

# Modification of multi-walled carbon nanotubes with tannic acid for the adsorption of La, Tb and Lu ions

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**Abstract** We have prepared an environmental friendly sorbent by modifying multi-walled carbon nanotubes with tannic acid. The adsorption of La (III), Tb (III) and Lu (III) as a function of contact time, initial solution pH, and quantity of adsorbent was studied using a batch technique. Both Langmuir and Freundlich isotherms can be used to describe the process. The major adsorption mechanisms were attributed to ion exchange and surface complexation. The kinetics of the adsorption follows a pseudo-second-order model. The thermodynamic functions  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  indicate that the sorption is endothermically driven. The adsorbed ions can be readily desorbed from the surface with 1 M hydrochloric acid.

**Keywords** Modification · Multi-walled carbon nanotubes · Tannic acid · Adsorption · Rare earth elements

## Introduction

Rare earths elements (REEs) have obtained considerable attention because of their unique properties, such as the

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production of superconductors, super-magnets and geo-chemical natures. REEs are important elements not only in industrial applications but also in energy and environmental problems [1]. It is essential to find appropriate methods to satisfy the needs for quality control, certification, and evaluation of material performance.

The most widely used techniques for the separation and removal of trace REEs include precipitation [2], solvent extraction [3], adsorption [4] and ion-exchange [5], etc. Although solvent extraction has been widely used since effective extraction ability and separation selectivity, the large amount of organic solution strongly destroys the environment and harms human health.

Among the various methods, adsorption technique is undoubtedly the most frequently used method. As an economical and efficient method, adsorption technique has found its extensive applications to this field, in which many kinds of sorbents are used as adsorption materials including inorganic oxides [6–9], zeolites [10], silica [11–15], activated carbon [16], various resins, [4, 5, 17–24], biological adsorbents [25–27], and etc. [28, 29]. In our previous work [5], a sensitive and rapid on-line method has been developed for the determination of trace amounts REEs by microwave plasma torch-atomic emission spectrometry (MPT-AES) combined with micro-column filled with a strong basic cinnamene anion exchange resins for matrix elimination and enrichment of the analytes. The adsorbed metal ions are eluted and transferred into the detector with nitric acid solutions for the simultaneous multi-element determination. The method has been validated through measurements of La, Ce, Nd, and Y in high purity REE oxide samples.

In recent years, great attention has been paid to the application of nano-structure materials, especially carbon nanotubes (CNTs). Due to their high mechanical strength,

large specific surface area, high chemical and thermal stabilities, and low cost, CNTs have been widely used as a promising adsorbent for the removal of metal ions or organic contaminants [30–32]. In addition, their surface properties can be modified through chemical treatments to satisfy some special needs [33–35]. Based on the structure of CNTs, they can introduce oxygen-containing negatively functional groups such as  $-\text{COOH}$ ,  $-\text{OH}$ , or  $-\text{C}=\text{O}$  on their surface site after treatment with oxidants. In order to obtain high adsorption capacity, it is being paid more and more attention to find an effective modification method of CNTs. Tannic acid (TA,  $\text{C}_{76}\text{H}_{52}\text{O}_{46}$ ), with several *o*-dihydroxy and trihydroxy aromatic rings (polyhydroxy polyphenols), has attracted much attention because of their metal-binding properties, antimicrobial and anticorrosive activities in aqueous solutions [36, 37]. Furthermore, some previous studies have indicated that TA may be adsorbed onto CNTs surface with a sorption affinity comparable to that of dissolved organic matter [33–35]. All the facts mentioned above reveal to us that CNTs modified with TA may have great potential as an effective adsorbent. However, such study has received little attention so far.

The basic objectives of the present work are: (1) to study the adsorption of TA with multi-walled carbon nanotubes (MWCNTs) for optimizing the modification method of MWCNTs with TA; (2) to investigate the adsorption of REEs with the synthesized TA-MWCNTs by varying experimental parameters, such as pH, initial concentration, contact time, and temperature, etc.; (3) to obtain the adsorption isotherms and kinetics of REEs with TA-MWCNTs.

