–7].

Many methods were recorded for removal of uranium ions from the aqueous solutions such as solvent extraction, precipitation, electrochemical techniques, ion-exchange methods, flotation and coagulation [8–13]. Among these techniques adsorption method was considered as the best and economic for separation of uranium species [14–19]. However the most problem in this method is how to select a suitable adsorbent with a high capacity, more selectivity and with a low economic cost rather than polymeric resin. For this target silica gel was recommended as an inorganic solid support due to it has many advantages in comparing with polymeric resin for removing different metal ions from aqueous solutions [20]. It includes high selectivity, insoluble in water, no swelling, rapid sorption of metal ions, and good mechanical stability [21]. The modification of silica gel based organic–inorganic hybrid materials for the removal of U(VI) has become an interesting subject [12, 13, 22–29].

In our previous work silica gel was functionalized with polyamidoamine (PAMAM) dendrimers which contain large numbers of nitrogen and oxygen groups to improve the binding ability toward uranium ions due to the prevalence of peripheral amine groups [30]. In the present work, we extend our previous results to prepare a polyamidoamine dendrimers modified silica gel terminated with phenylphosphonic acid-amide (Si-6G PAMAM-PPAAM) for using in adsorption of U(VI) from aqueous solution using batch and column techniques. As the modified silica gel containing phosphorus groups have exhibited superior adsorption characteristics such as high adsorption rate, improved capacity and good selectivity toward uranium ions. The effects of various parameters on adsorbent capacity for U(VI) were
studied using batch and column methods then applied to adsorb uranium(VI) from real samples.

**Experimental**

**Materials**

Phenylphosphonic dichloride and Arsenazo III were obtained from Sigma-Aldrich, Germany. Xylene, Ethanol, sodium hydroxide and sodium chloride were of analytical grades. U(IV) stock solution (1000 mgL⁻¹) was prepared by dissolving 2.11 g of UO₂(NO₃)₂·6H₂O (Sigma-Aldrich, Germany) in 1 L of 0.05 MHNO₃.

**Preparation of Si-6G PAMAM**

Si-6G PAMAM was prepared according to our previous work [30]. Briefly activated silica gel reacts with 3-aminopropyltrimethoxysilane to give Si-APMS. The latter was reacted with methyl acrylate in methanol to obtain Si-0.5G PAMAM. After that Si-0.5G PAMAM reacted with ethylene diamine to give the complete generation of modified silica gel (Si-1G PAMAM). These last two steps repeated six times to obtain Si-6G PAMAM.

**Preparation of Si-6G PAMAM-PPAAM**

The modified Si-6G PAMAM-PPAAM is prepared by refluxing Si-6G PAMAM (10 g) with phenyl phosphonic dichloride in the presence of xylene in an oil bath for 12 h. The prepared adsorbent is washed several times with ethanol and double distilled water then dried under vacuum at 70 ºC. The synthetic route of Si-6G PAMAM-PPAAM is illustrated in Scheme 1.

**Characterization of Si-6G PAMAM-PPAAM**

FTIR spectra for Si-6G PAMAM and Si-6G PAMAM-PPAAM before and after uranium adsorption were determined using Nexus-Nicolite Model 640-MSA. Thermal gravimetric analysis (TGA) for Si-6G PAMAM-PPAAM was determined under N₂ atmosphere using temperature range from room temperature to 800 ºC and heating rate of 10 ºC min⁻¹ using SDT Q600 V20.5 Build15. The surface morphology was observed using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit. Porous structure parameters for Si-6G PAMAM and Si-6G PAMAM-PPAAM were characterized by Brunauer–Emmett–Teller (BET) and BJH methods (Quanta chrome Instruments v1.03) through N₂ adsorption–desorption methods using nitrogen gas as adsorbent at 77 K. Before analysis the adsorbent was pretreated in vacuum at 100 ºC for 8 h.

**Uptake of U(VI) using batch method**

In volumetric flask, a suitable amount of Si-6GPAMAM-PPAAM was added to 100 mL of uranium solution of initial concentration (100–800) mg g⁻¹. The flasks were shaken using a Vibromatic-384 shaker at 120 rpm for (1–30) min at different temperatures (15 ºC, 25 ºC, 35 ºC) and pH range (2–9). The residual concentration of U(VI) was determined at equilibration using arszenazo III [31].

The removal percentage (R) and the adsorption capacity (Qₑ) for uranium were calculated according to Eqs. 1 and 2, respectively.

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where Qₑ is the adsorption capacity (mg g⁻¹), C₀, Cₑ is the initial and equilibrium U(VI) concentration (mg L⁻¹) respectively, V is the volume of uranium solution, (L) and W is the weight of dry Si-6G PAMAM-PPAAM (g).

