Green Removal of Toxic Th(IV) by Amino-Functionalized Mesoporous TiO$_2$-SiO$_2$ Nanocomposite

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ABSTRACT: Mesoporous TiO$_2$-SiO$_2$ nanocomposite (TS) was synthesized via sol-gel method and Amino-functionalized using 3-(aminopropyl) triethoxysilane. prepared amino-functionalized TiO$_2$-SiO$_2$ (NH$_2$TS) was evaluated for eliminating radioactive Th(IV) ion in comparison with (TS). The prepared nanocomposites were characterized using FT-IR, XRD, DSC-TGA, SEM, EDS, BET, and BJH analyses. DSC and TGA analyses revealed that the total organic content of the NH$_2$TS was at about 4%. According to the XRD patterns, synthesized nanocomposites exhibited only the crystalline anatase phase, and the sizes of the anatase crystallites in the prepared TS and NH$_2$TS calculated to be 10.4 and 14.1 nm, respectively. Moreover, the pore diameters of TS and NH$_2$TS estimated to be 4.65 and 3.632 nm according to their BJH plot. The kinetic data of Th(IV) uptake process on both of two nanocomposites corresponded well to the pseudo-second-order equation. Adsorption thermodynamic parameters including the standard enthalpy, entropy, and Gibbs free energy revealed that the ion exchange reactions on both of NH$_2$TS and TS nanocomposites were endothermic and spontaneous processes. The results indicated that NH$_2$TS exhibited higher adsorption affinity toward Th(IV) compared to TS. Moreover, based on the Langmuir model, the maximum adsorption capacity of NH$_2$TS nanocomposite towards the Th (IV) was found to be 1000 mg/g.

KEYWORDS: TiO$_2$-SiO$_2$; Amino-functionalization; Th (IV) ion removal; Nanocomposite; Gibbs free energy.

INTRODUCTION
Thorium has received great attention owing to its unique properties and a wide range of applications. Thorium, as an alternative to uranium, has found multiple applications as a nuclear fuel in power plants. Unlike uranium, thorium and its compounds pave the way for widespread industrial productions common as well as high-temperature ceramics, carbon arc lamps, strong alloys, and catalysts [1]. Radioactive thorium intake albeit in small quantities with water, or at the working place under the shadow of this element. Unfortunately, thorium remains in the body, emitting harmful alpha radiation as it decays. The danger of developing leukemia, liver

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and bile duct cancer in the industrial workers dealing with thorium has been estimated to be well above 20 times the risk of the rest of the population [2]. So, adverse effects of thorium contamination necessitate its clean up, a great challenge to human society. A good number of processes for the scooping of thorium ions out of wastewaters and radioactive wastes by natural and synthetic materials have been reported [3]. Adsorption technology has been confirmed to be an effective method for heavy metals enrichment and clean up by using a series of adsorbent materials, such as carbon nanotubes, activated carbons [4], zeolite, porous alumina, etc [5–7]. However, the reported low adsorption capacity is unsatisfactory and undesirable for universal application of the unclear technology. Hence, new sorbents with high adsorption capacities for eliminating harmful radionuclides are required [8]. Some of the surface functionalized nano oxides are known as promising materials with improved adsorption capacity [9–11]. In this research, titania-silica mixed oxide as a recognized sorbent in the field of eliminating hazardous heavy metal ions with cation exchange property of SiO$_2$ and both cation and anion exchange properties of TiO$_2$ [12] was applied for amino functionalization and adsorption studies towards thorium (IV) ion removal. Sorption of Th(IV) on amino functionalized and non-functionalized TiO$_2$-SiO$_2$ were evaluated versus time, pH, and temperature. The thermodynamic data such as $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$ were calculated from temperature relevant sorption isotherms and used to investigate the sorption properties of Th(IV) on amino-functionalized TiO$_2$-SiO$_2$ nanocomposite.

**EXPERIMENTAL SECTION**

**Materials**

Titanium tetrachloride (TiCl$_4$, 99.9%) was purchased from Fluka. Tetraethylorthosilicate (TEOS, 98%), HNO$_3$ (70 wt%, $d=1.42$g cm$^{-3}$), NH$_4$OH (25 wt%), APTES (3-aminopropyltriethoxysilane), anhydrous ethanol (C$_2$H$_5$OH) and thorium nitrate pantahydrate (Th(NO$_3$)$_4$.5H$_2$O) were supplied by Merck.

