Decontamination of $^{137}$Cs, $^{95}$Zr, $^{154}$Eu and $^{144}$Ce from aqueous solutions using polyacrylamide titanium tungstosilicate

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Abstract
Polyacrylamide titanium tungstosilicate (PAM/TiWSi) composite was synthesised using a sol–gel process and characterized via FT-IR, SEM, XRD, and TGA methods. The effects of several factors on the adsorption of Cs+, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ have been studied, including contact duration, pH, temperature, and starting concentration. PAM/TiWSi sorption of Cs+, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ was studied in terms of isotherms and kinetics. The Freundlich model was better linked with isotherm data than the Langmuir model. Cs+, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ have maximum sorption capacities (Q$_{max}$) of 30.7, 26.6, 25.3 and 29.7 mg g$^{-1}$, respectively. Furthermore, the sorption process was found based on pseudo-second-order.

Keywords Polyacrylamide titanium tungstosilicate · Adsorption technique · $^{137}$Cs · $^{154}$Eu · $^{95}$Zr · LLW

Introduction
The escalation of the peaceful use of nuclear energy and radioactive materials in several areas such as medicine, agriculture, industry, and the whole nuclear industry has increased the production of different forms of radioactive waste. The significant parameters that increase the risk of radioactive waste are long half-lives, high radiation toxicity, high solubility, and easy transfer into organs via internal contamination via food and water resources. Many researchers are working seriously to find a means to treat this hazardous waste [1–15]. One of the main hazard radionuclides generated in the nuclear industry from $(n, fission)$ reaction are $^{134}$Cs and $^{137}$Cs, with a half-life of ($T_{1/2} = 2.064$ and 30.1 y, respectively), has a lower hydrated radius and a greater diffusion coefficient. Moreover, $^{154}$Eu is a fission product with a relatively long half-life and highly energetic gamma-ray emission. Furthermore, rare earth radionuclides such as cerium, samarium, and lanthanum ($^{144}$Ce, $^{141}$Sm and $^{140}$La) can also be generated in the backend cycle of uranium and thorium used as a nuclear fuel with a relatively short half-life. $^{95}$Zr can be produced as an activation product $(n, \gamma)$ reaction in nuclear reactors from fuel cladding materials in the processing of the spent fuel. Different techniques were established to treat these radioactive liquid wastes generated during the front and back of the nuclear fuel cycle. For example, chemical precipitation, coagulation, sorption, ion exchange, flotation, and membrane technologies were used. Since it is easy, cost-effective, and practicable, sorption is the most commonly used among these approaches [5–7, 10–16].

This technique is based on the preparation of inorganic, organic, hybrid of inorganic and organic (composite materials) and biological sorbent materials. Sorbent materials are favourable when they have high sorption efficiency, chemical, mechanical and radiological stability, durability, and cost-effectiveness. One significant disadvantage of employing organic material is low thermal and radiation stability. A second constraint is the non-reproducibility of inorganic material [17–21]. So, hybrid materials have received more attention than organic and inorganic ones. Recently, several authors have investigated the application of organic/inorganic or composites for the adsorption of different radionuclides [7, 8, 10–15].
The present work scope is an attempt to synthesise an organic–inorganic hybrid sorbent material (composite) with remarkable selectivity for certain radionuclides. The prepared composite is novel and it is the first time been utilized in the removal of certain radionuclides from liquid radioactive waste effluents. The selected sorbent composite is based on using acrylamide with some inorganic metals such titanium, tungsten and silicon in different chemical forms. To better understand the nature of the composite, it is physically and chemically examined using several approaches. The optimum experimental conditions for the present study proposed composite were examined using the batch approach. Finally, the proposed composite ability to absorb chosen radionuclides in a gravitational column was investigated.

**Experimental**

All upcoming symbols and abbreviations are defined in Table 9 at the end of the paper.

**Materials**

Sodium tungstate (Na₂WO₄·2H₂O), acrylamide (CH₂CH–CO–NH₂), potassium persulfate (K₂S₂O₈) and sodium metasilicate (Na₂SiO₃·9H₂O) obtained from BDH (England) and Loba Chemie (India). The other chemicals and reagents were pure enough to be employed as analytical reagents without additional purification.

**Preparation of PAM/TiWSi**

Graphical abstract for the preparation method of Polyacrylamide titanium tungstosilicate (PAM/TiWSi) composite is presented in Fig. 1.