**Uptake of U(VI) using column method**

The synthesized Si-6G PAMAM-PPAAM was packed in a glass column with an inner diameter of 1.0 cm and length of 10 cm. The adsorption experiments were carried out at different bed heights (1 and 2 cm), flow rates (1, 3 and 5 mL min⁻¹), U(IV) concentration (150 mg L⁻¹), pH = 4.5 at T = 25 ºC. The outlet U(VI) solutions were collected at definite time intervals and analyzed using (UV–Visible) spectrophotometer as previously described. The fixed bed column experiments were stopped when the column reached exhaustion.

The fixed-bed adsorption is conveniently described by the breakthrough curve Cₑ/Co vs. volume (where Cₑ and Co are the effluent and inlet metal ions concentration, respectively) for a given bed height. The value of total adsorbed U(VI) quantity of a given influent concentration and flow rate from the area under the breakthrough curve was determined by integrating the adsorbed U(VI) concentration versus time as illustrated in the following equation [32]:

$$q_{total} = \frac{Q}{1000} \int_0^{\text{tot}} C_{ads} dt = \frac{Q}{1000} \int_0^{\text{tot}} (C_o - C_{eff}) dt \quad (3)$$

where, Q and Cₐₜ₅ are the volumetric flow rate (mL min⁻¹) and concentration of adsorbed metal ion (mg L⁻¹), respectively.
The equilibrium adsorption capacity $q_e$ (mg g$^{-1}$) of Si-6G PAMAM-PPAAM [33] is calculated from Eq. (4)

$$q_e = \frac{q_{total}}{W}$$  \hspace{1cm} (4)

where $W$ is the total dry weight of Si-6G PAMAM-PPAAM (g).

The total amount of uranium ions fed into the column (X, mg) is calculated from the following equation:

$$X = \frac{C_o V_{eff}}{1000}$$  \hspace{1cm} (5)

where $V_{eff}$ is the effluent volume of the uranium solution (mL).

The column performance by Si-6G PAMAM-PPAAM or the ratio of the maximum capacity of uranium sorption ($q_{total}$, mg) to the total amount of uranium ions fed into the column (X, mg) can be calculated from the following equation:

$$R(\%) = \frac{q_{total}}{X} \times 100$$  \hspace{1cm} (6)

Also, the mass transfer zone $\Delta t$ is given by the following equation:

$$\Delta t = t_e - t_p$$  \hspace{1cm} (7)

The length of mass transfer zone ($Z_m$, cm) is obtained from the break-through curve using the following equation [33]:

Scheme 1  The synthetic routes of a (Si-nG PAMAM-PPAAM) and b The product (Si-6G PAMAM-PPAAM)
\[ Z_m = Z \left( 1 - \frac{t_b}{t_e} \right) \]  

where \( Z \) is the bed height in cm, \( t_b \) is the time at breakthrough point (min) and \( t_e \) is the time at exhaustion point (min).

**Elution experiment**

Elution experiments were carried out by placing 0.25 g of Si-6G PAMAM-PPAAM in the column then loaded with U(VI) at the flow rate of 1 mL min\(^{-1}\). The maximum uptake was obtained in the first run, thereafter the adsorbent was washed by flowing distilled water crossing the column. The synthesized adsorbent loaded by U(VI) was subjected to elution using 1 M HNO\(_3\), then washed carefully with a diluted aqueous solution of NaOH and finally with distilled water to become ready for using again.

**Results and discussion**

**Characterization of adsorbents**

FT-IR spectrum of Si-6G PAMAM and Si-6G PAMAM-PPAAM before and after adsorption of U(VI) were presented in Fig. 1a–c, respectively. For all adsorbents in Fig. 1a–c the absorption bands in the range of 3450–3200 cm\(^{-1}\) are related to –OH and –NH groups. The strong band at 1100 cm\(^{-1}\) is due to Si–O–Si stretching vibration. The bands at 770 and 435 cm\(^{-1}\) were related to the symmetric and bending vibration of Si–O–Si in the silica gel network [20]. Strong peaks at 2950 cm\(^{-1}\) and 2800 cm\(^{-1}\) were corresponding to asymmetric and symmetric CH\(_2\) bands. The absorption bands at 1650 cm\(^{-1}\) and 1555 cm\(^{-1}\) were referred to amide I and amide II groups. The spectrum of Si-6G PAMAM-PPAAM had strong bands at 1211 cm\(^{-1}\) group in Fig. 1b was due to the P=O group [3]. The peak for uranyl ions appearing around 900 cm\(^{-1}\) in Fig. 1c, while the absorption intensity spectrum of –NH, –OH and P=O group vibrations around 3430 cm\(^{-1}\) and 1211 cm\(^{-1}\) were decreased after uranium adsorption.