**TS and NH$_4$TS Preparation**

TiO$_2$-SiO$_2$ nanocomposite (TS) was provided using the method previously described [13]. The reaction sequence for the synthesis of TS is summarized as follows:

1. TiCl$_4$ was added to water under stirring in an ice water bath. The prepared dispersion was treated with NH$_4$OH and the pH was adjusted to 7. The produced solid was collected via filtration and washed with water. The resulted precipitate was dispersed in 200mL of 0.3 mol/L HNO$_3$. The mixture was refluxed under stirring at 70°C for 16 h. After that, 25mL of tetraethylorthosilicate was added dropwise to the above prepared sol and stirred at 70°C. The produced powder was filtered and washed with water and then dried at room temperature. The prepared mixed oxide was calcined in air, at 400°C for 1 h. The prepared powder was labeled as TS.

2. In order to prepare amino-functionalized TiO$_2$-SiO$_2$, 1.2 g of the synthesized TS powders was dispersed in 200 mL ethanol. After that, 2mL of 3-aminopropyltriethoxysilane (APTES) was added to the suspension and the mixture was refluxed for 7 h. The powders were filtered and washed with ethanol and water several times. The powder dried at room temperature was labeled as NH$_4$TS.

**Characterization of prepared adsorbents**

X-ray powder diffractometry was carried out using an 1800 PW Philips diffractometer with CuKa beam and the average crystallite size of the synthesized samples was determined by Scherrer equation [14]. The infrared spectra were recorded using a Brucker-Vector22 spectrometer. The morphology of the products was studied by Scanning Electron Microscopy (SEM, Philips XL30). Oxford INCA Energy-Dispersive X-ray (EDX) was used to analyze the elemental constituents of amino-functionalized composite. The Brunauer–Emmett–Teller (BET) specific surface area and Barret–Joyner–Halenda (BJH) pore size distribution plot of the samples were determined through nitrogen adsorption–desorption (Quantachrome NOVA 2200 e). ThermoGravimetry and Differential Scanning Calorimetry (TG–DSC) was carried out using STA 150 Rheometric Scientific unit. Measurements were taken at a heating rate of 10 °C/min from 25 to 800°C in argon atmosphere.

**Adsorption experiments**

Batch experiments using TS and NH$_4$TS composite adsorbents and 200 mg/L initial thorium ion concentration were conducted to investigate the effects of solution pH, temperature and contact time on sorption performance of the prepared composites.
Th(IV) solutions were placed in 50 mL polypropylene bottles and 0.1 g of sorbent was added to each of the test solution. After that, the sample bottles were placed in a thermostated shaker. After regular time intervals, the suspensions were centrifuged and then the supernatant solutions were passed through milipore filters to remove the suspended sorbents particles. Finally, the concentration of Th(IV) was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP–AES). The experiments were adjusted at 298.15 K and pH 5 except for the temperature and pH dependence studies. NaOH and HNO₃ solutions were used to adjust the pH values, monitored with a digital pH meter.

The amount of adsorbed thorium ion was presented in terms of the distribution coefficient (Kd). The distribution coefficient (Kd) of adsorbed Th(IV) on the composite adsorbents was calculated according to the following equation:

\[
K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} (mL/g) \tag{1}
\]

where \(C_0\) and \(C_e\) are the initial and final Th(IV) ion concentrations in the aliquots, respectively. \(V\) (mL) is the solution volume and \(m\) (g) is the mass of sorbent. A higher \(K_d\) reveals a higher selectivity or adsorption.

The adsorption Th (IV) ions expressed in terms of adsorption percentage (Ads %) was obtained from Eq. (2)

\[
Ads\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}
\]

The effect of temperature on Th (IV) adsorption was examined between 288.15 K and 308.15 K. Furthermore, the thermodynamic parameters such as \(\Delta H^0\), \(\Delta S^0\) and \(\Delta G^0\) were calculated.

**RESULTS AND DISCUSSION**

**Characterization of TS and NH₂TS**

Differential scanning calorimetry and thermogravimetric curves of synthesized NH₂TS are shown in Fig. 1. The decrease in weight, up to 100°C is related to desorption of the physically sorbed water which is confirmed by a small endothermic peak on the DSC curve. The total organic content of the mater determined from the total mass weight, apart from water loss stage, is 4%. Thermal organic weight loss follows a two step process, the first one illustrates an explicit exothermic peak on the DSC curve at 300°C attributed to the presence of amine groups [15, 16].The second one correspond to the decomposition of organic moieties from the organosilane [15, 17].

