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## Ethyl thiosemicarbazide intercalated organophilic calcined hydrotalcite as a potential sorbent for the removal of uranium(VI) and thorium(IV) ions from aqueous solutions

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### Abstract

This work was conducted to determine the practicability of using a new adsorbent 4-ethyl thiosemicarbazide intercalated, organophilic calcined hydrotalcite (ETSC-OHTC) for the removal of uranium (U(VI)), and thorium (Th(IV)) from water and wastewater. The FT-IR analysis helped in realizing the involvement of nitrogen and sulphur atoms of ETSC in binding the metal ions through complex formation. Parameters like adsorbent dosage, solution pH, initial metal ions concentration, contact time and ionic strength, that influence adsorption phenomenon, were studied. The optimum pH for maximum adsorption of U(VI) and Th(IV) was found to be in the range 4.0–6.0. The contact time required for reaching equilibrium was 4 hr. The pseudo second-order kinetic model was the best fit to represent the kinetic data. Analysis of the equilibrium adsorption data using Langmuir, Freundlich and Sips models showed that the Freundlich model was well suited to describe the metal ions adsorption. The  $K_F$  values were 25.43 and 29.11 mg/g for U(VI) and Th(IV), respectively, at 30°C. The adsorbent can be regenerated effectively from U(VI) and Th(IV) loaded ones using 0.01 mol/L HCl. The new adsorbent was quite stable for many cycles, without much reduction in its adsorption capacity towards the metals.

**Key words:** hydrotalcite; 4-ethyl thiosemicarbazide; uranium(VI); thorium(IV); adsorption.

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### Introduction

The discharge of radioactive waste into the environment is a major issue. Uranium (U), a radioactive material, is an environmental pollutant, being present in mining industry wastewater. Other uranium sources include mainly soils and seawater (Rao et al., 2006). In view of the anticipated exhaustion of terrestrial uranium reserves in the near future, research was directed towards the recovery of U from sources like coal and natural water (Kavakli and Güven, 2004). The main sources of thorium (Th) are monazite, rutile and thorianite. It occurs in the tetravalent form in its compounds in nature. The recent attention to extract Th from waste streams is due to its application as a good fertile nuclear fuel for breeder reactors. Since U and Th ions are radioactive, they emit electromagnetic radiations that can give permanent damage to cells and ultimately resulting to cancer. Methods for removing U and Th ions in water include precipitation, solvent extraction, adsorption, ion-exchange, and reverse osmosis. Adsorption is a relatively simple, cheap and effective method for wastewater

treatment. Different adsorbents have been reported in the literature for the removal of U(VI) and Th(IV) ions, such as cellulose triacetate (Villalobos-Rodríguez et al., 2012), magnetic chitosan composite (Hritcu et al., 2012) and sepiolites (Kilislioglu and Aras, 2010).

Synthetic hydrotalcites have attracted attention as inorganic adsorbents because clay minerals have high adsorption capacity and selectivity for various radionuclides (Kang et al., 1996). On heating, hydrotalcites expel carbon dioxide and water molecules from the interlayers resulting increased exchange properties (Châtelet et al., 1996). Calcined hydrotalcites (HTC) are better adsorbents than hydrotalcites because the former has higher surface area and higher adsorption capacity than the latter. Chemical modification of HTC is needed for enhancing the adsorptive removal of cations from aqueous systems. The association of particular functional groups onto chelating ligands gives potential adsorbents for water treatment processes. The HTC was converted into organophilic (OHTC) by treatment with a surfactant before the introduction of an organic chelating agent, which in turn is capable for metal ion adsorption. Metal cations can be removed by

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complexation via nitrogen and sulphur atoms of thiosemicarbazide in near neutral solutions. There are a very few reports for the removal of metal ions by means of these thiosemicarbazide derivatives.

This article describes the adsorption properties for U(VI) and Th(IV) ions by ethyl thiosemicarbazide intercalated organophilic calcined hydrotalcite (ETSC-OHTC).

## 1 Materials and methods

### 1.1 Materials

Magnesium nitrate, aluminium nitrate, sodium hydroxide and sodium carbonate were obtained from E. Merck, India Ltd. Sodium dodecyl sulphate (SDS) and 4-ethyl thiosemicarbazide (ETSC) were supplied by Aldrich Chemical Company. Solutions of uranium and thorium were prepared from  $\text{UO}_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  and  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  respectively (Fluka, Switzerland). Rest of the chemicals and reagents needed in the present study were of analytical grade and purchased from E. Merck, India Ltd. They were used without any additional purification. Double distilled water was used throughout the study.

### 1.2 Adsorbent preparation

Hydrotalcite required for developing ETSC-OHTC was prepared by the co-precipitation method (Pavlovic et al., 2005).  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.75 mol/L, 50 mL) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.25 mol/L, 50 mL) solutions were added simultaneously to a 50 mL mixture containing 1.7 mol/L NaOH and 0.5 mol/L  $\text{Na}_2\text{CO}_3$  under vigorous stirring at 60°C and was kept under stirring for 24 hr at the same temperature. The thick gel like precipitate obtained was filtered, washed repeatedly with double distilled water and dried at 80°C. The product was then powdered and calcined in a muffle furnace at 450°C for 5 hr to get HTC. About 5 g of HTC in 100 mL distilled water was treated with SDS solution (2.36 g) equivalent to the anion exchange capacity of HTC (1.60 meq/g) for 30 min, and then added ETSC (1.16 g), dissolved in alcohol. The total volume of the mixture should be 500 mL and was kept at pH 6.0 and 30°C for 24 hr under continuous stirring. The product was washed several times with double distilled water until it was free from excess reactants and dried at 60°C. The adsorbent (ETSC-OHTC), thus obtained was powdered and sieved to get particles of uniform size.