The TGA curve indicated that Si-6G PAMAM-PPAAM undergoes degradation through three stages. The first degradation stage was from 15 to 200 °C with a partial weight loss of 9.87% due to physically adsorbed water which presented in the external surface and the internal pores or the cavities of the adsorbent. The second stage was from 200 to 400 °C with a partial weight loss of 18.28% which assigned to the decomposition of dendrimers layer and the condensation of the remaining silanol groups. The third stage was from 400 to 800 °C with a weight loss of 7.66% due to the decomposition of phenylphosphonic acid-amide moieties Fig. 2.

The BET surface area, BJH desorption cumulative volume of pores and BJH desorption average pore radius for Si-6G PAMAM-PPAAM indicated that the surface area and pore size of the prepared adsorbent became smaller when Si-6G PAMAM modified with phenylphosphonic acid-amide moieties, as described in Table 1. These results confirmed that a large amount of functional groups have been chemically grafted on the surface of Si-6G PAMAM-PPAAM. This indicates that increasing the number of functional groups on Si-6G PAMAM-PPAAM surface is very important than high surface area and pore volume when the prepared adsorbent is used for adsorption [34, 35].

The change of the surface morphologies of Si-6G PAMAM-PPAAM before and after uranium adsorption is presented in Fig. 3a, b. As shown in this figure, a lot of the
crevices were clearly disappeared due to the adsorption of uranium ions on the surface of the adsorbent. EDX elemental analysis of Si-6G PAMAM-PPAAM showed a chemical composition of 29.76% C, 4.08% N, 24.42% O, 37.16% Si and 4.58% P Fig. 3c. After U(VI) adsorption process, the characteristic peaks of uranium and the percentage (in mass) of U(VI) was 44.12% were clearly shown in Fig. 3d.

**Uptake of U(VI) by batch method**

**Effect of pH**

The pH effect on U(VI) adsorption by Si-6G PAMAM-PPAAM was studied by varying the solution pH between 2 to 9 as shown in Fig. 4. The uptake capacity of Si-6G PMAM-PPAAM increases with the increase of pH value and reaches its maximum at pH 4.5 then decreases again at higher pH. The NH and O = P–OH functional groups of adsorbent surface make complex with U(VI). At pH below 4.5, the uptake capacity was decreased due to protonation of NH and O = P–OH groups. Also the observed decrease in the uptake of UO$_2$$^{2+}$ at pH > 4.8 can be explained on the basis of the formation of different uranyl species with lower adsorption affinities. At pH ≥ 4.5 various oligomeric and monomeric hydrolyzed species of UO$_2$$^{2+}$ are reported [36, 37].

**Effect of the adsorbent dosage**

The effect of adsorbent amount was carried out using Si-6G PAMAM-PPAAM dosage ranging from 0.03 to 0.15 g and with initial concentration of U(VI) (100 mg L$^{-1}$, 100 mL) at room temperature and pH 4.5. As can be illustrated in Fig. 5, the adsorption percentage of U(VI) increased with increasing Si-6G PAMAM-PPAAM dosage until reached to 99.9% at 0.07 g of adsorbent. After that, a tendency to show a plateau was observed.

**Adsorption Kinetics**

The kinetics experiments for adsorption of U(VI) onto Si-6G PAMAM-PPAAM are conducted at pH 4.5 at different temperatures and different contact times. The obtained data indicates that the equilibrium time is attended during 15 min as shown in Fig. 6. In this respect two different kinetic models namely Lagergren’s pseudo-first-order and pseudo-second-order kinetic models [38, 39] are applied to discuss the kinetic mechanism of adsorption as shown in Fig. 6a, b.

The values of kinetics parameters of these models are summarized in Table 2. It is obvious that pseudo-second-order model provides higher correlation coefficients (R2) than those of pseudo-first-order model, suggesting that pseudo-second-order model is more suitable to describe the adsorption kinetics of U(VI). It is also observed that the equilibrium adsorption capacity calculated (Qe,cal) based on pseudo-second-order model are much better in agreement with the experimental data (Qe,exp), further demonstrating that the kinetic adsorption processes follow pseudo-second-order model better than pseudo-first-order model and the reaction is a chemisorption process. It proceeds via reaction on an exposed surface, which creates a chemical bond between the surface of Si-6G PAMAM-PPAAM and the uranium ions. Chemisorption reaction is irreversible and involves more heat during the experiment than physical adsorption [40].

