Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1177734

57 (2016) 27754–27767
December

Taylor & Francis
Taylor & Francis Group

Amino phosphate on the surface of nanotitania as attractive group to improve the adsorptive properties for lanthanides removal: adsorption, kinetic, equilibrium, and thermodynamic studies

Z. Shojaei[a], E. Iravani[b,*], M.A. Moosavian[a], M. Torab-Mostaedi[b]

[a]*Faculty of Engineering, Department of Chemical Engineering, University of Tehran, 11365-4563 Tehran, Iran, emails: z_shojaei@alumni-ut.ac.ir (Z. Shojaei), moosavian@ut-ac.ir (M.A. Moosavian)*
[b]*Nuclear Science and Technology Research Institute, 11365-8486 Tehran, Iran, emails: eiravani@aeoi.org.ir (E. Iravani), mmostaedi@aeoi.org.ir (M. Torab-Mostaedi)*

Received 27 September 2015; Accepted 7 April 2016

ABSTRACT

The present work focuses on the adsorption of La(III) from aqueous solutions by amino phosphate-functionalized nanotitania in a batch system. Surface modification was based on anchor group using chelating ligand, 2-aminoethyl dihydrogen phosphate. The effects of some important parameters including pH of solution, adsorbent dose, contact time, initial metal concentration, and temperature on the adsorption process were examined. The maximum adsorption of La(III) on the modified nanotitania was observed to occur at pH 6.0. Kinetic data showed that the adsorption process achieved equilibrium within 90 min and experimental data were fitted well by the pseudo-second-order model ($R^2 > 0.99$). The equilibrium data were correlated with Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models. The results indicated that La(III) adsorption was well described by Langmuir isotherm model. The maximum adsorption capacity was 14.33 mg g^{-1} for La(III). According to the evaluated thermodynamic parameters at different temperatures, the adsorption was a spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$) process. The effect of interfering cations on the adsorption of La(III) was studied. The presence of Mg and Ca ions up to 150 mg g^{-1} caused no considerable lowering effect on the La(III) adsorption. The presence of Ce(III) with a concentration in the range of 30–70 mg L^{-1} led to decreasing adsorption of La(III) from 84 to 76%. In addition, regeneration of the modified nanotitania was performed using HNO_3 (0.1 mol L^{-1}) with efficiency greater than 84%.

Keywords: Nanotitania; Amino phosphate; Surface modification; Adsorption; La(III)

1. Introduction

Lanthanum as a strategically important element is currently used as a pure element or in association with other compounds in catalysts, special ceramics, super alloys, and inorganic synthesis [1,2]. Because of many important applications for lanthanum in different industries and discharge of effluent from them to the environment, it's necessary to separate this metal ion from aqueous solutions.

Numerous conventional techniques such as chemical precipitation [3], ion exchange [4], floatation [5],

---

*Corresponding author.

coagulation [6], membrane processes [7,8], solvent extraction [9], and adsorption [10–13] have been developed for separation of heavy metals from aqueous solutions. Adsorption is considered as the most popular way to remove heavy metals due to its advantages e.g. high efficiency, easy operation, low-cost, and production of less sludge volume [14]. Several kinds of materials including activated carbons [15], carbon nanotubes [16], zeolites [17,18], chitosan [19], clays [20,21], and agricultural wastes [22] have been investigated to adsorb metal ions from aqueous solutions. Nanometal oxides are classified as the promising adsorbents for this purpose [23–25]. In particular, nanotitania has high potential for environmental applications due to its physical and chemical stability, non-toxicity, relatively low-cost, and the resistance to corrosion [26]. A number of nanotitania composites such as TiO_2/montmorillonite [27], TiO_2/fly ash [28], B_2O_3/TiO_2 [29], TiO_2-MCM-41 [30], titania/silica nanohybrid [31], and dendrimer/titania composites [32] have also been studied in recent years. Surface modification of nanomaterials is one of the promising ways to enhance the adsorption capacity [33–35].