### 1.3 Equipments

The FT-IR spectra of the samples were taken using a Shimadzu FT-IR spectrophotometer between 4000 and 400  $\text{cm}^{-1}$  with KBr background. The CHNS analysis of HTC and ETSC-OHTC was done using Thermo Finnigan Flash EA III CHNS analyzer. Glass-stoppered Erlenmeyer flasks and Borosil glasswares were used for adsorption experiments. Solution pH was measured with a Systronic Microprocessor pH Meter (model  $\mu$ -362). All the solu-

tions, for the adsorption equilibrium studies, were shaken in a temperature controlled water bath shaker purchased from Labline, India. It has accuracy up to  $\pm 1^\circ\text{C}$ . A UV-Vis spectrophotometer (V-530, JASCO) was used for estimating the amount of U(VI) and Th(IV) ions in solutions.

### 1.4 Adsorption experiments

To measure the equilibrium distribution of U(VI) and Th(IV) ions between the adsorbent and the liquid phase, an accurately weighed amount (0.1 g) of adsorbent was continuously shaken in 50 mL of the corresponding salt solutions with different initial metal concentrations at a fixed pH. Shaking was kept at 300 r/min for 4 hr to reach equilibrium. After attaining the equilibrium, the adsorbent was removed by filtration and the concentrations of U(VI) and Th(IV) ions in the corresponding filtrate were determined. Arsenazo III was used as the complexing agent for both U(VI) and Th(IV) ions and the absorbance was measured at  $\lambda = 665$  and 660 nm, respectively (Khan et al., 2001).

The amount of metal ions adsorbed at equilibrium,  $q_e$  (mg/g), was obtained by Eq. (1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where,  $C_0$  (mg/L),  $C_e$  (mg/L) are the initial and equilibrium concentrations of the metal ion respectively,  $V$  (L) is the volume of solution, and  $m$  (g) is the mass of the adsorbent. Each experiment was carried out in duplicate and the average value is reported.

### 1.5 Desorption studies

The reuse of the adsorbent was accessed by shaking the metal ion loaded adsorbent with 0.01 mol/L hydrochloric acid (the desorbing reagent) for 4 hr at 30°C. The suspension was filtered and the filtrate was analyzed for determining the desorbed metal amount. The recovered adsorbent was then washed gently with deionized water, dried and reused in the second cycle of adsorption. Both the adsorption and desorption studies were repeated for many cycles.

## 2 Results and discussion

### 2.1 Characterization of adsorbent

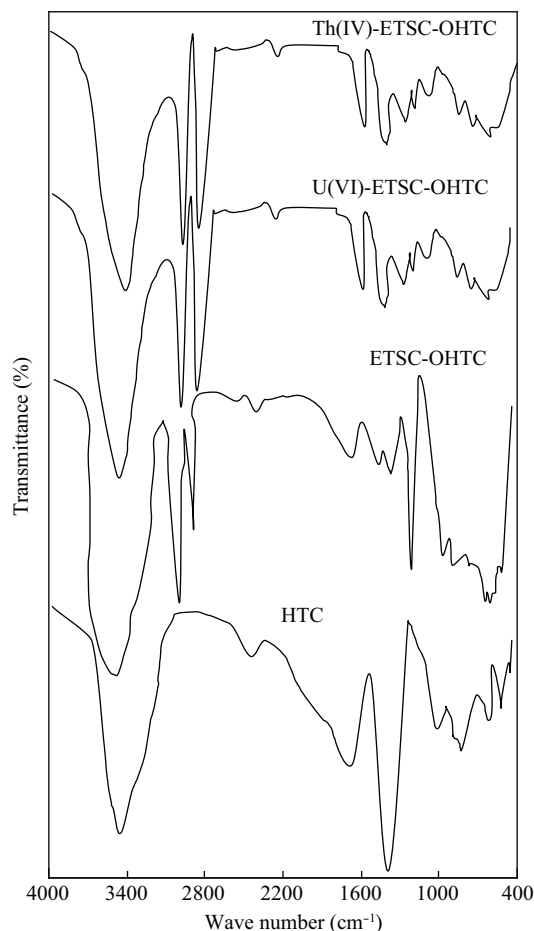
The elemental analysis results of HTC and ETSC-OHTC are as follows: the percentages of C, H, N, S in HTC were 1.8%, 1.9%, 0.2%, and 0, respectively, while in ETSC-OHTC were 17.1%, 4.5%, 4.1% and 6.3%, respectively. The increase of carbon, hydrogen, nitrogen and sulphur contents in ETSC-OHTC showed evidence of intercalation of organic moieties in HTC molecule. The amount of amine group in ETSC-OHTC was estimated using volumetric method (Zhu and Alexandratos, 2005) and was found to be 1.31 meq/g. Specific surface area values of

HTC and ETSC-OHTC were determined by BET, nitrogen adsorption method and the values were 201 and 72 m<sup>2</sup>/g respectively. The reduction in surface area after surface modification might be because of the filling of pores of HTC by SDS and ETSC molecules.