**Effect of initial concentration and equilibrium isotherm models**

The effect of initial U(VI) concentration on the adsorption capacity of Si-6G PAMAM-PPAAM was studied in concentration ranging from 100 to 800 mg L$^{-1}$ at pH 4.5 and T = 25 ºC with constant contact time (30 min). The adsorption capacity of Si-6G PAMAM-PPAAM increases by increasing U(VI) initial concentration until reaching the plateau as shown in Fig. 7. This can be due to the increase in mass driving force from the bulk solution to the

![Fig. 2 TGA curve of Si-6G PAMAM-PPAAM](image)

**Table 1** The parameters of porous structure for Si-6G PAMAM and Si-6G PAMAM-PPAAM

| Adsorbents          | BET Surface Area (m$^2$ g$^{-1}$) | BJH Desorption cumulative volume of pores (cm$^3$ g$^{-1}$) | BJH Desorption average pore radius (nm) |
|---------------------|-----------------------------------|-------------------------------------------------|----------------------------------------|
| Si-6G PAMAM         | 57.450                            | 0.024                                           | 1.231                                   |
| Si-6G PAMAM-PPAAM   | 25.640                            | 0.021                                           | 1.120                                   |
adsorbent surface which enhances the interaction between adsorbate and the adsorbent. The maximum adsorption capacity for uranium on Si-6G PAMAM-PPAAM was determined experimentally to be 400 mg g⁻¹. In order to define the mechanism of uranium adsorption onto Si-6G PAMAM-PPAAM, the experimental data were applied to Langmuir, Freundlich and Temkin linear isotherm models.
Langmuir isotherm model

The Langmuir isotherm model is proper for monolayer adsorption onto a surface. The model assumes uniform energies of adsorption onto the surface and no migration of adsorbate in the level of the surface. The adsorption process is homogeneous, where adsorption activation energy on the surface of adsorbent is uniform. Langmuir is represented on the linear form as the following [41]:

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}
\]

where, \( C_e \) is the equilibrium concentration of U(VI) in the solution (mg L\(^{-1}\)), \( Q_e \) is the adsorption capacity (mg g\(^{-1}\)) at equilibrium, \( Q_{max} \) is the maximum adsorption capacity (mg g\(^{-1}\)) and \( b \) (L mg\(^{-1}\)) is the binding constant. The fundamental features of the Langmuir isotherm may be expressed in terms of equilibrium parameter \( R_L \), which is a dimensionless constant referred to as separation factor or equilibrium parameter [42] which is defined as the following equation:

\[
R_L = \frac{1}{1 + bC_o}
\]

The value of \( R_L \) indicates the nature of the isotherm to be irreversible (\( R_L = 0 \)), favorable (\( 0 > R_L > 1 \)) and unfavorable (\( R_L = 1 \)). Plotting of \( R_L \) versus \( C_o \) is shown in Fig. 8, the calculated \( R_L \) values are greater than 0 but less than 1. This indicates that the adsorption of U(VI) onto Si-6G PAMAM-PPAAM is favorable under the used conditions in this study. The \( R_L \) values decreased as the \( (C_o) \) of uranium ion increased which showed that the adsorption of uranium ions is more effective at higher initial concentration. As shown in Fig. 9 the maximum monolayer capacity \( Q_{max} \) was determined to be 434.78 mg/g, \( b \) (Langmuir isotherm constant) is 0.047 L/mg, \( K_L \) (the separation factor) is 0.0.047 this, indicating that the equilibrium adsorption was favorable and the \( R^2 \) value is 0.99 proving that the adsorption data fitted well to Langmuir Isotherm model Table 3.

The Freundlich isotherm model

The Freundlich isotherm model is an empirical relation which is used to explain the adsorption characteristics of the heterogeneous surface. And consider that the adsorption occurs at sites with different energy of adsorption.

The linear form of Freundlich adsorption model can be written as illustrated by the following equation [43, 44]:

\[
\ln Q_e = \ln K_f + \frac{\ln C_o}{n}
\]

\( Q_e \) is the adsorption capacity at equilibrium (mg g\(^{-1}\)), \( K_f \) is the Freundlich constant (mg kg\(^{-1}\)), \( n \) is the Freundlich empirical constant, and \( C_o \) is the equilibrium concentration of U(VI) in the solution (mg L\(^{-1}\)). The Freundlich isotherm model is plotted in Fig. 5 for Si-6G PAMAM-PPAAM at different amounts of adsorbent. The adsorption process is favorable as the calculated values of \( K_f \) and \( n \) are greater than 1 and less than 1, respectively. The adsorption data fitted well to Freundlich isotherm model with \( R^2 = 0.99 \) as shown in Table 3.
Linear plots of $\ln Q_e$ vs $\ln C_e$ as shown in Fig. 10. Where, $K_f$ is constant for Freundlich adsorption model, $1/n$ is a function of strength of adsorption. The nature of Freundlich isotherm depends mainly on the values of $1/n$ when $1/n > 1$ the process is unfavorable and is to be favorable when $0 < 1/n < 1$ however when $1/n = 0$ the process becomes irreversible. Table 3 showed the obtained Freundlich isotherm parameters, the $1/n$ value was 0.184, indicating that the adsorption of U(VI) onto Si-6G PAMAM-PPA is favorable.