IR spectra of NH₂TS samples are shown in Fig. 2. The band at around 1100 cm⁻¹ is the asymmetrical vibration of the Si-O-Si bond in the tetrahedral SiO₄ unit of the SiO₂ matrix. The symmetrical Si-O-Si stretching vibration appears at 795cm⁻¹, along with a peak at 954cm⁻¹. This band is ascribed to the vibration involving a SiO₄ tetrahedron bonded to a titanium atom through Si-O-Ti bonds. The TiO₂-SiO₂ sample shows a band at around 490cm⁻¹ which is representative of the titania matrixes [13]. The broad band in the region of 3200–3650 cm⁻¹ is due to the stretching vibration of hydroxyl groups and the peak at 1620 cm⁻¹ can be assigned to the deformation vibration of the free water molecules [18, 19]. However,
according to Mureseanu et al. reports, the absorption band at 1630 cm\(^{-1}\) is not only related to the H\(_2\)O but also to the NH\(_2\) which seems to be some indication of the presence of the amine groups [20]. The typical C–H stretching vibrations of the propyl chains at 2900 cm\(^{-1}\), the C–H deformation vibration at 1485 cm\(^{-1}\), and the N–H deformation vibration at 1556 cm\(^{-1}\) confirmed the grafting of amino propyl groups in the sample [21].

Two absorption bands located in the region of 3300–3500 cm\(^{-1}\) related to the symmetry and asymmetry stretching modes of NH could not be exhibited due to the overlap of the wide band of water.

The X-Ray Diffraction (XRD) analyses of TS and NH\(_2\)TS nanocomposites are shown in Fig. 3. The XRD pattern of the TS composite shows that TiO\(_2\)-SiO\(_2\) has crystalline anatase phase in amorphous silica matrix. Comparing the XRD patterns of TS and NH\(_2\)TS reveals that both of the samples exhibit only anatase phase of TiO\(_2\) and functionalization with APTES does not change the crystal structure of the material. The sizes of the anatase crystallites in the prepared TS and NH\(_2\)TS nanocomposites measured by peak half-width according to the Scherrer equation, are calculated to be 10.4 and 14.1nm, respectively. It can be seen that the crystallite size of the obtained TS powder increases with grafting of amino groups to the mater.

Fig. 4a and b show scanning electron microscopy (SEM) images of TS and NH\(_2\)TS samples. SEM images reveal nanoscale dimensions for TS and NH\(_2\)TS particles. These images demonstrate that the morphology of the samples are not different from each other. However, the modification of TS with APTES agent enlarges the NH\(_2\)TS particles.

Fig. 4c illustrates the Energy-Dispersive X-ray spectroscopy (EDX) analysis of NH\(_2\)TS sample. On the basis of EDX analysis, the peak due to nitrogen is distinct at 0.3 KeV. Moreover, the content of nitrogen in the sample is estimated to be 3wt%.

N\(_2\) adsorption–desorption isotherms and the pore size distribution analyses of TS and NH\(_2\)TS samples are illustrated in Fig. 5. Isotherms of TS and NH\(_2\)TS composites are of type IV which indicating the presence of mesopore. However in the case of TS the hysteresis loop is of a H\(_2\) type with a triangular shape and a steep desorption branch. Such behavior is observed for many porous inorganic oxides and ascribed to the pore connectivity effects [22]. Indeed, H\(_2\) hysteresis loops are observed for materials with relatively uniform channel-like pores, when the desorption branch is located under relative pressures in the proximity of a lower pressure limit of adsorption–desorption hysteresis [23].

For the amino-functionalized nanocomposite, NH\(_2\)TS, hysteresis loop is an H\(_4\) type. Type H\(_4\) loops feature parallel and almost horizontal branches and their occurrence has been attributed to the adsorption–desorption in narrow slit-like pores [24]. The surface area of TS and NH\(_2\)TS composite samples calculated from BET are 405.3 and 205.1m\(^2\)/g, respectively. Furthermore, the pore diameters of TS and NH\(_2\)TS are 4.65 and 3.632 nm according to their BJH plot. It can be seen that grafting the organic functional moieties on TiO\(_2\)-SiO\(_2\) composite results in a decrease in the specific surface area compared to TS.
area and pore size. The surface area decreases by 49% after the grafting of APTES on TS mater.