**Figure 1** presents the FT-IR spectra of HTC, ETSC-OHTC, and U(VI) and Th(IV) loaded ETSC-OHTC (U(VI)-ETSC-OHTC, Th(IV)-ETSC-OHTC respectively), obtained between 4000 and 400 cm<sup>-1</sup>. In HTC spectrum, the peak centered at around 3445 cm<sup>-1</sup> was attributed to the -OH vibration from the brucite-like layers (Mg-OH-Al and Al-OH-Al) and from interlayer water molecules (Barriga et al., 2002). In ETSC-OHTC spectrum, the overlap of -OH stretching from HTC and -NH<sub>2</sub> stretching vibrations of ETSC molecule was revealed by the broad peak at 3470 cm<sup>-1</sup>. The peak (1220 cm<sup>-1</sup>) of thiocarbonyl group and the peaks (2920 and 2850 cm<sup>-1</sup> respectively) of -CH<sub>2</sub> and -NH group stretching vibrations (Silverstein, 1991), supported the presence of ETSC molecule in ETSC-OHTC. Furthermore in ETSC-OHTC spectrum, bands observed at 610 and 1420 cm<sup>-1</sup> belong to S-O stretching and SO<sub>2</sub> group respectively, show the presence of SDS molecules. The band at 1384 cm<sup>-1</sup> in the HTC spectrum corresponding to carbonate absorption (Rey et al., 1992) shifted to a lower wavelength at 1372 cm<sup>-1</sup> in ETSC-OHTC, might be due to the exchange of carbonate ions by SDS molecules. The spectra of U(VI)-ETSC-OHTC and Th(IV)-ETSC-OHTC had new bands at 3430 and 3410 cm<sup>-1</sup> respectively revealed the formation of complex between metal ions (U(VI), Th(IV)) and -NH<sub>2</sub> group. The shift of  $\nu$  (C=S) band to 1205 cm<sup>-1</sup> in U(VI)-ETSC-OHTC and 1207 cm<sup>-1</sup> in Th(IV)-ETSC-OHTC, showed the involvement of sulphur atoms in co-ordination. Thus, thiosemicarbazides are chelating bidentate ligands coordinated through the tenninal hydrazine N atom and S atom during complex formation.

## 2.2 Effect of pH

**Figure 2** represents the optimization study of pH for the maximum removal of U(VI) and Th(IV) ions using ETSC-OHTC from two different initial concentrations (25 and 50.0 mg/L). Uranium occurs as U(VI) in the form of mobile, hydrated uranyl UO<sub>2</sub><sup>2+</sup> ions in aqueous solutions. The pH of a solution strongly affects the solubility of metal species. Adsorption of U(VI) increased sharply with increase of pH up to 5.0 and then started decreasing. Hydrolysis of the uranyl ion practically begins at pH 3.0 and mononuclear [UO<sub>2</sub>(OH)]<sup>+</sup> as well as polynuclear [(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup>, [(UO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub>]<sup>+</sup> products of the general type [UO<sub>2</sub>]<sub>x</sub>(OH)<sub>y</sub>]<sup>(2x-y)+</sup> are formed (Al-Shaybe and Khalili, 2009). At pH ≤ 5.0, the uranium removal is mainly due to the predominant species, UO<sub>2</sub><sup>2+</sup> and UO<sub>2</sub>(OH)<sup>+</sup>, of U(VI). However at very low pH, since H<sub>3</sub>O<sup>+</sup> is predominant, its competition towards the adsorption site controls the metal ions adsorption efficiency. The pH increase



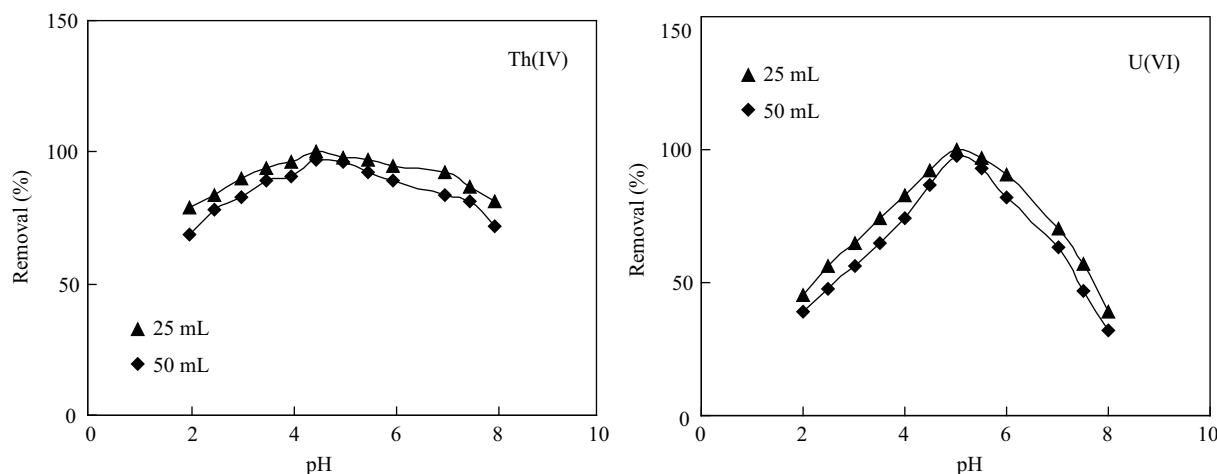
**Fig. 1** FT-IR spectra of HTC, ETSC-OHTC, U(VI)-ETSC-OHTC and Th(IV)-ETSC-OHTC.

enhanced the metal ion removal as a result of lowering of positive charge of the adsorbent, which in turn increased its attraction towards the metal cations (Anirudhan and Sreekumari, 2011). Soluble uranyl ions complexes are formed above pH 5.0 so that uranium adsorption decreased after this pH. The pH for maximum removal of U(VI) was found to be 5, and thus all the succeeding experiments of U(VI) were done at this pH value.

The pH study on the adsorption of Th(IV) ions indicated a pH optimum of 4.5. The decrease in thorium ions sorption at low pH range could be attributed to the increased competition by H<sub>3</sub>O<sup>+</sup> and its increased solubility (Baes and Mesmer, 1976). The higher adsorption at pH 4.5 could be associated with the predominance of [Th<sub>2</sub>(OH)<sub>2</sub>]<sup>6+</sup> and other polymerized species possessing a better binding affinity (Tsezos and Volesky, 1982). Adsorption was limited above pH 6.0 due to the formation of neutral Th(OH)<sub>4</sub>.