## Experimental section

### Reagents and materials

MWCNTs were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, (<http://www.cioc.ac.cn/>). The main range of the outer diameter, length and special surface area of MWCNTs are 20 to 30 nm, 30 to 40  $\mu\text{m}$ , and 110 to 300  $\text{m}^2 \text{g}^{-1}$ , respectively. High purity  $\text{La}_2\text{O}_3$  (99.999%),  $\text{Tb}_2\text{O}_3$  (99.999%) and  $\text{Lu}_2\text{O}_3$  (99.998%) were purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China, <http://www.ciac.jl.cn/>). Stock standard solutions of La, Tb, and Lu were prepared from these oxides by dissolving in concentrated hydrochloric acid and diluting with distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions ( $1000 \text{ mg L}^{-1}$ ). TA, with a structure characterized as five digallic acid units ester-linked to a glucose core, was supplied by Tianjin Guangfu chemical plant (Tianjin,

China, <http://guangfuchem.shuoyi.com/>). NaOH and HCl were used to adjust solutions pH. All the reagents used were of analytical grade or better. Deionized water was used throughout the work.

### Apparatus

The measurements of REEs were performed with an MPT-AES from Jilin University Little Swan Instruments Co., Ltd. (Changchun, China, <http://kgy.jlu.edu.cn/>). The MPT conditions were: microwave forward power 80 W, carrier gas (Ar) flow rate  $1.0 \text{ L min}^{-1}$ , support gas (Ar) flow rate  $0.6 \text{ L min}^{-1}$ , sheathing gas ( $\text{O}_2$ ) flow rate  $1.0 \text{ L min}^{-1}$ , wavelength range 200 to 900 nm, entrance slit width 5  $\mu\text{m}$ , CCD pixel elements 2048, optical resolution 0.065 nm, data transfer rate 13 ms, integration time 3 to 65000 ms. La, Tb, and Lu were determined at the wavelengths of 333.749 nm, 350.917 nm, and 261.541 nm, respectively. A UV-Vis spectrometer (TU-1800, Beijing Purkinje General Instruments Co., Ltd., China, <http://www.pgeneral.com/>) with 1 cm quartz cell was used for the spectrophotometric determination of TA (275 nm). A pHs-3 C digital pH meter (Rex Instruments Factory, Shanghai, China, <http://www.lei-ci.com/>) was employed for the pH measurements. Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA, <http://www.millipore.com/>).

### Preparation of modified MWCNTs

Briefly, the MWCNTs were suspended in mixture of concentrated sulfuric acid and nitric acid (3:1 v/v), then sonicated for 2 h in an ultrasonic bath. The suspension was stirred at 55  $^\circ\text{C}$  for 7 h [38]. After cooled to room temperature, the oxidized MWCNTs (ox-MWCNTs) were washed repeatedly with deionized water until the residual acid was completely removed, and dried under vacuum for further use. The ox-MWCNTs (0.1 g) were dispersed in 30 mL  $10 \text{ mg L}^{-1}$  TA solutions and shaken continuously for a period of time at pH 3. Experiments were repeated at different pH values (1 to 6), contact time (60 to 600 min), and initial concentration of TA ( $5$  to  $100 \text{ mg L}^{-1}$ ) to obtain the optimum modification method of oxidized MWCNTs with TA. The separated solid parts obtained after the adsorption step under the optimized conditions were washed, dried under vacuum and kept for the subsequent adsorption experiments.

### Batch adsorption experiments

0.05 g TA-MWCNTs mixed with 10 mL REEs solution in batch reactors were shaken under controlled temperature of 293 K unless otherwise stated. Batch adsorption experiments were conducted to investigate REEs adsorption as a

function of initial REEs concentration (5 to 50 mg L<sup>-1</sup>), aqueous pH (1 to 7), TA-MWCNTs dosage (0.02 to 0.2 g), and contact time (5 to 120 min). After reaching the sorption equilibrium, the aqueous phase was filtered with a syringe filter of 0.45 μm, and the final concentration of REEs was determined by MPT-AES. The adsorption capacity  $q_e$  (mg/g TA-MWCNTs) was obtained as follows:

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

where  $q_e$  is the amount of REEs adsorbed per unit amount of the adsorbent (mg g<sup>-1</sup>);  $C_0$  and  $C$  are the initial and final concentrations (mg L<sup>-1</sup>) of REEs after adsorption, respectively;  $V$  is the volume of REEs solution (L); and  $m$  is the weight of TA-MWCNTs (g). In all batch experiments, average values were taken from triplicate measurements.