In this study, nanotitania was surface modified using 2-aminoethyl dihydrogen phosphate, was characterized via various spectroscopic analysis methods. Then adsorption of La(III) was investigated using this novel adsorbent. The effects of experimental conditions such as pH of solution, the adsorbent dose, contact time, initial concentration of ions, and temperature were studied. The adsorption rate was determined and compared to the pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) equations were used to fit the equilibrium isotherm. The thermodynamic parameters were evaluated from the adsorption measurements at different temperatures. Effect of interfering cations on the adsorption of La(III) and also simultaneous adsorption of La(III) and Ce(III) was investigated and finally, the reusability of the modified nanotitania was also determined.

2. Experimental

2.1. Materials

Titania nanopowder (80% anatase, 20% rutile, 21 nm average particle size, 99.5%) and 2-aminoethyl dihydrogen phosphate (98%) were purchased from Degussa and Merck (Germany), respectively. Appropriate amounts of Lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, 99%) purchased from Merck were used to prepare La(III) solutions with needed concentrations in deionized water. Other chemicals such as cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 98.5%), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, 99%), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 98.5%), nitric acid (69%), acetate buffer (0.1 mol L^{-1}), and sodium hydroxide (≥99%) were obtained from Merck. Ethanol (99.5%) obtained from Bidestan, Iran, and distilled water were used for the reaction and washing proccess. The chemicals used in the ninhydrin dye test were ethyl acetate (99.9%, Fluka, Germany), ninhydrin (≥99%, Merck), acetic acid (100%, Merck), and heptane (99%, Aldrich). Ninhydrin solution was prepared according to the Paunikallio et al. [37].

2.2. Methods

Attenuated total reflectance (ATR) spectra were recorded on a BRUKER TENSOR 27 ATR-FT IR spectrometer equipped with a ZnSe single crystal. Nuclear magnetic resonance (NMR) spectra including ^{31}P MAS NMR and ^{13}C CP/MAS NMR spectra were recorded on BRUKER AVANCE SPECTROSPIN 400 MHz and BRUKER TOPSPIN spectrometer 500 MHz, respectively. Thermogravimetric analyses (TGA) were performed on a RHEOMETRICSCIENTIFIC STA 1500 thermal analyzer under air flow with heating rate of 10 °C min^{-1} and temperature range 25–900 °C. Specific surface area (BET) measurement was done with COVANTO CROM-NOVA 2000 apparatus. The adsorption gas was nitrogen. High-resolution transmission electron microscope images (HRTEM) and scanning electron microscope images (SEM) were obtained with a JEOL 3010 microscope at 300 kV and REM CamScan-4DV, respectively. The metal ion concentrations were determined by an inductive coupled plasma atomic emission spectrophotometer (ICP-AES, Optima, Model 7300DV American). The pH values of the aqueous solutions were adjusted as needed (2−7) using appropriate concentration of HNO_3 or NaOH and monitored using a pH meter (Sartorius PB–11). Acetate buffer (0.1 mol L^{-1}) was used to adjust the pH values of the aqueous solutions to 5 and 6. Mse Mistral 1000 centrifuge and GFL 1083 shaker water bath were also used for adsorption experiments.

2.3. Preparation of adsorbent

2-aminoethyl dihydrogen phosphate (0.141 g, 0.001 mol) was dissolved in 100-mL distilled water. Nanotitania (0.799 g, 0.01 mol) was added into the mixture and was stirred for 24 h at room temperature. Then the mixture was centrifuged for 30 min at 6,000 rpm. The resulted powders were eluted in a

Soxhlet extractor with distilled water for 12 h to remove the physically adsorbed modifying agent and probable titanium phosphates. Afterward, the powders were dried in an oven at 100˚C for 12 h [36].