**Adsorption studies**

*Effect of pH on thorium ion adsorption*

The pH of Th(IV) solution is a controlling factor in ions sorption. The pH of the solution may affect the surface charge of the sorbent as well as the degree of ionization of the metal ions present in the solution [25]. Depending on the pH, metal ions may form complexes with OH− such as M(OH)$_n$, M(OH)$_{n+1}$ and M(OH)$_{n+2}$[26]. Fig. 6 represents the effect of the initial pH of the solution on the adsorption percentage (Ads %) values of the Th(IV) ion on TS and NH$_2$TS. Results emphasize
that with enhancement of pH, the Th(IV) sorption increases in both of two systems. The increase of pH enhances the metal ion removal as a result of lowering the positive charge of the adsorbents, resulting in an increase in their attraction towards the metal cations [27]. The decrease in thorium ions sorption within low pH range could be ascribed to the competition between the excess of H\(^+\) ions in the medium and positively charged cationic species present in the solution [28]. Lower pH hinders hydrolysis of the metal ions. Moreover, the surfaces of exchangers are largely protonated at low pH. Hence, the electrical repulsion between the metal cations and positively charged surface of the sorbents brings about causing less sorption of Th(IV) ions [29–31]. Anirudhan et al. reported that the high adsorption at pH 5 could be ascribed to the predominance of polymerized thorium species such as [Th\(_2\)(OH)\(_6\)]\(^{6+}\) possessing a better binding affinity to the sorbents [32].

**Effect of temperature on removal of thorium ion and adsorption thermodynamic**

The thermodynamic parameters, the values of standard free energy (\(\Delta G^o\)), standard enthalpy (\(\Delta H^o\)), and standard entropy (\(\Delta S^o\)) of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic, and the spontaneity of the adsorption process. The amounts of \(\Delta H^o\), and \(\Delta S^o\) were calculated from the slope and intercept of the straight line obtained from plotting \(\ln K_d\) values versus reciprocal temperature (Fig. 7), respectively, by using the following equation [33]:

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

(3)

After obtaining \(\Delta H^o\) and \(\Delta S^o\) values of the adsorption, \(\Delta G^o\) of the adsorption process at each temperature was calculated from the well-known equation [34]:

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]

(4)

Thanks to Table 1, the obtained negative amounts of \(\Delta G^o\) at different temperatures and the positive amount of \(\Delta H^o\) reveal that the ion exchanger process is an endothermic and spontaneous sorption reaction on the surface of both TS and NH\(_2\)TS nanocomposites. The positive value of \(\Delta S^o\) and thus a decrease in the amount of \(\Delta G^o\) with an increase in the temperature indicate that Thorium adsorption on the sorbent is more spontaneous at higher temperatures.

The decrease of \(\Delta G^o\) with the increasing temperature indicates more efficient adsorption at higher temperatures. According to Wu and co-workers, at higher temperature, Th(IV) is readily dehydrated, and therefore, adsorption becomes more favorable [35]. The values of \(\Delta G^o\) for TS and NH\(_2\)TS at 298.15 K are -10.4152 and -15.137 kJ/mol, which indicate that the adsorption of Th(IV) on NH\(_2\)TS is more favorable than TS.

Sorption kinetics is one of the most important aspects of the adsorption process. Kinetic models control the mechanism of the adsorption process [37]. The rate of sorption of Th(IV) ions by TS and NH\(_2\)TS nanocomposites was studied by equilibrating the 0.1 g solid phase with 50 mL ion solution for different time
Table 1: Thermodynamic parameters of thorium adsorption on TS and NH₂TS nanocomposites.

<table>
<thead>
<tr>
<th>NH₂TS Sorbent</th>
<th>TS Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°(kJ/mol)</td>
<td>15.96</td>
</tr>
<tr>
<td>ΔS°(kJ/mol/K)</td>
<td>0.1043</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>ΔG°(KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>-14.094</td>
</tr>
<tr>
<td>293.15</td>
<td>-14.6155</td>
</tr>
<tr>
<td>298.15</td>
<td>-15.137</td>
</tr>
<tr>
<td>303.15</td>
<td>-15.6585</td>
</tr>
<tr>
<td>308.15</td>
<td>-16.18</td>
</tr>
</tbody>
</table>

Fig. 8: Effect of the contact time on removal of thorium ion and adsorption kinetics

Fig. 9: The pseudo-first-order kinetic plot of Th(IV) adsorption on TS and NH₂TS nanocomposites.