### Elution studies

The elution studies were carried out in two steps. Firstly, stability of TA-MWCNTs; secondly, the recovery of the adsorbed REEs from TA-MWCNTs were determined in different concentrations of HCl. The concentrations of TA and REEs in the resulting solutions were determined by UV-Vis spectrometer and MPT-AES, respectively.

## Results and discussion

### Modification of method study

In order to achieve the best performance of TA onto ox-MWCNTs, the modification conditions have been optimized, such as contact time, pH, and TA concentration. Experimental data of effect of contact time, pH, and TA concentration are shown in Electronic Supplementary Material (Figs. S1–S3). Therefore, the optimized experimental conditions of modifying oxidized MWCNTs with TA are: contact time of 2 h, pH of 3, and TA concentration of 10 mg L<sup>-1</sup>. After the adsorption under such experimental parameters, the separated solid parts were washed, dried, and employed for the subsequent experiments. For the proper adsorption of REEs, the optimum amount of tannic acid immobilized per unit mass of oxidized MWCNTs was 3.45 mg g<sup>-1</sup>.

### Characterization of adsorbents

The adsorbents were characterized using FT-IR spectra and transmission electron microscopy (TEM). The FT-IR spectra of MWCNTs, ox-MWCNTs, and TA-MWCNTs are studied and compared (Fig. S4 ESM). The HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> treatment produced carboxyl group on the surface of MWCNTs, as indicated by the presence of characteristic

peaks at 3430 and 1716 cm<sup>-1</sup> for stretching vibrations of O–H and C=O of the carboxyl group, respectively [38]. The intensity of the band representing –OH (3430 cm<sup>-1</sup>) stretching of alcoholic groups becomes stronger after MWCNTs compound with TA. 1535 cm<sup>-1</sup> was C–C stretching vibration from tetrasubstituted benzene rings [39], which is a main structure in the TA molecule. These FI-IR spectra confirm that MWCNTs have been successfully modified by tannic acid.

Figure 1 shows the TEM images of TA-MWCNTs. The nanotubes are curved with some open tips. The surfaces of MWCNTs are smooth and clean, and no obvious change of the surface structure and the framework of MWCNTs after modification with TA [38].

### Adsorption of REEs with TA-MWCNTs

#### *Effect of contact time on the adsorption of REEs with TA-MWCNTs*

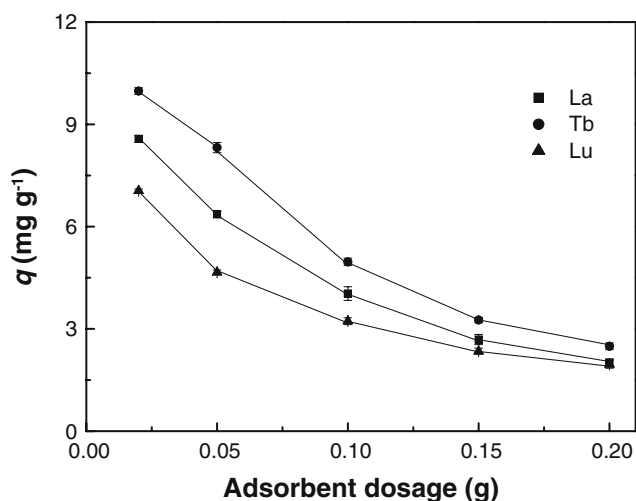
The effect of contact time on the adsorption of La, Tb, and Lu has been investigated when initial REEs concentrations are fixed at 40 mg L<sup>-1</sup> (Fig. S5 ESM). The results demonstrate that the adsorption increases with increasing agitation time and attains equilibrium rapidly at about 50 min. This is obvious from the fact that a large number of vacant surface sites are available for adsorption in short time. A period of 60 min is chosen as a suitable contact time for La, Tb, and Lu.