2.4. Batch adsorption experiments

Stock solutions of La(III) were prepared by dissolving appropriate amounts of $La(NO_3)_3·6H_2O$ in deionized water, and the initial concentrations (C_0) were adjusted to $50\ mg\ L^{-1}$ for each experiment. A mass of 0.2-g modified nanotitania was added into a flask containing 30-mL La(III) solution at room temperature and was shaken for 90 min. Afterward, the solutions were centrifuged at 6,000 rpm for 15 min to separate the solid adsorbents from the liquid phases. After determining the optimal pH, the effect of adsorbent dose was investigated in the range of 0.05–0.5 g of adsorbent at 25˚C and optimum pH. Kinetic experiments were conducted by varying the contact time from 5 to 150 min (5, 10, 15, 20, 30, 45, 60, 90, 120, and 150 min) at room temperature and optimum pH. The adsorption isotherms were performed using 0.2-g adsorbent in various metal ion concentrations in a range of $10–100\ mg\ L^{-1}$ at different temperatures (25, 35, and 45˚C). The simultaneous adsorption of La (III) and Ce(III) ions and the interfering effect of calcium and magnesium ions on La(III) adsorption were also investigated by contacting 30 mL of solution (containing $50\ mg\ L^{-1}$ of each ions) with 0.2 g of modified nanotitania in a shaker at 25˚C and pH 6 for 90 min. Adsorption process was quantified by calculating the adsorption percentage (%Ad) and the adsorption capacity (q_e, $mg\ g^{-1}$) by Eqs. (1) and (2), respectively:

$$\%Ad = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$q_e = (C_o - C_e) \times \frac{v}{m} \tag{2}$$

where C_o and C_e are the initial and equilibrium metal ion concentrations in $mg\ L^{-1}$, respectively. v is the aqueous solution volume in mL and m is the mass of adsorbent in mg.

The distribution coefficient (K_d) of metal ions between the aqueous phase and the solid phase can be directly obtained using Eq. (3) [38]:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{v}{m} \tag{3}$$

where C_o ($mg\ L^{-1}$) and C_e ($mg\ L^{-1}$) are the initial and equilibrium cerium concentrations, v/m is the ratio of the volume of metal solution (mL) to the amount of adsorbent (g) in a batch. Two determinations were utilized to check the standard deviation for each K_d value. Standard deviations were less than 10%.

The selectivity coefficient of La(III) ions over Ce (III) ions was investigated by batch procedure and determined by the ratio of the two distribution coefficients, K_d La(III) and K_d Ce(III), which are referred as the selectivity factors as follows:

$$\alpha = \frac{K_d Ce(III)}{K_d La(III)} \tag{4}$$

3. Results and discussion

3.1. Adsorbent characterization

The surface-modified nanotitania was characterized applying different characterization methods. SEM and HRTEM micrographs showed well dispersed, fairly homogeneous, and spherical shape nanoparticles with no considerable agglomeration (Fig. 1).

BET analysis result ($55.78\ m^2\ g^{-1}$) showed slightly increased surface area (5−7%) compared to the untreated nanotitania (about $50\ m^2\ g^{-1}$). Decomposition temperature for modified nanotitania particles was high (about 600˚C, ESM 1). This fact could be a proof, that there is no free capping agent in AP-modified nano-TiO_2. According to the CHN (Table 1), TGA, and BET analyses, the amount of amino phosphate groups on the surface of modified nanotitania was estimated to be about 3.17 wt% and the number of coupling agent conjugated to the surface was calculated to be ca. 2.43 molecules per nm^2.

According to ATR-FTIR spectra (Fig. 2), the observation of two sharp bands centered at 2,933 and $2,901\ cm^{-1}$ related to symmetric and asymmetric stretching vibration of methylene groups, together with positive ninhydrin test (ESM 2) demonstrated the presence of ethylamine ($-CH_2-CH_2-NH_2$) into nanotitania matrix.

In the study of modified nanotitania by magic angle spinning NMR spectroscopy, a distinct downfield shift for ^{31}P signal at δ 2.11 ppm has been seen comparing to the pure capping agent (δ 0.17 ppm) due to P–O–Ti bond formation (Fig. 3).

^{13}C CP MAS NMR showed two signals at δ 41.48 and 58.12 ppm related to N–C and O–C, respectively, confirming that aminoethyl chain stayed on the phosphate groups (ESM 3). Considerable upfield shift of ^{13}C signal of O–C was a proof for amino phosphate