Effect of the contact time on removal of thorium ion and adsorption kinetics

The pseudo-first-order model equation is written in Eq. (5):

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]  

(5)

Where qe and qt are the amounts of metals adsorbed on the sorbent (mg/g) in equilibrium and at time t, respectively, and k₁ is the rate constant of the first-order adsorption (min⁻¹). The straight line plots of log (qe-qt) against t were used to determine the rate constant (k₁) and correlation coefficient (R²) values of the model (Fig. 9). The calculated pseudo-first-order correlation coefficients for TS and NH₂TS sorbents and the values of constants are given in Table 2.
Table 2: Kinetic Parameters for Th(IV) sorption onto the NH$_2$TS and TS nanocomposites.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{e,exp}$ (mg/g)</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
<th>$K_2$ (g/mg min)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS</td>
<td>13.8</td>
<td>6.909x10$^{-3}$</td>
<td>14.2</td>
<td>0.9754</td>
<td>8.95.3x10$^{-4}$</td>
<td>14.2</td>
<td>0.9924</td>
</tr>
<tr>
<td>NH$_2$TS</td>
<td>52.1</td>
<td>9.212x10$^{-3}$</td>
<td>48.5</td>
<td>0.9749</td>
<td>3.170x10$^{-4}$</td>
<td>54.9</td>
<td>0.9981</td>
</tr>
</tbody>
</table>

Fig. 10: The pseudo-second-order kinetic plot of Th(IV) adsorption on NH$_2$TS and TS nanocomposites.

was due to the abundance of active binding sites on the adsorbents, and as these sites were saturated, only a reduced amount of adsorption was occurred. This finding is in consistence with Costa et al. reports [36].

The mathematical expression of the pseudo-second-order model is shown in Eq. (6):

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (6)

Where $t$ is time (min), $q_t$ and $q_e$ are the quantity of the adsorbed ions on the surface of the sorbent (mg/g) at time $t$ and in equilibrium, respectively. $k_2$ denotes the pseudo-second-order rate constant (g/mg·min). The values of constants and correlation coefficients for pseudo-second-order can be calculated from the slope and intercept of the plot of $t/q_t$ versus $t$ (Fig. 10). The calculated pseudo-second-order correlation coefficients for TS and NH$_2$TS sorbents and the values of constants are shown in Table 2.

The $R^2$ values obtained from the pseudo-first-order kinetic plots are relatively small and the experimental $q_e$ values are not consistent with the values calculated from the linear plots.

The correlation coefficients of pseudo-second order kinetics are higher than those of the pseudo-first order ones. Besides, the nearly comparable experimental $q_e$ and calculated $q_e$ values obtained from pseudo second-order equations imply that the the adsorption of Th(IV) on TS and NH$_2$TS is more fitted to the pseudo-second order kinetic.