## 2.3 Effect of adsorbent dose

The effect of adsorbent dose on the removal of U(VI) and Th(IV) ions was studied by carrying out the adsorption experiments using various amounts of ETSC-OHTC at the optimum pH 5.0 for U(VI) and 4.5 for Th(IV) at 30°C (**Fig. 3**). The time needed to attain equilibrium



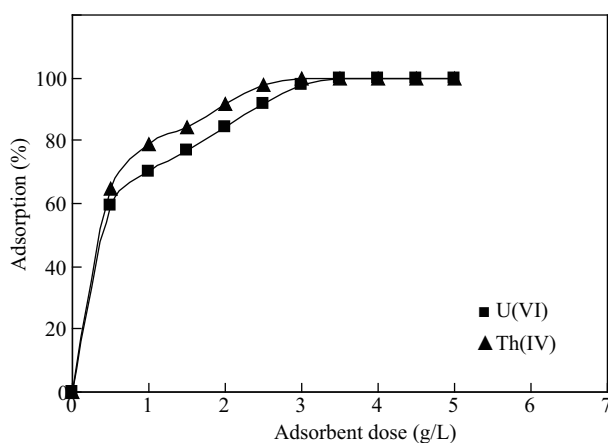
**Fig. 2** Effect of pH on the adsorption of U(VI) and Th(IV) onto ETSC-OHTC. Conditions: adsorbent dose 2 g/L; equilibrium time 4 hr; temperature 30°C.

was taken as 4 hr. The removal percentage of U(VI) and Th(IV) ions was noted as a function of adsorbent dose. The removal of metal ion increased from 59.0% for U(VI) and 65.0% for Th(IV) to 100.0% with an increase of dose from 0.5 to 3.5 and 3.0 g/L respectively from the corresponding metal solutions of initial concentration 100.0 mg/L. As adsorbent dosage was increased, the number of unoccupied effective sites and the surface area also increased and thus it improved the percentage of adsorption.

#### 2.4 Effect of contact time and initial concentration

In order to ascertain an appropriate contact time between the adsorbent and metallic ions in solution, the adsorption of U(VI) and Th(IV) onto ETSC-OHTC was tested as a function of contact time at room temperature by batch method at different initial concentrations (50 to 200 mg/L) of metal ion solutions (**Fig. 4**). The rate of adsorption for U(VI) and Th(IV) was initially fast and then reached a plateau value. The high adsorption rate was due to the abundance of active binding sites on the adsorbent, and as these sites get saturated, only a reduced amount

of adsorption was occurred (da Costa and Leite, 1991). The equilibrium time was found to be a constant and was independent of the initial U(VI) and Th(IV) ion concentrations. The quantity of U(VI) and Th(IV) ions adsorbed at equilibrium onto ETSC-OHTC was found to be improved from 26.5 and 31.09 mg/g to 70.42 and 73.2 mg/g, respectively, on increasing the initial concentration from 50 to 200 mg/L indicating that the metal removal was concentration dependent. The increase of metal ion concentration accelerated the diffusion of metal ion from the bulk solution onto the adsorbent phase because of the enhanced force of the higher concentration (Hameed et al., 2008). If metal ion/adsorbent ratios are low, metal adsorption takes place at higher energy sites. When the metal ion/adsorbent ratio is increased, the higher energy sites become saturated and lower energy sites are involved in adsorption and consequently the adsorption efficiency is decreased (Bhattacharya et al., 2006). Since the amount of metal ions adsorbed did not change after 4 hr, the succeeding adsorption experiments were done keeping 4 hr as an appropriate equilibrium time.



**Fig. 3** Effect of adsorbent dose on the adsorption of U(VI) and Th(IV) onto ETSC-OHTC. Conditions: equilibrium time 4 hr; concentration 100 mg/L; pH 5.0 for U(VI); pH 4.5 for Th(IV); 30°C.

#### 2.5 Kinetics of adsorption

Kinetics of adsorption is determined by the rate at which an adsorbate is adsorbed at the surface of an adsorbent and hence it is a measure of the efficiency of the process. The adsorption kinetics of U(VI) and Th(IV) ions was evaluated by testing the experimental data with pseudo first-order (Rudzinski and Plazinski, 2006) and pseudo second-order (Ho and McKay, 1999) equations.

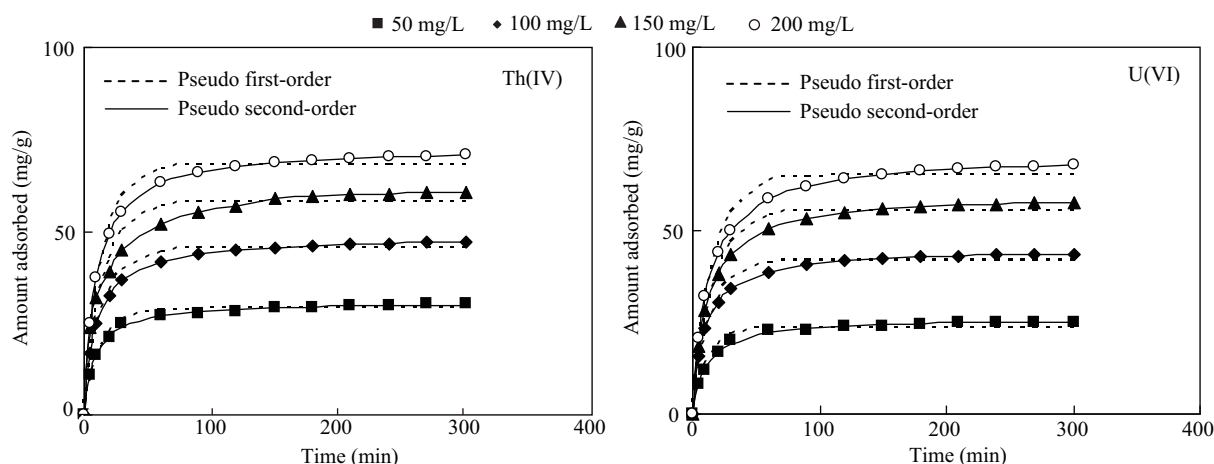
Pseudo first-order:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