Temkin isotherm model

Temkin isotherm has one factor that declares the interaction between adsorbent and adsorbing particle so vividly. It is represented by the Eq. (17), Fig. 11. As $BT$ and $AT$ are constants related to surface heterogeneity of the adsorbent and the equilibrium binding constant corresponding to the maximum binding energy, respectively. Where, $B_T = R_T/b_T$, $T$ is the absolute temperature, $R$ is universal gas constant. Also, $b_T$ is related to the heat of adsorption. Temkin calculated parameters are given in Table 3.

After comparing the correlation coefficients of the three models, it is clear that Langmuir model closely fits to the experimental data very well with high correlation coefficient ($R^2 = 0.99$) as compared to the ones given by Freundlich model ($R^2 = 0.89$) and Temkin model ($R^2 = 0.83$).

Adsorption thermodynamic

Thermodynamic parameters obtained for U(VI) adsorption process were calculated according to the following equations [44–46]:

\[
\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{14}
\]
where $K_c$ is the thermodynamic equilibrium constant, $T$ is the temperature of solution (K), and $R$ (8.314 J (mol K)$^{-1}$) is the universal gas constant, $ΔH^°$ (kJ mol$^{-1}$) is the enthalpy change and $ΔS^°$ is the standard entropy (J mol$^{-1}$ K$^{-1}$).

Thermodynamic parameters such as ($ΔH^°$) and ($ΔS^°$) were determined by plotting ln $K_c$ versus $1/T$ (Fig. 12) according to Van’t Hoff Eq. (16). The thermodynamic experiments are carried out at 288, 298 and 308 K using 100 mg L$^{-1}$ of U(VI). Free energy change ($ΔG^°$) is calculated and the obtained data are tabulated in Table 4.

$$ΔG^° = ΔH^°TΔS^°$$  \tag{16}

Our results indicate that the adsorption of uranium onto Si-6G PAMAM-PPAAM slightly increases by increasing the temperature. $ΔH^p$ associated consist of a) enthalpy change for dehydration ($ΔHd^p$) which can be expected to be positive because energy required to break the ion-water and water-water bonding of the hydrated ions and b) enthalpy change for complexing ($ΔHc^p$) which will make $ΔH^p$ more negative due to the formation of metal complex. The positive $ΔH^p$ value obtained for the adsorption of uranium ions indicates that dehydration seems to be more significant than complexation. Also, the positive value of $ΔH^p$ means that the adsorption of uranium using Si-6G PAMAM-PPAAM is an endothermic process as seen in Table 4 [47]. The positive value of $ΔS^°$ suggests an increase in randomness at the solid/liquid interface during the adsorption process. The negative value of free energy change ($ΔG^°$) proves the feasibility and

Table 3: Adsorption isotherm parameters for U(VI) adsorption onto Si-6G PAMAM-PPAAM

| Adsorption isotherm | Langmuir isotherm | Freundlich isotherm | Temkin isotherm |
|--------------------|-------------------|---------------------|-----------------|
|                    | $Q_{max}$ (mg g$^{-1}$) | $B$ (L mg$^{-1}$) | $R^2$ | $K_f$ | $1/n$ | $R^2$ | $1/n$ | $b_T$ | $R^2$ | $b_T$ | $A_T$ (Lmin$^{-1}$) | $R^2$ |
|                    | 434.78 | 0.047 | 0.99 | 133.31 | 0.18 | 0.89 | 0.28 | 40.29 | 38.09 | 0.83 | 6.5 |

Fig. 10 Freundlich isotherm for the adsorption of U(VI) onto Si-6G PAMAM-PPAAM at T = 25 °C

![Fig. 10](image1)

Fig. 11 Temkin isotherm for the adsorption of U(VI) onto Si-6G PAMAM-PPAAM at T = 25 °C

![Fig. 11](image2)

Table 4: Thermodynamic parameters for U(VI) adsorption by Si-6G PAMAM-PPAAM

| T(°C) | $ΔG^°$ (kJ mol$^{-1}$) | $ΔH^p$ (kJ mol$^{-1}$) | $ΔS^°$ (J (mol K)$^{-1}$) |
|-------|----------------------|------------------------|--------------------------|
| 15    | −168.57              |                        |                          |
| 25    | −174.43              | 161.11                 | 585.88                   |
| 35    | −180.29              |                        |                          |

![Fig. 12](image3)
the spontaneous nature of uranium adsorption onto Si-6G PAMAM-PPAAM. The increase in the negative values of $\Delta G^\circ$ by increasing the temperature indicates the formation of more stable bonding between U(VI) and amino groups of Si-6G PAMAM-PPAAM at the higher temperature, consequently more adsorption capacity.