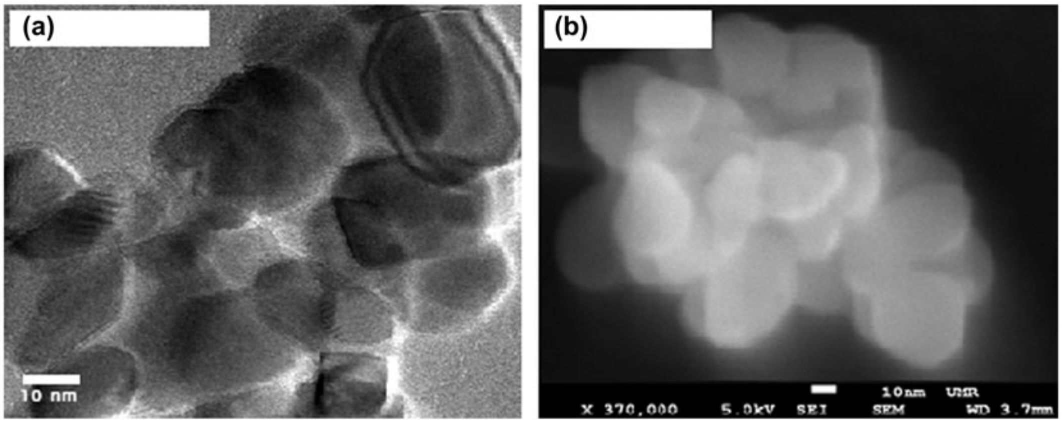

Fig. 1. (a) HRTEM and (b) SEM images of modified nanotitania.

Table 1
Elemental analysis (CHN) results

	Modifying agent (theoretical values)	Modified nanotitania (experimental values)
C wt%	16.95	0.539
H wt%	5.65	0.253
N wt%	9.89	0.356
H/C	0.33	0.47

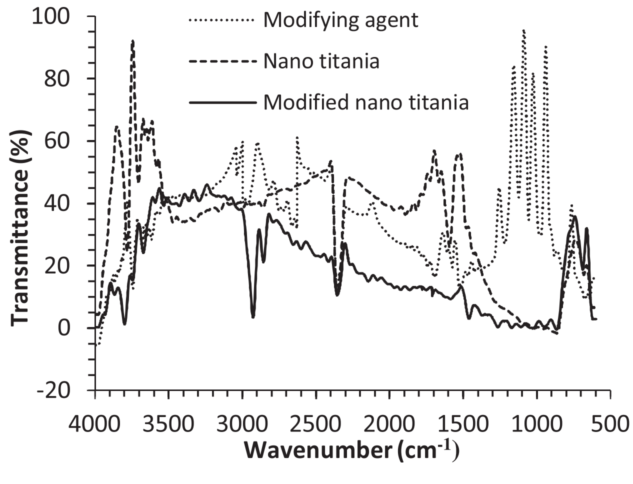

Fig. 2. ATR-FTIR spectra of modifying agent, pure, and modified nanotitania.

group bonding with nanotitania through phosphate groups. The phosphate groups interact with the surface via quite strong covalent interaction, while according the analyses results, the surface amine groups remained uncoordinated.

Positive ninhydrin test by a color change from white to hell violet would be probably sufficient to prove the existence of free amine groups on the surface of modified nanotitania (Fig. 4).

In this study, untreated (as the reference) and treated nanotitania were separately soeked in ninhydrin solution. After drying, the color of modified sample changed from white to hell violet, which confirmed the presence of amines; there was no color change to observe for the reference. The observed colors during ninhydrine dye test are given in Online Resource (ESM 2).

3.2. Effect of surface modification

The results of comparative tests performed for La (III) adsorption on the modified nanotitania with different modification degrees showed that increasing modifier: nanotitania mole ratio from 0.01 to 0.1 led to the increase in adsorption percentage from about 53% to more than 97%. La(III) was adsorbed by untreated nanotitania about 46%. No more adsorption enhancement was observed by increasing the modifier: nanotitania mole ratio any more (Fig. 5). Apparently, the described surface modification plays an important role in adsorption behavior. The considerably enhanced adsorption of La(III) onto treated nanotitania comparing with untreated one could be due to the ability of