Pseudo second-order:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) denote the amounts adsorbed at equilibrium and at time  $t$ , respectively, and  $k_1$



**Fig. 4** Adsorption kinetics at different initial U(VI) and Th(IV) concentrations (50–200 mg/L). Conditions: adsorbent dose 2 g/L; pH 4.5 for Th(IV); pH 5.0 for U(VI); temperature 30 °C.

( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}/(\text{mg}\cdot\text{min})$ ) represent the rate constants of pseudo first- and second-order reactions, respectively. The kinetic parameters  $k_1$  and  $k_2$ , and the values of correlation coefficients ( $R^2$ ) and chi-squared ( $\chi^2$ ) were determined using nonlinear regression analysis and the results are given in **Table 1**. The pseudo second-order kinetic model was found to be the best fit for the adsorption data (**Fig. 4**). The  $R^2$  values for the pseudo second-order kinetic model was  $> 0.99$  for both U(VI) and Th(IV) adsorption and the estimated values of  $q_e$  also agreed with the experimental ones. These results show that the adsorption of U(VI) and Th(IV) ions obeyed the pseudo second-order kinetic model, suggesting that the process is chemical adsorption between metal ions and ETSC-OHTC (Dundar et al., 2008).

As the metal ion concentrations were increased, the  $q_e$  values were also increased but the rate constants ( $k_1$  and  $k_2$ ) were decreased. The pseudo second-order rate constant ( $k_2$ ) values decreased from  $2.93 \times 10^{-3}$  to  $1.25 \times 10^{-3} \text{ g}/(\text{mg}\cdot\text{min})$  for U(VI) and from  $3.50 \times 10^{-3}$  to  $1.40 \times 10^{-3} \text{ g}/(\text{mg}\cdot\text{min})$  for Th(IV), with increasing metal ion concentration from 50 to 200 mg/L. This might be because of the direct relation between initial metal ion concentration and the mass-transfer resistance. The low concentration of metal ion in solution increased the probability of adsorption and showed greater rate. In dilute solutions, the ions are more mobile and it will increase the interaction of these ions with the adsorbent (Humelnicu et al., 2010).

Because of quick and constant shaking, the adsorbate molecules may enter slowly into the inner parts of the adsorbent pores. In order to explore the mass transfer behaviour of metal adsorption by ETSC-OHTC, intraparticle mass transfer diffusion model (Weber and Morris, 1963) was applied.

$$q_t = k_{id}t^{1/2} + C \quad (4)$$

where,  $q_t$  (mg/g),  $k_{id}$  ( $\text{mg}/(\text{g}\cdot\text{min}^{1/2})$ ) and  $C$ , represent

amount adsorbed at time  $t$ , the rate parameter or intraparticle diffusion rate constant and the intercept, respectively. When  $q_t$  is plotted against  $t^{1/2}$ , the graph will be linear, if intraparticle diffusion has an important function in the adsorption mechanism. The  $q_t$  versus  $t^{1/2}$  plots, for the adsorption of U(VI) and Th(IV) ions onto ETSC-OHTC are presented in **Fig. 5**. The deviation from linearity might be because of the change in the mechanism of adsorption.

All the  $q_t$  vs  $t^{1/2}$  curves have three portions and each part represents a particular stage in the process. The first region is curved, the second part is linear and the third portion is a plateau one. Surface adsorption took place in the initial stage which was followed by intraparticle diffusion in the next stage, represented by the straight line part whereas the equilibrium state was shown by the last region. The intraparticle diffusion rate constant ( $k_{id}$ ) and the boundary layer thickness were got from the slope and intercept of the linear portion, respectively. The larger the intercept the greater is the boundary layer effect (Kannan and Sundaram, 2001). At the third region, the intraparticle diffusion was somewhat stopped because of decreased concentration of the solution (Sun and Yang, 2003). The deviation of the curve from linearity indicated that the adsorption process involved some other mechanisms in addition to intraparticle diffusion. As initial metal ion concentration was varied from 50 to 200 mg/L, the intraparticle diffusion rate constant, got from the slope of the linear portion corresponding to 10 to 60 min, increased from 2.21 to 5.63  $\text{mg}/(\text{g}\cdot\text{min}^{1/2})$  for U(VI) and 2.40 to 5.68  $\text{mg}/(\text{g}\cdot\text{min}^{1/2})$  for Th(IV) (**Table 1**). The  $R^2$  values for intraparticle diffusion model were found to be 0.99 for both the ions, indicated that the adsorption of U(VI) and Th(IV) ions onto ETSC-OHTC was controlled by this mechanism during 10–60 min.