#### *Effect of sample pH on the adsorption of REEs with TA-MWCNTs*

To determine the experimental conditions at which REEs are effectively adsorbed with TA-MWCNTs, the sorption



**Fig. 1** TEM images of TA-MWCNTs



**Fig. 2** Effect of adsorbent dosage on the adsorption of La, Tb, and Lu with TA-MWCNTs (pH 5.0, concentration of La, Tb, and Lu: 40 mg L<sup>-1</sup>)

studies have been carried out at different initial pH levels (Fig. S6 ESM). The oxidation of MWCNTs with concentrated HNO<sub>3</sub> leads to the surface functionalization with oxygen containing groups, and the isoelectric point (IEP) of MWCNTs shift to lower pH values [40]. Furthermore, Lin et al. have demonstrated that Zeta potentials of the oxidation of CNTs in TA solutions do not significantly reduce [35]. In order to evaluate effect of pH, a series of sample solution are adjusted to a pH range of 1.5 to 7.0 and process according to recommended procedure. The adsorption capacity increases rapidly from 0.4 mg g<sup>-1</sup> to approximately 6.0 mg g<sup>-1</sup> with increasing pH from 1.5 to 4.0, and then gently increases from 4.0 to 7.0. At low pH range all metals are expected to exist predominantly in the M<sup>n+</sup> form. The concentration of H<sup>+</sup> ions increases with decreasing pH, which competes with La, Tb, and Lu and makes the ion exchange reaction in the composite very difficult. The adsorption capacity rises in the pH range of 4.0 to 7.0. A possible reason may be that MWCNTs modified with TA having a number of functional groups is capable of forming chelates easily with REEs and thus improves the MWCNTs surface like humic substances [36]. The pH of 5.0 is selected in subsequent work.

**Table 1** Parameters of Langmuir and Freundlich adsorption isotherm models for La, Tb, and Lu with TA-MWCNTs

Elements	Langmuir			Freundlich		
	$q_{\max}$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_f$ (mg g <sup>-1</sup> )	$n$	$R^2$
La	5.35	1.947	0.9937	3.04	4.255	0.9876
Tb	8.55	3.441	0.9924	5.61	4.338	0.9989
Lu	3.97	1.467	0.9918	2.49	6.502	0.9926

### Effect of adsorbent dosage on the adsorption of REEs with TA-MWCNTs

The amount of the adsorbent is an important parameter because it determines the adsorption capacity of an adsorbent for given initial concentration of the adsorbate. Figure 2 shows the effect of TA-MWCNTs amount on the adsorption capacity of La, Tb, and Lu in the dose range from 0.02 to 0.2 g, indicating that the adsorption capacity decreases almost linearly with increasing amount of adsorbent. This result indicates that the amount of La, Tb, and Lu adsorbed per unit weight of TA-MWCNTs decreases with an increase of adsorbent dosage. The decrease in unit adsorption with increasing adsorbent dosage is mainly due to the fact that the adsorption sites remain unsaturated during the adsorption reaction [28]. When the TA-MWCNTs dose is 0.1 g, the maximum adsorption capacities are 100% for REEs.

### Sorption isotherms

In order to illustrate the interaction between the adsorbate and adsorbent, the obtained equilibrium isotherm adsorption data have been analyzed by the Langmuir and Freundlich isotherm models, which are most popular isotherm theories: [41]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (2)$$

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of the solute,  $q_e$  is the amount adsorbed at equilibrium (mg g<sup>-1</sup>),  $q_{\max}$  is the maximum adsorption at monolayer coverage (mg g<sup>-1</sup>),  $b$  is the adsorption equilibrium constant (L mg<sup>-1</sup>);  $x/m$  is the amount adsorbed per unit mass of the adsorbate,  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>),  $K_f$  (L mg<sup>-1</sup>) and  $n$  are the Freundlich isotherm constants.

The Langmuir and Freundlich constants are presented in Table 1. The calculated  $R^2$  values indicate that both Langmuir and Freundlich isotherms model fit well. This

**Table 2** Adsorption capacity for La, Tb and/or Lu of different common adsorbents

Adsorbents	Ions	Adsorption capacity (mg/g)	Reference
H, PEG400, PW <sup>a</sup>	La	220.8	[29]
H, PEG400, PMo	La	214.4	[29]
Soils	La	2.1	[27]
Magnet chitosan	La	41.2	[26]
Sargassum biomass	La	111.1	[25]
XAD-4-(MADB18C6) <sup>b</sup>	La	9.2	[24]
XAD-4-OVSC <sup>c</sup>	La	2.3	[20]
Magnetic calcium alginate beads	La	123.5	[28]
Iron oxide nanoparticles	La	2~8	[28]
Nanometer TiO <sub>2</sub>	La	15.3	[7]
Nanometer Al <sub>2</sub> O <sub>3</sub>	La	26.7	[8]
TA-MWCNTs	La, Tb, Lu	5.35, 8.55, 3.97	Present work