At 25 ± 1 °C, the inorganic precipitate of titanium tungstosilicate was fabricated by combining equal volumes of titanium chloride (0.5 M), sodium tungstate (0.5 M), and sodium metasilicate solutions (0.5 M). A pale-yellow precipitate was formed by adding aqueous ammonia (NH₄OH) to make the mixture pH ~ 0.95. The inorganic precipitate was mixed with acrylamide and potassium persulfate

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Fig. 1 The graphical abstract for the preparation method of Polyacrylamide titanium tungstosilicate (PAM/TiWSi) composite

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(prepared by gently heating the mixture at 70 ± 1 °C while stirring constantly). The resulting pale-yellow precipitate was left at room temperature for 24 h to digest. The liquid supernatant was decanted, and the gel was filtered using a centrifuge (approximately 4 × 10³ rpm) and then dried at 50 ± 1 °C.

**Characterization of PAM/TiWSi**

Various characterization methodologies were used to determine the physical and chemical characteristics of the synthesized composite material. Thermal gravimetry analysis TGA (Shimadzu DTG-60/60H-Thermal Analyzer, Japan) was performed in conjunction with X-ray diffraction XRD (Shimadzu XD-D1, Japan), X-ray fluorescence (XRF), Flash elemental analyzer (EA), Fourier transform infrared FT-IR (Nicolet spectrometer, Meslo, USA) and scanning electron microscopy SEM (JEOL-JSM-6510LA, Tokyo, Japan).

**Adsorption experiments**

Batch studies were conducted in 15 mL glass vials containing 50 mg powdered PAM/TiWSi and 5 mL of the examined metal ion solution to determine the PAM/TiWSi ability to adsorb Cs⁺, Eu³⁺, Ce³⁺, and Zr⁴⁺ ions from metal ion prepared solutions. The temperature was then set to 25 ± 1 °C, and the vials were sealed and shaken at 250 rpm. A suitable amount of (0.1 M) HCl or NH₄OH was used to adjust the pH; double distilled water was used to make the metal ion solutions for the experiments. With solution concentrations ranging from 50 to 500 mg L⁻¹, the effect of initial adsorbate concentration was examined. Furthermore, all experiments were carried out under identical circumstances, including a contact time of 10 to 300 min, a temperature of 25 ± 1 °C, and a V/m of 100 mL g⁻¹.

The percent removal (%R) was calculated in [22] as:

\[
\% (R) = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

The following equations can be used to determine the adsorption capacity at any time (qt) and equilibrium (qe):

\[
q_e \text{ (mg} \cdot \text{g}^{-1}) = (C_i - C_e) \times \left( \frac{V}{m} \right)
\]

and

\[
q_t \text{ (mg} \cdot \text{g}^{-1}) = (C_i - C_t) \times \left( \frac{V}{m} \right)
\]

Using the formula below, the distribution coefficient (Kd) and separation factor (\(a_B^A\)) as a function of pH were computed.

\[
K_d \text{ (mL} \cdot \text{g}^{-1}) = \left( \frac{C_i - C_f}{C_f} \right) \frac{V}{m}
\]

\[
a_B^A = \frac{K_d(A)}{K_d(B)}
\]

where V is the solution volume (mL), and m is the weight (g). All results were repeated three times and the average value was taken with an error percent does not exceed 5%.

**Point zero charge (PZC) determination**

PZC for PAM/TiWSi was measured using 5 mL of DDW and 50 mg of sample. The pH was adjusted with (0.1 M) HCl and NH₄OH to produce the desired pH range (1–12 ± 0.1). The samples were shaken for 24 h using a rotary agitator set to 200 rpm. The pH of the supernatant was measured and recorded as pHf for each tube. The PZC was generated by plotting ΔpH (pHf-pHi) versus pHi.

**Results and discussion**

**Characterization**

**Scanning electron microscope**

In the SEM micrographs in Fig. 2, the surface morphology of the prepared composite (PAM/TiWSi) is displayed at different magnifications.

The synthesized PAM/TiWSi has a random morphology with no defined direction and discrete titanium and tungsten distribution on the polyacrylamide surface. The surface appears to be heterogeneous. At a low magnification power of ×100, the surface appears rugged, but at a high magnification power of ×1000, it becomes smoother with fairly spaced porosity [2].