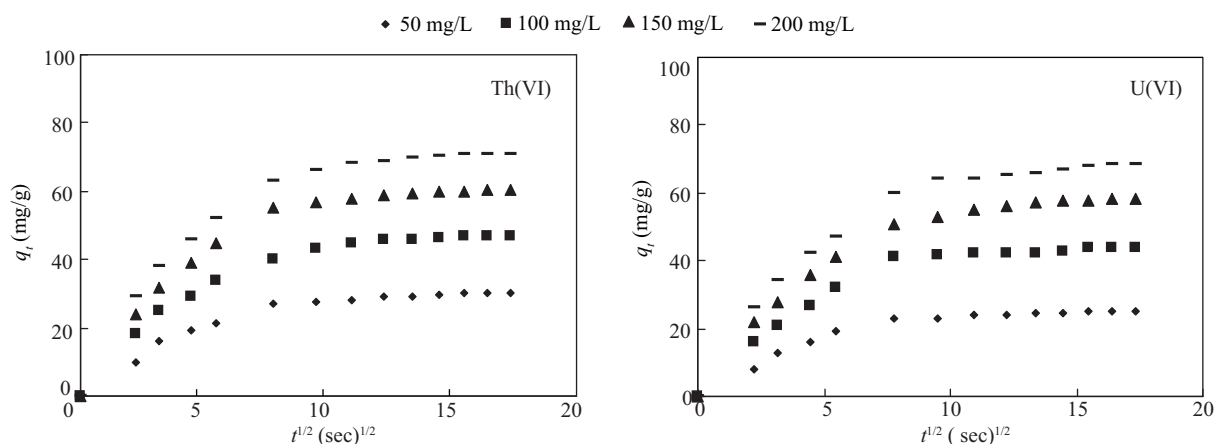
## 2.6 Adsorption isotherm

The adsorption data are usually collected in terms of the total amount of the adsorbate adsorbed at the adsorbent's



**Table 1** Kinetic parameters for the adsorption of U(VI) and Th(IV) onto ETSC-OHTC

Concentration (mg/L)		Pseudo first-order		Pseudo second-order		Intra particle diffusion	
		$k_1$ ( $\times 10^{-2} \text{min}^{-1}$ )	$R^2$	$k_2$ ( $\times 10^{-3} \text{g}/(\text{mg}\cdot\text{min})$ )	$R^2$	$k_{id}$ ( $\text{mg}/(\text{g}\cdot\text{min}^{1/2})$ )	$R^2$
U(VI)	50	6.20	0.983	2.93	0.998	2.21	0.988
	100	5.82	0.977	1.91	0.997	4.37	0.995
	150	5.81	0.965	1.42	0.993	4.96	0.992
	200	5.72	0.961	1.25	0.998	5.63	0.995
Th(IV)	50	6.17	0.971	3.50	0.996	2.40	0.992
	100	6.20	0.957	1.93	0.997	4.39	0.989
	150	6.66	0.968	1.91	0.994	5.02	0.994
	200	6.67	0.959	1.40	0.996	5.68	0.996

**Fig. 5** Intraparticle diffusion plots for the adsorption of U(VI) and Th(IV) onto ETSC-OHTC. Conditions: adsorbent dose 2 g/L; pH 4.5 for Th(VI); pH 5.0 for U(VI); temperature 30 °C.

surface. When the amount adsorbed at equilibrium is plotted against the equilibrium concentration of the adsorbate at constant temperature, adsorption isotherms are obtained. Since an adsorption isotherm gives an idea about the adsorption capacity of the adsorbent, this can be used for optimizing the application of an adsorbent. The common adsorption isotherm models are Langmuir, Freundlich, and Sips (Langmuir-Freundlich). These equations were tested to fit the experimental adsorption data of U(VI) and Th(IV) ions. The Langmuir model suggests a monolayer adsorption onto the adsorbent having uniform surface sites with equivalent energies and the adsorbed species do not interact with one another (Langmuir, 1918). The Freundlich model is an empirical one relating adsorption onto heterogeneous surface (Freundlich, 1906). This model is typical of heterogeneous surfaces and suggests that the surface active sites of the adsorbent have unequal binding energies. The Sips isotherm (Sips, 1948) is a fusion of the Langmuir and Freundlich isotherm models.

Langmuir equation:

$$q_e = \frac{Q^0 b_L C_e}{1 + b_L C_e} \quad (5)$$

Freundlich equation:

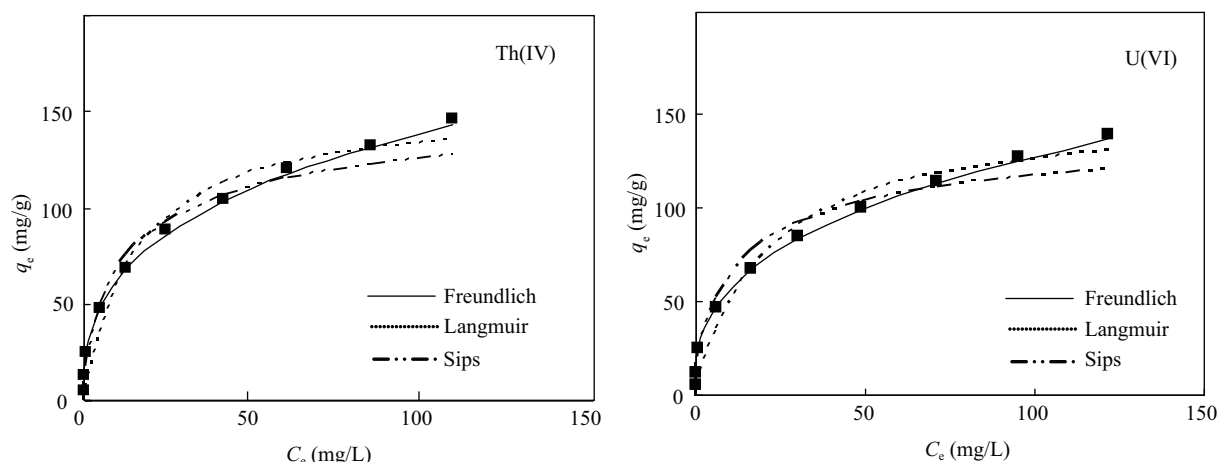
$$q_e = K_F C_e^{\frac{1}{n_F}} \quad (6)$$