<sup>a</sup> Polyethyleneglycol (PEG)-phosphomolybdic (PMo)/phosphotungstic (PW) heteropolyacids

<sup>b</sup> Amberlite XAD-4 - monoaza dibenzo 18-crown-6 ether

<sup>c</sup> Amberlite XAD-4-*o*-vanillinsemicarbazone

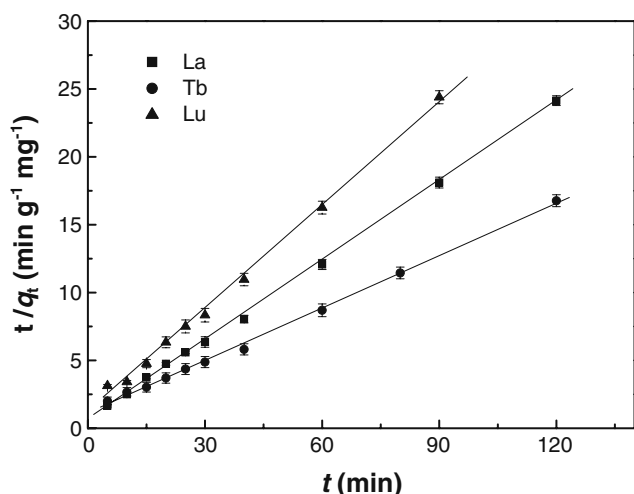
implies that both monolayer sorption and heterogeneous surface conditions exist under the experimental conditions used. Therefore, the sorption of REEs with TA-MWCNTs is complex, involving more than one mechanism.

Adsorption capacity of TA-MWCNTs has been evaluated to be 5.35, 8.55, and 3.97 mg g<sup>-1</sup> for La, Tb, and Lu, respectively. Such adsorption capacities are comparable to those reported in other papers. The adsorption capacities of REEs with various adsorbent are summarized in Table 2. For instance, Jain et al. [20] have reported that the adsorption capacity of XAD-4 functionalized with *o*-vanillinsemicarbazone is 2.3 mg g<sup>-1</sup> for La. Hang et al. [7] have employed nanometer TiO<sub>2</sub> as a new type of adsorption material to separate and concentrate trace REEs. The adsorption capacity of nanometer TiO<sub>2</sub> for REEs is in the range of

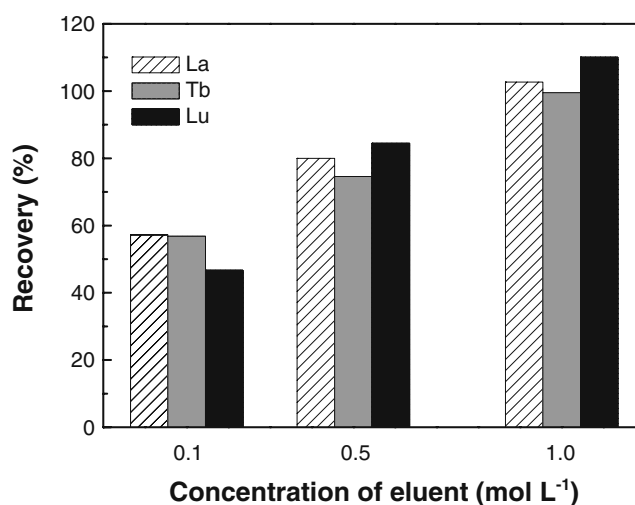
11.3~21.6 mg g<sup>-1</sup>. However, it should be noted that compared with biomasses [25] or magnetic materials [28], the adsorption capacity of TA-MWCNTs is low. A possible strategy to enhance the adsorption capacity may be achieved by using MWCNTs with smaller sizes or exploring more effective modification methods on MWCNTs.