**X-ray diffraction**

The atoms in amorphous materials are not arranged in a regular pattern but are randomly scattered in 3D space. As a result, their diffraction patterns do not produce sharp Bragg peaks but rather very broad peaks. As can be seen in Fig. 3, the PAM/TiWSi XRD diffraction pattern exhibits an amorphous structure in nature, which is expected from the organic part of the composite.

**Elemental analysis**

To identify the elemental composition of PAM/TiWSi, elemental analysis can be employed. Table 1 summarizes the results of the elemental analysis.

The suggested empirical formula of the prepared composite is shown below:
$Na_2WO_4 \cdot 2H_2O + 2Na_2SiO_3 \cdot 9H_2O + 4TiCl_4 + nCH_2CH - \xrightarrow{\text{initiator}} (WO_3(TiO_2)_4(SiO_2)_2)_2 \rightarrow CH_2 - CH - \text{bands} - NH$

FT-IR

The FT-IR analysis for PAM/TiWSi is presented in Fig. 4, and the identified bands for function groups are listed in Table 2.

At 3428 cm$^{-1}$, the vibration corresponding band to the OH group of adsorbed water might also be for the NH group [23]. The bands around 2955 and 2855 cm$^{-1}$ may be due to asymmetric and symmetric C–H stretching vibration [7]. At 1657 cm$^{-1}$ and 1457 cm$^{-1}$, stretching and deformation
vibrations corresponding to the C=O and NH linkages from the amidic group appear, respectively. The C–N stretching vibration has a peak at 1381 cm$^{-1}$. The peak at 1228 cm$^{-1}$ is consistent with the asymmetric vibration of NH$_2$. Deformation vibrations of the –C–N– links and CH$_2$ group are attributed to absorption bands in the 1121–1033 cm$^{-1}$ range [24]. Finally, the two peaks at ≈816 and ≈600 cm$^{-1}$ are associated with metal–oxygen bonds [8].

**Thermal analysis TGA**

The result of the TGA study for PAM/TiWSi is shown in Fig. 5. The thermal breakdown of PAM/TiWSi is divided into three stages. At (50–250) °C, the initial phase of dehydration of PAM/TiWSi occurs, resulting in a weight loss of 9.6% [8]. The weight loss increases to 17.2% in the second phase due to the polyacrylamide chain breaking at (250–530) °C. Finally, Polyacrylamide decomposes completely at (530–700) °C with a weight loss of 3.35% [24]. In the temperature range of (50–700) °C, the overall calculated weight loss for the PAM/TiWSi is 30.174%.

**Point Zero Charge (PZC)**

Point Zero Charge is the pH value at which the surface of the adsorbed substance has no charges. The surface of PAM/TiWSi possesses a positive charge below this pH range, allowing it to engage with negative species [25]. The negatively charged surface above it interacts with positive species. The PZC for PAM/TiWSi is 2.14, as shown in Fig. 6; this value is consistent with the sorption results, as shown subsequently.

| Wave number (cm$^{-1}$) | Functional group                                |
|------------------------|-------------------------------------------------|
| 3428.05                | Overlapping between –NH$_2$ and –OH stretching vibrations |
| 2955.35                | C–H asymmetric stretching vibration              |
| 2855.85                | C–H symmetric stretching vibration               |
| 1657.09                | C=O stretching vibration                         |
| 1457.66                | N–H deformation vibration                        |
| 1381.20                | C–N stretching vibration                         |
| 1228.75                | Asymmetric vibration of NH$_2$                  |
| 1121 and 1033          | Deformation vibrations of –C–N– and CH$_2$      |
| 816 and 600            | Metal–oxygen bonds (SiO$_2$–TiO$_2$–WO$_4$)     |
Adsorption batch experiments

Effect of initial concentration

As shown in Fig. 7, the relationship between initial metal ion concentrations ($C_0$) and the amount sorbed ($q_e$) of examined metal ions on the surface of PAM/TiWSi was investigated. The amount of metal ions sorbed is found to grow as the initial metal ion concentrations increase [10].

Effect of pH

The surface charge of PAM/TiWSi and the active sites available to interact with metal ions are influenced by the pH of Cs⁺, Eu³⁺, Ce³⁺, and Zr⁴⁺ solutions. So, with unchanged conditions (contact time = 2 h, temp = 298 K, initial conc. = 50 ppm), experiments were done to identify the optimum pH for each metal ion in different pH ranges from 1 to 9. The %removal increased with increasing pH value till saturation was achieved at pH = 5 for Cs⁺, Eu³⁺, and Ce³⁺ and pH = 3 for Zr⁴⁺, as shown in Fig. 8. The electrostatic attraction force between the studied cations and the PAM/TiWSi surface rises owing to the increased pH surface charge is negative [17, 26, 27].