Sips (Langmuir-Freundlich):

$$q_e = \frac{q_{\max} (b_s C_e)^{n_s}}{1 + (b_s C_e)^{n_s}} \quad (7)$$

where,  $q_e$  (mg/g) is the amount adsorbed at equilibrium and  $C_e$  (mg/L) is the equilibrium concentration of the metal ions in solution.  $Q^0$  and  $b_L$  are Langmuir constants associated with adsorption capacity and binding energy of adsorption, respectively.  $K_F$  and  $1/n_F$  represent Freundlich's constants connected to adsorption ability and the heterogeneity factor, respectively.  $q_{\max}$ ,  $b_s$  and  $n_s$  denote Sips isotherm constants connected to adsorption ability, equilibrium constant and heterogeneity factor, respectively.

The isotherms of U(VI) and Th(IV) ions onto ETSC-OHTC are illustrated in **Fig. 6**. The  $q_e$ , was studied as a function of  $C_e$ . The metal removal mechanism is related to the initial metal ion concentration. Adsorption of metal ions takes place at definite sites only when the metal ion concentration is low, but as the concentration is increased, the sites become saturated and exchange sites are filled (Patel et al., 2007). Based on the correlation coefficients (**Table 2**), the Freundlich equation gives a better fit of experimental data than the Langmuir and Sips, for the adsorption of U(VI) and Th(IV) ions. This gives the inference that the surface of ETSC-OHTC is mainly made up of heterogeneous adsorption patches. The experimental



**Fig. 6** Comparison of isotherm data for the adsorption of U(VI) and Th(IV) onto ETSC-OHTC. Conditions: adsorbent dose 2 g/L; equilibrium time 4 hr; pH 4.5 for Th(IV); pH 5.0 for U(VI).

**Table 2** Various isotherm parameters for the adsorption of U(VI) and Th(IV) onto ETSC-OHTC

Metal ion	Langmuir	Freundlich	Sips
U(VI)	$Q^0$ : 150.48 mg/g $b_L$ : 0.052 L/mg $R^2$ : 0.963 $X^2$ : 99.	$K_F$ : 25.43 $1/n_F$ : 0.35 $R^2$ : 0.999 $X^2$ : 1.98	$q_{max}$ : 154.10 mg/g $b_s$ : 0.061 $n_s$ : 0.65 $R^2$ : 0.979 $X^2$ : 46.1
Th(IV)	$Q^0$ : 154.25 mg/g $b_L$ : 0.066 L/mg $R^2$ : 0.965 $X^2$ : 105.7	$K_F$ : 29.10 $1/n_F$ : 0.34 $R^2$ : 0.999 $X^2$ : 1.51	$q_{max}$ : 162.24 mg/g $b_s$ : 0.065 $n_s$ : 0.671 $R^2$ : 0.987 $X^2$ : 42.66

values of  $K_F$  of the adsorbent towards uranyl and thorium ions were 25.43 and 29.10, respectively. The Freundlich constant  $1/n_F$  was below 1 at all the experimental concentrations, indicative of high adsorption intensity (Tsai et al., 2003).

### 2.7 Comparing adsorptivity between Th(IV) and U(VI) ions

Values of different isotherm constants connected to adsorption capacity,  $Q^0$ ,  $K_F$  and  $q_{max}$ , are higher for Th(IV) than U(VI) ions (Table 2) indicating that the adsorption of Th(IV) is more favourable than U(VI) ions onto ETSC-OHTC at the same temperature. Smaller ion is hydrated easily and it has got greater hydrated ionic radius whereas ion with greater ionic radius has smaller hydrated ionic radius. Since adsorptive power depends inversely on the size of the species, smaller hydrated ions are adsorbed readily. Ionic radii of Th(IV) and U(VI) are 1.19 and 0.97 Å and it agrees with the greater adsorption of Th(IV) over U(VI) ions. Similarly, ions having lower hydrolytic constant as well as hydration energy experience greater adsorption than those with higher hydrolytic constant and hydration energy. Thorium and uranium have the hydrolytic constant and hydration energy as 4.0 and -3332 kJ/mol and 4.7 and -3958 kJ/mol respectively (Al-Shaybe and Khalili,

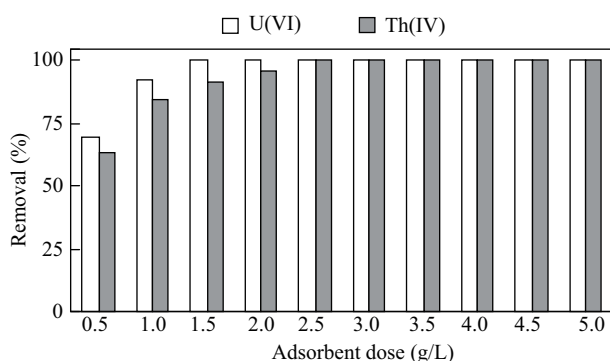
2009). Based on hydration nature, Th(IV) adsorption is more favoured and so the amount of Th(IV) adsorbed is greater than that of U(VI).