### Uptake of U(VI) using fixed-bed column technique

**Effect of bed height**

Adsorbent bed height is an effective component that influences the dynamic performance of the column in adsorption studies. The break-through curves of adsorption of U(VI) onto Si-6G PAMAM-PPAAM at bed height (1 and 2 cm), flow rates (1, 3 and 5 mL min$^{-1}$) and 150 mg g$^{-1}$ as initial concentration of U(VI) were described in (Fig. 13a–c). The shape of break-through curves of U(VI) at different flow rates was significantly different as the bed height changed from 1 to 2. From the calculated results shown in Table 5, the break-through time ($t_b$), exhaustion time ($t_e$), ($\Delta t$) and the height of mass transfer zone ($Z_m$) were increased with increasing of bed height. A larger volume of uranium solution could be treated, as there was increasing in the ratio of the adsorbent, whereas extra binding sites of Si-6G PAMAM-PPAAM were ready for adsorption. The calculated results indicate that, uptake capacities ($q_e$ mg g$^{-1}$) were decreased by increasing the bed height at different flow rates is owing to the change in volume to mass ratio of ion exchange [48]. The sorption capacity of Si-6G PAMAM-PPAAM for U(VI) was calculated as about (400 mg g$^{-1}$) at bed height 1 cm and flow rate 1 mL min$^{-1}$.

**Effect of flow rate**

The breakthrough curves for the adsorption of uranium ions at different flow rates (1, 3 and 5 mL min$^{-1}$) were given in Fig. 13(a–c). The breakthrough time was decreased with flow rate increase due to the inadequate residence time of the U(VI) with Si-6G PAMAM-PPAAM [49]. Also, the uranium sorption capacity was decreased from 397.59 mg g$^{-1}$ at (1 cm, 1 mL min$^{-1}$) to 153.27 mg g$^{-1}$ at (2 cm, 5 mL min$^{-1}$). Due to a longer time is needed between the uranium solution and Si-6G PAMAM-PPAAM to reach equilibrium state. The percentage of U(VI) removal Table 5 was decreased with increasing in flow rates because the uranium ions left the column before reaching equilibrium. Therefore, this increase in flow rate causes a shorter presence time of the solute in the column and so, the metal ions leave the column rapidly before equilibrium occurs [50]. In general, the adsorption of U(VI) increased as the contact time increased provided at the lower flow rate.

The total quantity of adsorbed uranium ions by Si-6G PAMAM-PPAAM ($q_{\text{total}}$, mg), the adsorption capacity ($q_e$), removal percentage (R%), the break-through time ($t_b$), exhaustion time ($t_e$), mass transfer zone ($\Delta t$) and the length of mass transfer zone ($Z_m$) were calculated from the break-through curves using Eqs. (3–8) and presented in Table 5.

U(VI) adsorption capacity of Si-6G PAMAM-PPAAM at column bed height (1 cm) and flow rate (1 mL min$^{-1}$) was found 397.59 mg g$^{-1}$. This value was lower than that one obtained by batch method (434.78 mg g$^{-1}$). The difference in adsorption capacities between the two methods is due to insufficient contact time which was given for the adsorption of uranium by Si-6G PAMAM-PPAAM under fixed bed column technique, as compared with batch technique.

### Fixed bed column models

**Thomas model** The Thomas model is based on the assumption that the adsorption behavior follows Langmuir kinetics and assumes that the rate driving forces conform to the
second-order reversible reaction kinetics. This model can be represented by Eq. (17) [51]:

\[
\frac{C_{\text{eff}}}{C_o} = \frac{1}{1 + \exp \left( \frac{K_{\text{th}} q_0 M - C_{\text{eff}} V_{\text{eff}}}{Q} \right)}
\]

(17)

where, \( C_{\text{eff}} \) is the effluent metal ion concentration (mg L\(^{-1}\)), \( K_{\text{th}} \) is Thomas rate constant (mL mg\(^{-1}\) min\(^{-1}\)), \( q_0 \) is the equilibrium adsorbate uptake (mg g\(^{-1}\)), \( M \) is the adsorbent amount in the column (g), \( V_{\text{eff}} \) is the effluent volume of the solution (mL), and \( Q \) is volumetric flow rate (mL min\(^{-1}\)). The linear form of this model is represented as:

\[
\ln\left( \frac{C_{\text{eff}}}{C_o} - 1 \right) = \ln\left( \frac{K_{\text{th}} q_0 M}{Q} \right) - \frac{K_{\text{th}} C_{\text{eff}} V_{\text{eff}}}{Q}
\]