Effect of contact time

At a temperature of 298 K and an initial concentration of 50 ppm, the effect of contact time on the adsorption of Cs⁺, Eu³⁺, Ce³⁺, and Zr⁴⁺ on the surface of PAM/TiWSi was examined from 10 min to 5 h. According to Fig. 9, the %removal for selected metal ions reached equilibrium at 60, 30 min for Cs⁺ and Zr⁴⁺, respectively and 2 h for Eu³⁺ and Ce³⁺. This might occur because there is a considerable active site accessible at first contact time for metal ions to occupy until equilibrium is attained. Adsorption has a slow escalation for remaining metal ions diffusion into the adsorbent material surface as contact time increases. Moreover, Cs⁺ and Zr⁴⁺ ions were equilibrated faster than Eu³⁺ and Ce³⁺ due to their smaller hydrated ionic radii [28].

Fig. 7 The effect of concentration of Cs⁺, Eu³⁺, Ce³⁺and Zr⁴⁺ on the amount sorbed by PAM/TiWSi

Fig. 8 The effect of solution pH in removing Cs⁺, Eu³⁺, Ce³⁺and Zr⁴⁺ by PAM/TiWSi

Fig. 9 The effect of contact time in removing Cs⁺, Eu³⁺, Ce³⁺and Zr⁴⁺ by PAM/TiWSi
Effect of temperature

The effect of different temperatures was evaluated at 298, 313, and 338 K and graphically displayed in Fig. 10. The % removal significantly improved as the temperature was increased, indicating the sorption mechanism of the examined metal ions is endothermic [14].

Distribution studies

The distribution coefficients ($K_d$) of Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ on PAM/TiWSi as a function of pH were calculated using batch equilibration. When log($K_d$) values are plotted against the pH of the solutions, a straight line with a slope ($n$) is established [25]. The results are reported in Fig. 11, which elaborate on the pH dependence of $K_d$ values of the metal ions studied. For the cations, Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ the slopes of the linear correlations between log($K_d$) and pH are 0.4, 0.3, 0.3, and 0.6, respectively. These slopes do not equal the sorbed metal ions valences, indicating that the exchange process is non-ideal. A summary of the obtained $K_d$ and separation factor ($\alpha_{AB}$) values for studied metal ions is in Table 3.

From Table 3, it appears that the highest separation factors obtained are the following:

(i) For Cs$^+$ and Zr$^{4+}$, the highest $\alpha$ is obtained at pH = 1.
(ii) For Cs$^+$ and Eu$^{3+}$, the highest $\alpha$ is obtained at pH = 5.
(iii) For Cs$^+$ and Ce$^{3+}$, the highest $\alpha$ is obtained at pH = 3.
(iv) For Zr$^{4+}$ and Eu$^{3+}$, the highest $\alpha$ is obtained at pH = 3.
(v) For Zr$^{4+}$ and Ce$^{3+}$, the highest $\alpha$ is obtained at pH = 3.
(vi) For Eu$^{3+}$ and Ce$^{3+}$, the highest $\alpha$ is obtained at pH = 4.

Thermodynamic studies

Using the Van’t Hoff relation given by Eq. (7), the slope and intercept obtained from the plotting of the ln($K_d$) plot against $1/T$ can be used to derive the values of $\Delta H^o$ and $\Delta S^o$ as follows:

| pH | Cs$^+$ | Zr$^{4+}$ | Eu$^{3+}$ | Ce$^{3+}$ |
|----|--------|----------|----------|----------|
| Kd (mL g$^{-1}$) | Kd (mL g$^{-1}$) | $\alpha_{Cs/Zr}$ | Kd (mL g$^{-1}$) | $\alpha_{Cs/Eu}$ | Kd (mL g$^{-1}$) | $\alpha_{Zr/Eu}$ | Kd (mL g$^{-1}$) | $\alpha_{Zr/Ce}$ | Kd (mL g$^{-1}$) | $\alpha_{Eu/Ce}$ |
| 1  | 566.65 | 448.23 | 1.16 | 257.1 | 2.20 | 1.74 | 198.5 | 2.85 | 2.25 | 1.29 |
| 2  | 1150.25 | 1718.18 | 0.66 | 437.3 | 2.62 | 3.90 | 344.4 | 3.33 | 4.98 | 1.26 |
| 3  | 3900 | 9900 | 0.39 | 1011.1 | 3.85 | 9.79 | 566.6 | 6.88 | 17.47 | 1.78 |
| 4  | 8233.33 | – | – | 2280.9 | 3.60 | – | 1233.3 | 6.67 | 1.74 | 1.84 |
| 5  | 24900 | – | – | 4900.0 | 5.80 | – | 3764.1 | 6.61 | 1.74 | 1.30 |
where \( \Delta S^\circ \) represents the entropy change, \( \Delta H^\circ \) represents the enthalpy change, \( R \) represents the gas constant, and \( T \) represents the absolute temperature. The specific adsorption Gibbs free energy change (\( \Delta G^\circ \)) was computed using the formulas:

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)
\]

\[
\Delta G^\circ = -RT \ln (K_d) \quad (8)
\]

The result is shown in Table 4 and presented in Fig. 12, where the positive value of \( \Delta H^\circ \) indicates that the adsorption process is endothermic, and the positive value of \( \Delta S^\circ \) indicates that the surface randomness increases during the adsorption process. The studied metal ions had negative free energy change (\( \Delta G^\circ \)) values, indicating that the adsorption process is spontaneous and that these cations preferentially adsorb on PAM/TiWSi. Furthermore, the increase in negative Gibbs free energy with increasing temperature implies that the adsorption process is highly spontaneous and endothermic [12, 22, 29].

**Kinetic studies of adsorption**

Pseudo-first and pseudo-second-order kinetic models were used to analyse the adsorption of Cs\(^+\), Eu\(^{3+}\), Ce\(^{3+}\), and Zr\(^{4+}\) at 298 K.

**Pseudo-first-order kinetic model**

According to (Lagergren, 1907), the pseudo-first-order kinetic model is described by the following Eq.:

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t \quad (9)
\]

Plotting \(\ln(q_e - q_t)\) versus \(t\) and calculating the slope and intercept, respectively, yields the values of \(q_e\) and \(k_1\). Figure 13a depicts the calculation results, which are summarised in Table 5. The model is insignificant if the experimental and theoretical \(q_e\) disagree [30].

**Pseudo-second-order kinetic model**

According to Ho and Mckay, (1999), the pseudo-second-order kinetic model is calculated using the following equation:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad (10)
\]

The pseudo 2\(^{nd}\) order model fitted diagram is provided in Fig. 13b and Table 5. As obtained from Fig. 13b and Table 5, the pseudo 2\(^{nd}\) order model has a better correlation coefficient (\(R^2 > 0.999\)) than the pseudo 1\(^{st}\) order model (\(R^2 > 0.937\)). Furthermore, the estimated capacity of the sorbed metal ions at equilibrium \(q_{e(cal.)}\) values are almost identical to the experimental data \(q_{e(exp.)}\) values. This clearly shows that the pseudo 2\(^{nd}\) order model is appropriately fitted for metal ion sorption kinetics.
Isotherm studies of adsorption

The isotherm equation, whose variables reflect the adsorbent’s surface properties and affinity, is often used to express the adsorbent's surface features and affinity. Also, the adsorption isotherm describes the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid phase at equilibrium. Furthermore, the maximum capacity obtained from the adsorption isotherm is critical for the adsorption process design. Four theoretical isotherm models; Langmuir, Freundlich, Dubinin–Redushkevich and Flory Huggins; were utilised to assess the adsorption mechanisms of PAM/ TiWSi adsorbent. They’re known to be employed to model monomolecular layer adsorption with a consistent adsorption energy and multilayer adsorption on heterogeneous surfaces, evaluate whether the adsorption occurred physically or chemically and calculate the degree of surface coverage of adsorbate on the adsorbent. The adsorption models are described as follows:

Langmuir equation

Following [32], it can be calculated as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{bQ} \quad (11)$$

Freundlich equation

Following [33], it can be calculated as:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (12)$$