#### Sorption kinetics

In order to investigate the rate controlling step of adsorption process, the kinetic adsorption experiments of La, Tb and Lu on TA-MWCNTs are performed. After 60 min contact time for La, Tb and Lu, the adsorption equilibrium is reached in a solid solution (Fig. S5, *ESM*). The pseudo-first-order and pseudo-second-order kinetic



**Fig. 3** Pseudo-second-order kinetic model for the adsorption of La, Tb, and Lu with TA-MWCNTs



**Fig. 4** Effects of eluent concentration on the recovery of La, Tb, and Lu. (Dosage of TA-MWCNTs: 0.1 g, concentration of La, Tb, and Lu: 40 mg L<sup>-1</sup>, pH 5.0)

model have been employed to fit the kinetic adsorption data [42–44]. The pseudo-first-order and pseudo-second-order kinetic model can be expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the amounts of metal ions adsorbed at any time  $t$  (min) and at equilibrium, respectively,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the adsorption rate constant of pseudo-first-order and pseudo-second-order adsorption.

For the studied concentration, the rate constants ( $k_1$  and  $k_2$ ) and theoretical equilibrium sorption capacities,  $q_e$  are calculated from the slope and the intercept of the linear plot of the pseudo-first-order and pseudo-second-order kinetic models. It is important to note that for a pseudo-first-order model, the correlation coefficient is always less than 0.90, which is indicative of a bad correlation (Fig. S7 ESM). In contrast, the application of a pseudo-second-order model leads to much better regression coefficients, all greater than 0.99 (Fig. 3). Thus, the pseudo-second-order model is suitable to model the adsorption curves of La, Tb, and Lu with TA-MWCNTs. The values of  $k_2$  and  $q_e$  are calculated from the slope and intercept, respectively, of a linear plot of  $t/q_t$  versus  $t$  and are given in Table S1, ESM.

#### Recovery and reusability of TA-MWCNTs

For an effective recycling process, adsorbed REEs should be easily desorbed without destroying the adsorbent materials under suitable conditions. Firstly, the stability of TA-MWCNTs has been investigated when HCl is employed as the eluent. When  $1.0 \text{ mol L}^{-1}$  HCl is employed to desorb TA, the recovery reaches no more than 5.0%. Secondly, 0.1 g TA-MWCNTs have been used to adsorb La, Tb, and Lu ( $40 \text{ mg L}^{-1}$ ), and then the quantitative recovery of La, Tb, and Lu is performed using 20 mL various concentrations of HCl. As can be seen in Fig. 4,  $1.0 \text{ mol L}^{-1}$  HCl is sufficient for complete elution of La, Tb, and Lu from TA-MWCNTs and the recovery is more than 95%. Therefore,  $1.0 \text{ mol L}^{-1}$  HCl solution is selected for the elution of La, Tb, and Lu in the experiments. The adsorption process has been repeated by using the regenerated adsorbent. It can be found that after three cycles there is no significantly change in the sorption capacity of TA-MWCNTs. Thus, TA-MWCNTs are regenerable and can be used several times.

#### Thermodynamic parameters

The effect of temperature on the adsorption of La, Tb, and Lu with TA-MWCNTs has been studied at different temperatures from 293 K to 323 K. Thermodynamic parameters associated with the sorption viz., free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) were calculated as follows [45]:

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (7)$$

$$\Delta G = -RT \ln b \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

Where  $D$  is distribution ratios,  $b$  is the adsorption equilibrium constant ( $\text{L mg}^{-1}$ ) shown in Eq. 2. The values of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  are calculated and summarized in Table S2, ESM.  $\Delta H$  values are all positive, i.e., increasing temperature is advantageous for the reactions, indicating that the three systems are all endothermically driven. Negative values of  $\Delta G$  suggest that the sorption process is spontaneous with high preference of REEs for TA-MWCNTs. The positive entropy changes indicate that the degree of freedom increases at the solid-liquid interface during the adsorption of REEs with TA-MWCNTs.

#### Conclusions

In this research, the preparation and application of a sorbent based on the modification of MWCNTs with TA have been demonstrated. The preparation of TA-MWCNTs is proved to be relatively simple and rapid. TA-MWCNTs are effective adsorbents for the removal of REEs. The influence of various experimental parameters, contact time, initial solution pH, and adsorbent dose, on the adsorption of REEs has been investigated. Equilibrium data have been fitted to Langmuir isotherms and Freundlich isotherms, indicating that both monolayer sorption and heterogenous surface conditions exist under the experimental conditions used. The sorption process is found to be endothermic in nature. The rate of sorption follows the pseudo-second-order kinetic model.

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