(18)

The values of \( K_{\text{th}} \) and \( q_0 \) can be determined from the slope and intercept of the linear graph between \( \ln(C_{\text{eff}}/C_o) \) vs \( V_{\text{eff}} \) at different flow rates and bed heights. As can be observed in Table 5, for an increase in flow rate from (1 to 5 mL min\(^{-1}\)), the value of \( K_{\text{th}} \) increased. Whereas the value of the calculated adsorption capacity of Si-6G PAMAM-PPAAM \( (q_0) \) exhibited a reverse trend with increasing flow rate and bed height [30, 49]. From Thomas model the value of the calculated adsorption capacity of the adsorbent \( (q_0) \) is similar to the experimental adsorption capacity \( (q_e) \), as the higher correlation co-efficient \( (R^2) \) values for U(VI) ions onto Si-6G PAMAM-PPAAM.

**Yoon–Nelson model** The breakthrough curves of U(VI) onto Si-6G PAMAM-PPAAM were examined using the Yoon–Nelson model. The theoretical model based on the concept of the decrease in the adsorption for each adsorbate molecule is directly proportional to the probability of adsorbate breakthrough on the adsorbent. It can be represented as:

\[
\frac{C_{\text{eff}}}{C_o - C_{\text{eff}}} = \exp \left( K_{YN} t - \tau K_{YN} \right)
\]

(19)

where \( K_{YN} \) is the kinetic adsorption rate constant (min\(^{-1}\)); \( t \) is the breakthrough time (min) and \( \tau \) is the time required for 50% adsorbate breakthrough (min).

The linear form of this model is represented as:

\[
\ln\left( \frac{C_{\text{eff}}}{C_o - C_{\text{eff}}} \right) = K_{YN} t - \tau K_{YN}
\]

(20)

The values of \( K_{YN} \) and \( \tau \) can be calculated from a plot of \( (\ln(C_{\text{eff}}/C_o - C_{\text{eff}}) \) vs. \( t \) at different flow rates, and bed heights [52]. The values of \( K_{YN} \), \( \tau \) were tabulated in Table 5. The results show that \( K_{YN} \) increased with increasing flow rate and bed height. The data also indicate that values of \( \tau \) and \( \tau_{\text{exp}} \) are close to each other. The observed increase in the value of the time required for 50% adsorbate breakthrough \( (\tau) \) for U(VI) with increasing the bed height but the value of \( (\tau) \) decreases with increasing the flow rate, due to less residence time of uranium ions in adsorbent bed [53]. It was observed that Thomas and Yoon-Nelson models were appropriate for describing all or a specific part of the dynamic behavior of continuous operation.

**Column desorption studies**

Column desorption studies were performed to desorb U(VI) from Si-6G PAMAM-PPAAM using 1 M HNO\(_3\) as an elution agent at 25 °C. In order to test the reusability of the prepared adsorbent, it was subjected to five successive adsorption–desorption cycles according to the following equation [20]:

\[
\text{Regeneration efficiency} \% = \left( \frac{\text{uptake of metal ion in the second cycle}}{\text{uptake of metal ion in the first cycle}} \right) \times 100
\]

(21)

The Regeneration efficiencies decreased from 100% to 99.5, 98, 97, 95 and 94%, respectively over five cycles. The

| Variables | Calculated parameter | Thomas model | Yoon–Nelson model |
|-----------|----------------------|--------------|-------------------|
| Q mL min\(^{-1}\) | Z cm | q_{total} mg | q_{e} mg g\(^{-1}\) | R% | t h min | t \(_{\text{exp}}\) min | Z m cm | q_{d} mg/g | K_{th} mL mg\(^{-1}\) min\(^{-1}\) | R\(^2\) | K_{YN} min\(^{-1}\) | T min | R2 |
| 1 | 1 | 99.390 | 397.590 | 40 | 75 | 1575 | 1500 | 0.96 | 693.16 | 400 | 0.0268 | 0.970 | 0.004 | 665.880 | 0.970 |
| 1 | 2 | 169.350 | 338.690 | 43.110 | 140 | 2420 | 2280 | 1.900 | 1281.76 | 335.780 | 0.019 | 0.920 | 0.003 | 1101.370 | 0.920 |
| 3 | 1 | 73.260 | 293.040 | 35.500 | 16.66 | 425 | 408.340 | 0.960 | 167.260 | 293.430 | 0.128 | 0.960 | 0.019 | 164.730 | 0.960 |
| 3 | 2 | 136.930 | 273.860 | 37.700 | 40 | 740 | 700 | 1.890 | 283.330 | 275.360 | 0.056 | 0.930 | 0.008 | 305 | 0.930 |
| 5 | 1 | 38.820 | 155.270 | 33.440 | 6 | 135 | 192 | 0.955 | 49.220 | 160 | 0.310 | 0.940 | 0.047 | 48.350 | 0.940 |
| 5 | 2 | 76.640 | 153.270 | 35 | 10 | 275 | 265 | 1.927 | 82.690 | 151.250 | 0.160 | 0.920 | 0.024 | 100 | 0.920 |
decrease in adsorption efficiency is due to the loss of adsorbent mass in subsequent adsorption–desorption cycles.