Table 5  Comparison between the experimental and calculated $q_e$ values of the first and second-order adsorption kinetics for a Cs⁺, Eu³⁺, Ce³⁺ and Zr⁴⁺ on PAM/TiWSi

| Cation | Temperature (K) | $q_e$ exp (mg g⁻¹) | Kinetic model | $k_1$ (min⁻¹) | $q_e$ cal (mg g⁻¹) | $R^2$ | $k_2$ (g mg⁻¹ min⁻¹) | $q_e$ cal (mg g⁻¹) | $R^2$ |
|--------|-----------------|---------------------|---------------|----------------|---------------------|------|----------------------|---------------------|------|
| Cs⁺    | 298             | 4.98                | Pseudo first order | 0.021          | 7.09                | 0.558 | 0.171                | 5.01                | 0.999 |
| Zr⁴⁺   | 298             | 4.95                | Pseudo second order | 0.015          | 20.0                | 0.571 | 0.471                | 4.97                | 0.999 |
| Eu³⁺   | 298             | 4.90                |                | 0.035          | 3.83                | 0.937 | 0.017                | 5.15                | 0.999 |
| Ce³⁺   | 298             | 4.87                |                | 0.036          | 3.71                | 0.894 | 0.016                | 5.12                | 0.999 |

Fig. 13  Pseudo first and second-order kinetic models
Dubinin–Radushkevich equation

It can be calculated as:

\[ \ln(q_e) = \ln(q'_{m}) - \beta \epsilon^2 \quad \text{and} \quad \epsilon = RT \ln(1 + \frac{1}{C_e}) \]  

(13)

A data plot between \( \ln(q_e) \) and \( \epsilon^2 \) at constant temperature was used to determine both \( q'_{m} \) and \( \beta \). The mean sorption energy (\( E \)) is the free energy transfer of one mole of solute from infinity to the surface of the adsorbent and was calculated as:

\[ E = (-2\beta)^{-1/2} \]  

(14)

The \( E \) value produced from the Dubinin–Radushkevich isotherm model is used to identify the kind of interaction during the adsorption process. When the value of (\( E \)) is between (1–8) kJ.mol\(^{-1}\), physical adsorption is present; an ion-exchange mechanism defines the adsorption process in the field of (8–16) kJ.mol\(^{-1}\), more than 16 kJ.mol\(^{-1}\), the adsorption process is chemical [10].

Flory-Huggins model

The degree of surface coverage of adsorbate on adsorbent can be expressed in linear form according to Flory–Huggins model as:

\[ \log(\frac{\theta}{C_e}) = \log(K_{FH}) + \alpha_{FH} \log(1 - \theta) \]  

(15)

where \( \theta \) is the degree of surface coverage, can be computed as:

![Fig. 14 a Langmuir, b Freundlich, c D-R and d Flory–Huggins isotherm models calculation results](image-url)
The values of $K_{FH}$ and $\alpha_{FH}$ are obtained from the intercept and slope of the plot of $\log(\theta / C_i)$ versus $\log(1 − \theta)$, respectively [34]. Moreover, the equilibrium constant $K_{FH}$ can be used to compute the Gibbs free energy for the sorption process. The Gibbs free energy is related to the equilibrium constant as follows:

$$\Delta G^o = −RT \ln (K_{FH})$$

(17)

The Langmuir plot of $C_e$ vs $C_e/q_e$ is shown in Fig. 14a, and the isotherm yields a straight line with $R^2 > 0.98$. The slope and intercept of the resultant straight line were used to calculate the $Q_{\text{max}}$ and $b$ of the PAM/TiWSi adsorbent for Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ respectively. These findings suggest that the Langmuir monomolecular layer adsorption mode might be used to describe this adsorption process. Figure 14b depicts a visual representation of $\log(C_e)$ vs $\log(q_e)$ using the Freundlich isotherm equation. The slope and intercepts of the straight line with an $R^2$ value of 0.99 are used to derive the numerical values of the constants $1/n$ and $K_F$. Table 6 displays the parameters, implying that Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ adsorption onto PAM/TiWSi adsorbent under the experimental conditions are more compatible with the Freundlich isotherm than Langmuir isotherm model. Figure 14c and Table 6 demonstrate the results of the Dubinin–Radushkevich isotherm model. The obtained $E$ values for Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ were 2.5, 1, 0.9 and 1.5 kJ mol$^{-1}$, respectively, showing that physical adsorption was involved in the adsorption process. Moreover, Table 6 and Fig. 14d $\alpha_{FH}$ values indicate the high surface coverage for the PAM/TiWSi for the adsorption of Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$.