### 2.8 Effect of ionic strength

The effect of ionic strength on the adsorption of U(VI) and Th(IV) ions with ETSC-OHTC was studied in the presence of different NaCl concentrations at an initial metal ion concentration of 100.0 mg/L. Results showed that these metal ions binding by ETSC-OHTC was not much affected by ionic strength. However, a slight increase in adsorption was found with increase in ionic strength. The adsorption capacity values with NaCl concentrations 0.001, 0.005, 0.01, 0.02, 0.05, .075 and 0.1 mol/L were found to be 89.0%, 90.6%, 91.1%, 92.3%, 95.2%, 96.1% and 97.3% for U(VI) and 93.0%, 94.2%, 95.0%, 97.5%, 98.0%, 99.1% and 99.8% for Th(IV) ions, respectively. According to Guoy-Chapman theory (Osipow, 1972) regarding the electrical double layer, when two phases (adsorbent and adsorbate) are in contact with each other, they are surrounded by an electrical diffuse double layer. The increase in ionic strength might reduce the thickness of the above double layer and helped the adsorbent and adsorbate molecules to approach faster, resulting greater adsorption.

### 2.9 Test with industrial wastewater

The practical value and effectiveness of the adsorbent material for treating U(VI) and Th(IV) solutions was tested using simulated nuclear industry wastewater (Jansson-Charrier et al., 1996) and artificial sea water (Parsons et al., 1984) respectively. The simulated nuclear industry wastewater has the composition (mg/L): U(VI) 10;  $Ca^{2+}$  10;  $Mg^{2+}$  10;  $Cl^-$  20;  $SO_4^{2-}$  80;  $NO_3^-$  40;  $PO_4^{3-}$  20;  $C_2O_4^{2-}$  60; detergent 20 and pH 6.7. The composition of artificial sea water (mg/L) is:  $Th(NO_3)_4 \cdot 5H_2O$  0.061; NaCl 41.52;  $Na_2SO_4$  6.95; KCl 10.17;  $NaHCO_3$  0.340; KBr 0.17;  $H_2BO_3$  0.05; NaF 0.005;  $MgCl_2 \cdot 6H_2O$  18.80;



**Fig. 7** Effect of adsorbent dose for the removal of U(VI) and Th(IV) ions from wastewater by ETSC-OHTC. Conditions: equilibrium time 4 hr; temperature 30°C.

CaCl<sub>2</sub>·2 H<sub>2</sub>O 2.63; SrCl<sub>2</sub>·6H<sub>2</sub>O 0.0428. It contains 25 mg/L of Th(IV) solution. Batch adsorption studies were conducted by shaking 50 mL of wastewater samples with different masses of ETSC-OHTC to determine its amount for the complete removal of U(VI) and Th(IV) ions. These metal ions removal increased with increase in mass of the adsorbent (**Fig. 7**) which might be due to the increase in the availability of more unoccupied surface active sites. Experiments were also conducted with a series of 50 mL samples (separately) of 10 mg/L of U(VI) and 25 mg/L of Th(IV) aqueous solutions. Results show that 1.5 g ETSC-OHTC was needed to remove U(VI) ions, almost completely from both the simulated nuclear industry wastewater and aqueous solutions. Above 99.0% removal of Th(IV) ions was possible with 2.5 g of the adsorbent which is in good agreement with that obtained from the single solute batch experiment. The results demonstrate that ETSC-OHTC can be effectively employed for removing U(VI) and Th(IV) ions from industrial wastewater.

### 2.10 Desorption and regeneration studies

Desorption studies are conducted mainly for regenerating and reusing the adsorbent materials over a number of cycles. The adsorption can be physical or chemical. In the chemical adsorption regeneration can be achieved by acid or alkali solution. In the present study HCl solution was used as the desorbing agent. The desorption efficiency was examined for four cycles. The metal ion loaded adsorbent was placed in the desorbing solution and was kept shaking for 3 hr. After the experiment, the suspension was filtered and analysed the filtrate to estimate the metal ion concentration. Desorption was found to be increased from 43.0% to 94.6% for U(VI) and 39.0% to 93.5% for Th(IV) loaded adsorbents when the concentration of HCl was changed from 0.001 to 0.01 mol/L. Desorption medium should not cause any damage to the adsorbent. Highly concentrated acids/alkali can damage the adsorbent. Maximum desorption, 94.6% and 93.5% respectively for U(VI) and Th(IV) adsorbed samples, was possible with 0.01 mol/L HCl (**Table 3**). The adsorbent can be successfully re-used for at least 4 cycles with no significant

**Table 3** Adsorption-desorption cycles of U(VI) and Th(IV) using 0.01 mol/L HCl as the desorbing agent

Metal ion	No. of cycles	Adsorption (%)	Desorption (%)
U(VI)	1	99.6	94.6
	2	98.5	93.1
	3	98.0	92.5
	4	97.1	91.2
Th(IV)	1	99.7	93.5
	2	98.9	92.0
	3	98.2	91.2
	4	97.5	89.0

adsorption drop. After four cycles, the adsorption capacity of the ETSC-OHTC for U(VI) decreased from 99.6% to 97.1% and for Th(IV) decreased from 99.7% to 97.5%, while the desorption of U(VI) decreased from 94.6% to 91.2% and of Th(IV) decreased from 93.5% to 89.0% in the fourth cycle. As the regenerated ETSC-OHTC showed high affinity towards U(VI) and Th(IV) ions, ETSC-OHTC can be utilised for the design of continuous adsorption process.

### 3 Conclusions

Batch adsorption studies proved that the new adsorbent, ETSC-OHTC has high adsorption capacity for U(VI) and Th(IV) ions in the pH range 4.0–6.0. Kinetics data fitted well with pseudo second-order model confirming the chemisorptions of the metal ions onto ETSC-OHTC. The adsorption equilibrium experiments matched well with the Freundlich isotherm model. The adsorbent loaded by U(VI) and Th(IV) could be regenerated for constant use using 0.01 mol/L HCl solution. The results of this work showed that the new adsorbent ETSC-OHTC can be effectively used for the removal of metal ions from aqueous solutions and other industrial effluents.

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