**Application**

The proposed method is applied to adsorb U(VI) from the leach liquor of (granitic rock sample collected from Gabal El-Missikat), located at midway along Qena-Safaga road, Egypt. Uranium selectively leached using sulfuric acid solution (0.4 M) for 8 h at T = 70 °C. The reacted slurry is filtered and washed with hot water. The concentration of metal ions in leach liquor is determined and presented in Table 6.

The obtained filtrate is diluted as the concentration of uranium become (128 mg L⁻¹) before treated with Si-6GPAMAM and Si-6GPAMAM-PPAAM for uranium adsorption and separation at the optimum parameters. The results of treatment of the diluted leach liquor sample with the prepared adsorbents are presented in Table 7.

The uptake results of U(VI) indicate that Si-6GPAMAM-PPAAM and Si-6GPAMAM displayed higher removal efficiency toward uranium ions relative to other metal ions present in the sample solution.

**Conclusion**

Si-6G PAMAM-PPAAM was synthesized and characterized using FTIR, SEM–EDX, TGA and porous structure analysis for using in U(VI) adsorption from aqueous solution. The maximum adsorption capacity of Si-6G PAMAM-PPAAM was 434.78 mg g⁻¹ at T = 25 °C and pH 4.5 was described effectively by Langmuir isotherm model. The thermodynamic parameters of Si-6G PAMAM-PPAAM show a negative value for ΔG and a positive value for ΔH indicating the spontaneous and endothermic nature of the adsorption process. Breakthrough curves for the adsorbent were plotted for the different parameters affecting the column performance. The sorption capacity of Si-6G PAMAM-PPAAM for U(VI) was found 400 mg g⁻¹ at column bed height 1 cm and flow rate 1 mL min⁻¹. The adsorption of U(VI) increased as the contact time increased provided at the lower flow rate. The continuous adsorption behavior of U(VI) ions onto Si-6G PAMAM-PPAAM in fixed-bed columns was examined using theoretical models as Thomas and Yoon–Nelson. The studied models agreed well with the experimental data. Regeneration of Si-6G PAMAM-PPAAM for U(VI) was effectively achieved using 1 M HNO₃ at 25 °C. The prepared phosphorus modified silica gel is recommended as effective materials for separation of uranium ions from aqueous solutions particularly in the presence of other competitive metal ions.

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**Declarations**

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Table 6** Concentration of metal ions in leach liquor of the granite sample

| Metal ions | Conc (mg L⁻¹) |
|------------|---------------|
| U          | 1925          |
| ΣREEs      | 1370          |
| Fe         | 820           |
| Cu         | 96.3          |
| Mn         | 98.7          |
| Zn         | 86.5          |
| Ni         | 3.9           |
| Cd         | 0.1           |
| Pb         | 90.4          |
| Co         | 4.7           |
| Ca         | 300           |
| Mg         | 240           |
| Ba         | 20            |
| Cr         | 40            |

**Table 7** Results of treatment the leach liquor of the granite sample with Si-6GPAMAM and Si-6GPAMAM-PPAAM

| Metal ions | Removal efficiency (%) |
|------------|------------------------|
|            | Si-6GPAMAM | Si-6GPAMAM-PPAAM |
| U          | 94.8        | 90.2            |
| ΣREEs      | 28.5        | 31.3            |
| Fe         | 19.7        | 26.8            |
| Cu         | 0.0         | 0.0             |
| Mn         | 8.7         | 10.7            |
| Zn         | 0.3         | 0.3             |
| Ni         | 0.0         | 16.6            |
| Cd         | 0.0         | 0.0             |
| Pb         | 2.8         | 2.8             |
| Co         | 0.0         | 0.0             |
| Ca         | 1.7         | 6.7             |
| Mg         | 0.0         | 8.3             |
| Ba         | 0.0         | 0.0             |
| Cr         | 0.5         | 0.4             |
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