### Application

400 mL of a diluted real radioactive waste sample (pH = 5.56) generated in the Radioisotope Production Facility (RPF) in the Second Egyptian Research Reactor Complex (ETRR-II) characterized radiometrically using P-type coaxial HPGe (GEM-series, ORTEC, USA) connected to a multichannel analyzer system (MCA, Inspector 2000 Series, Canberra, USA) for 300 min. The characterization result is that the sample contains $^{137}$Cs, $^{154}$Eu, and $^{144}$Ce with radioactivity levels of 2800 ± 52.9, 1860 ± 43.12, and 700 ± 26.4 Bq L$^{-1}$, respectively. One gram of the PAM/TiWSi with a particle size < 500 µm was placed in a glass column (1.4 cm diameter and 5 cm height) to provide a

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**Table 6** Langmuir, Freundlich, D-R and Flory- Huggins adsorption isotherm models for Cs$^+$, Eu$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ adsorption on PAM/TiWSi at 298 K and initial concentration of 50 mg L$^{-1}$

| Isotherm model | Parameters | Temperature (K) | Cation | Cs$^+$ | Zr$^{4+}$ | Eu$^{3+}$ | Ce$^{3+}$ |
|---------------|------------|-----------------|--------|--------|---------|---------|---------|
| Langmuir      | $Q_{\text{max}}$ (mg g$^{-1}$)$\gamma$ | 298.0           |        | 30.70  | 29.7    | 26.6    | 25.3    |
|               | $b$ (L mg$^{-1}$)                  |                 |        | 0.073  | 0.062   | 0.042   | 0.037   |
|               | $R^2$                                 |                 |        | 0.987  | 0.988   | 0.972   | 0.957   |
| Freundlich    | $1/n$                                 | 298.0           |        | 0.26   | 0.29    | 0.30    | 0.29    |
|               | $k_f$ (mg g$^{-1}$)                  |                 |        | 7.69   | 6.14    | 4.90    | 4.47    |
|               | $R^2$                                 |                 |        | 0.999  | 0.997   | 0.999   | 0.999   |
| Dubinin-Radushkevich | $\chi_m$ (mg g$^{-1}$) | 298.0          |        | 23.80  | 23.1    | 20.28   | 18.17   |
|               | $\beta$ (kJ mol$^{-2}$)                |                 |        | 0.079  | 0.208   | 0.482   | 0.686   |
|               | $E$ (kJ mol$^{-1}$)                   |                 |        | 2.50   | 1.5     | 1.01    | 0.9     |
|               | $R^2$                                 |                 |        | 0.904  | 0.901   | 0.876   | 0.881   |
| Flory–Huggins | $K_{FH}$ (L mol$^{-1}$)                | 298.0           |        | 73.9   | 67.5    | 60.1    | 52.6    |
|               | $\Delta G^o$ (kJ mol$^{-1}$)           |                 |        | -10.6  | -10.4   | -10.1   | -9.8    |
|               | $\alpha_{FH}$                          |                 |        | 5.2    | 5       | 4.4     | 4.2     |
|               | $R^2$                                 |                 |        | 0.989  | 0.991   | 0.995   | 0.995   |

$\gamma$ saturation capacity
bed height of 2.2 cm³ volume for chromatographic column breakthrough investigations. At a flow rate of 6–7 drops/min, the 400 mL radioactive waste sample was passed down the column beds, equal fractions were collected in a volume of 5.0 mL, and the radioactivity level was continuously monitored using coaxial HPGe. A schematic diagram for the column experiment under investigation is presented in Fig. 15.

The values of breakthrough capacity under the conditions of the experiment can be easily estimated from the following equation as mentioned in [12]:

\[
\text{Breakthrough Capacity} = V_{(50\%)} \times \frac{C_i}{m}
\]

(18)

where \(V_{(50\%)}\) is the effluent volume at 50% breakthrough (mL), \((C_i)\) is the concentration of feed solution, \((\text{mg.L}^{-1})\) but in the present work, radioactivity-level in \((\text{Bq.L}^{-1})\) was used instead of concentration and \((m)\) is the amount of the column bed per gram. Once working adsorption experiments through columns, the breakthrough curve (a plot of metal ion concentration in the effluent to the feed solution, \(C/C_0\) vs effluent volume \(V\) (mL)) is very beneficial. At 95% of effluent concentration, the column reaches saturation. The resulting breakthrough curves are presented in Fig. 16.