The difference in the sorption efficiency of the Th(IV) metal ions onto TS and NH$_2$TS can be explained on the basis of more affinity of the surface of NH$_2$TS with the thorium metal ions. As far as we are concerned, the NH$_2$TS as an inorganic–organic hybrid material can act as a good chelating agent in pollutant Th(IV) ion removal from aqueous solution. Essentially, NH$_2$TS shows good sorption performance for Th(IV) in comparison with many adsorbents reported in literature. In order to evaluate the maximum adsorption capacity ($q_{max}$) of Th(IV) adsorption on the surface of NH$_2$TS, some adsorption experiments with varying Th(IV) concentration have been performed at the pH 5 and temperature 298.15 K. The corresponding experimental data, which is well fitted by the Langmuir isotherm ($R = 0.946$) are presented in Fig. 11. Langmuir equation which is used for monolayer adsorption on finite and similar surfaces has the form of Eq. (7) [39].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}$$  \hspace{1cm} (7)
Table 3: Comparison of maximum adsorption capacity (q_{max}) of synthesized NH\textsubscript{2}TS nanocomposite towards Th(IV) with various adsorbents for thorium ions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q_{max} (mg/g)</th>
<th>pH</th>
<th>Temperature (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin oxide</td>
<td>62.5</td>
<td>6</td>
<td>298.15</td>
<td>[1]</td>
</tr>
<tr>
<td>Silica-SH</td>
<td>412.54</td>
<td>4</td>
<td>298.15</td>
<td>[40]</td>
</tr>
<tr>
<td>Silica-NH2</td>
<td>431.19</td>
<td>4</td>
<td>298.15</td>
<td>[40]</td>
</tr>
<tr>
<td>Sodium clinoptilite</td>
<td>333.3</td>
<td>4</td>
<td>313.15</td>
<td>[41]</td>
</tr>
<tr>
<td>PEO/PLLA (poly ethylene oxide/ polyL-lactide)</td>
<td>50.1</td>
<td>6</td>
<td>298.15</td>
<td>[42]</td>
</tr>
<tr>
<td>bi-functionalized biocomposite</td>
<td>26.92</td>
<td>4</td>
<td>298.15</td>
<td>[43]</td>
</tr>
<tr>
<td>chitosan entrapped in polyacrylamide hydrogel</td>
<td>118.34</td>
<td>5</td>
<td>298.15</td>
<td>[44]</td>
</tr>
<tr>
<td>Titanium phosphate</td>
<td>81.2</td>
<td>3</td>
<td>333.15</td>
<td>[45]</td>
</tr>
<tr>
<td>Al-pillared rectorite</td>
<td>30.16</td>
<td>1.88</td>
<td>293.15</td>
<td>[46]</td>
</tr>
<tr>
<td>oxidized multi-wall carbon nanotubes</td>
<td>13.22</td>
<td>1.9</td>
<td>293.15</td>
<td>[47]</td>
</tr>
<tr>
<td>nanocrystalline MOR type zeolite</td>
<td>360</td>
<td>5</td>
<td>303.15</td>
<td>[26]</td>
</tr>
<tr>
<td>nanoporous ZnO</td>
<td>1500</td>
<td>5</td>
<td>303.15</td>
<td>[48]</td>
</tr>
<tr>
<td>NH\textsubscript{2}TS</td>
<td>1000</td>
<td>5</td>
<td>298.15</td>
<td>This study</td>
</tr>
</tbody>
</table>

**Fig. 11: Langmuir isotherm for adsorption of Th(IV) by NH\textsubscript{2}TS.**

where q_{max} is the maximum monolayer adsorption capacity (mg/g), KL is the Langmuir constant related to the free energy of adsorption (L/mg), and a plot of Ce/qe versus Ce yields a straight line with slope 1/qm.

The obtained q_{max} value is compared to the values reported in the literature for different adsorbent materials in Table 3. A higher adsorption capacity for NH\textsubscript{2}TS compared to most of the presented absorbents in the Table 3 is seen.

**CONCLUSIONS**

Mesoporous TiO\textsubscript{2}-SiO\textsubscript{2} (TS) and amino-functionalized TiO\textsubscript{2}-SiO\textsubscript{2} (NH\textsubscript{2}TS) nanocomposites were successfully synthesized and used as sorbents for thorium ion removal. The specific surface area decreased by 49% after the grafting of APTES on TS matrix. In detail, the pore size of NH\textsubscript{2}TS (3.63 nm) was smaller than that of TS (4.65 nm) due to the organic chain, but the particle size of NH\textsubscript{2}TS was larger.

In spite of the poorer porosity properties of NH\textsubscript{2}TS, it exhibited exceptional ability of sorption into the Th(IV) ion compared to TS. In conclusion, the study of the thorium ion adsorption onto the TS and NH\textsubscript{2}TS nanocomposites demonstrated that the NH\textsubscript{2}TS inorganic–organic hybrid material could act as a promising chelating agent in pollutant Th(IV) ion removal from aqueous solution. The batch studies for TS and NH\textsubscript{2}TS were followed to give a good number of favourable thermodynamic and kinetic sets of data such as endothermic enthalpy, negative free Gibbs energy, positive entropic values, and pseudo second-order sorption model. These thermodynamic and kinetic data suggest the application of the amino-functionalized TiO\textsubscript{2}-SiO\textsubscript{2} (NH\textsubscript{2}TS) material for more effective sorption of thorium ion from aqueous solution. Also, according to Langmuir isotherm, maximum adsorption capacity (qm) is 1000 mg/g for NH\textsubscript{2}TS which is a high value in comparison with value reported for other adsorbents and implies a high capability of NH\textsubscript{2}TS for the adsorption of Th(IV) ion from an aqueous solution.

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[2] Thorium Dioxide