The calculated breakthrough capacities are listed in Table 7. Breakthrough curves show that the breakthrough capacities for \(^{137}\text{Cs}\), \(^{154}\text{Eu}\), and \(^{144}\text{Ce}\) are 434.56, 401.574, and 175.0 Bq.g\(^{-1}\), respectively.

Finally, to compare the performance of the present work prepared sorbent material, Table 8 represents a comparison with different materials sorption for \(\text{Cs}^+, \text{Eu}^{3+}, \text{Ce}^{3+}\) and \(\text{Zr}^{4+}\) metal ions. (Table 9).

**Conclusion**

The present work prepared material Polycrylamide titanium tungstosilicate shows a high sorption capacity for the selected radionuclides \(^{137}\text{Cs}, \text{Eu}^{154}, \text{Ce}^{144}\) and \(^{95}\text{Zr}\) from radioactive liquid waste samples. The obtained optimum pH values were 5 for \(\text{Cs}^+, \text{Eu}^{3+}, \text{Ce}^{3+}\) and 3 for \(\text{Zr}^{4+}\). Also, the optimum contact time was 60, and 30 min for \(\text{Cs}^+\) and \(\text{Zr}^{4+}\), respectively and 2 h for \(\text{Eu}^{3+}\) and \(\text{Ce}^{3+}\). The sorption mechanism is well fitted with the pseudo-2nd-order kinetic model. Moreover, the findings suggest that the Langmuir

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**Table 7** Breakthrough capacities for \(^{137}\text{Cs}, \text{Eu}^{154}, \text{Ce}^{144}\) on PAM/TiWSi

| Radionuclide | \(V_{(50\%)}\) (mL) | Radioactivity level (Bq L\(^{-1}\)) | Breakthrough capacities (Bq g\(^{-1}\)) |
|--------------|---------------------|-----------------------------------|--------------------------------------|
| \(^{137}\text{Cs}\) | 155.2 | 2800.0 | 434.56 |
| \(^{154}\text{Eu}\) | 215.9 | 1860.0 | 401.57 |
| \(^{144}\text{Ce}\) | 250.0 | 700.0 | 175.0 |

**Table 8** Comparison of the performance of PAM/TiWSi and other materials for the sorption of the present study metal ions

| Sorbent material | Maximum capacity \((Q_{max})\) mg.g\(^{-1}\) | Ref |
|------------------|---------------------------------------------|-----|
| \(\text{Cs}^+\)  | \(\text{Ce}^{3+}\)  | \(\text{Eu}^{3+}\)  | \(\text{Zr}^{4+}\)  |
| Polyaniline/SiO\(_2\) composite | – | – | – | 24.26 | [26] |
| Charcoal | – | – | – | 17.54 | [29] |
| Chitosan derivatives | – | – | 29.47 | – | [27] |
| Sodium lauryl-sulfonate modified silicon dioxide | – | 52.5 | – | [28] |
| Activated Carbon Developed from Rice Straw | 2.5 | – | – | [35] |
| Potassium bismuthate | 19.2 | – | – | [36] |
| \(\text{Fe}_3\text{O}_4/\text{Graphene Oxide}\) | 14.8 | – | – | – | [37] |
| \(\text{SiO}_2/\text{Fe-CN}\) | 32.0 | – | – | – | [22] |
| Cellulose/\(\text{HO}_3\text{Sb}_3\) | 14.31 | – | – | – | [12] |
| PAM/TiWSi | 30.70 | 25.30 | 26.60 | 29.70 | Present work |

Fig. 16 Breakthrough curves of the mixture of \(^{137}\text{Cs}, \text{Eu}^{154}, \text{Ce}^{144}\) on PAM/TiWSi composite at pH = 5.56 and 25 ± 1°C.
Monomolecular layer adsorption mode might be used to describe this adsorption process. In addition, the obtained $E$ values from the D-R model for $\text{Cs}^+$, $\text{Eu}^{3+}$, $\text{Ce}^{3+}$ and $\text{Zr}^{4+}$ show that physical adsorption was involved in the adsorption process. Breakthrough capacities for $\text{Cs}^{+}$, $\text{Eu}^{154}$ and $\text{Ce}^{144}$ are 434.56, 401.574, and 175.0 Bq $\cdot g^{-1}$, respectively, were calculated from the column study with a real radioactive liquid waste sample.

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