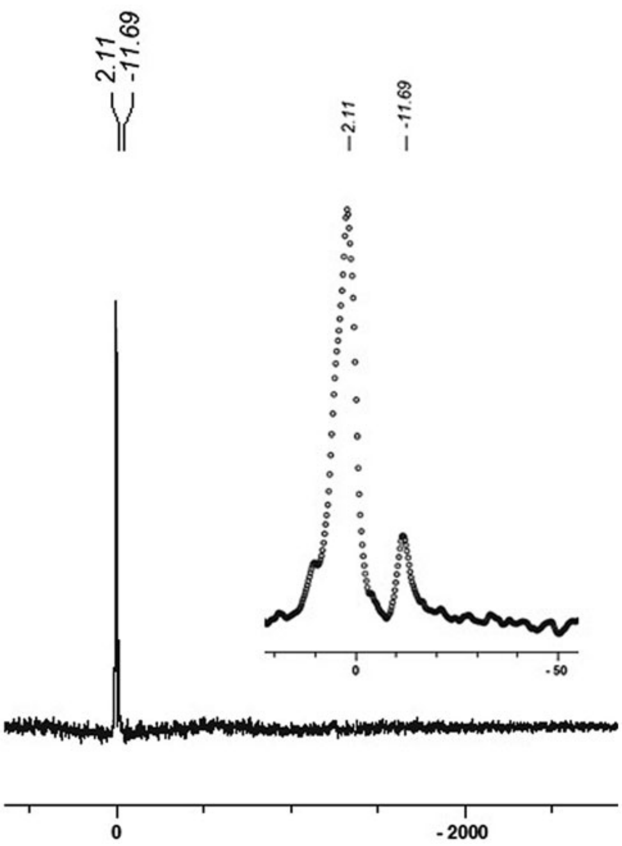

Fig. 3. ^{31}P MAS NMR spectra of modified nanotitania.

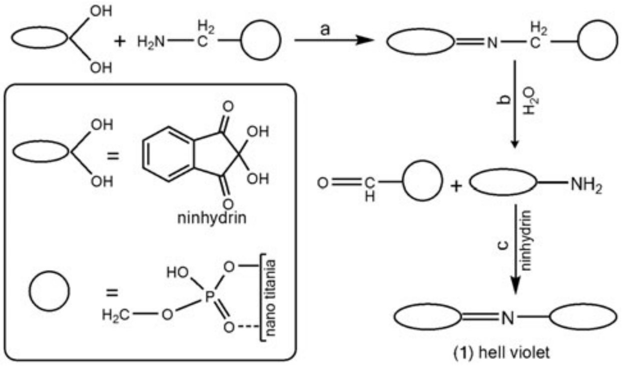

Fig. 4. The reaction between ninhydrin and free amino groups on the surface leads to the formation of compound 1 showing hell violet color.

free $–NH_2$ groups to form complexes with La(III). Tendency of lanthanides to be surrounded by phosphate oxygen atoms could be another reason for enhanced adsorption of La(III) (ESM 4).

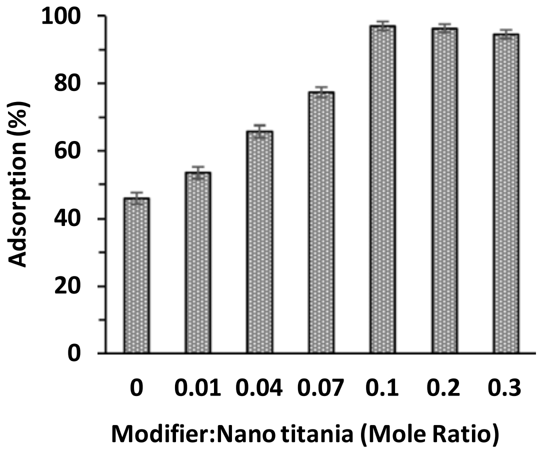

Fig. 5. Effect of modification degree on La(III) adsorption by modified nanotitania.

3.3. Effect of initial pH

The initial pH value is one of the most important parameters affecting the adsorption because of the pH dependency of the various complexation reactions or electrostatic interactions at the surface [39]. Since 2-aminoethyl dihydrogen phosphate with its zwitterion structure has aliphatic, phosphate, and amine functional groups in various portions, pH dependency of the lanthanide ions adsorption has to be determined. Thus, the pH effect on the adsorption of La(III) ions was examined by varying the initial pH values of the solutions in the range of 2–6 (Fig. 6). Measurement of the equilibrium pH at the end of each adsorption

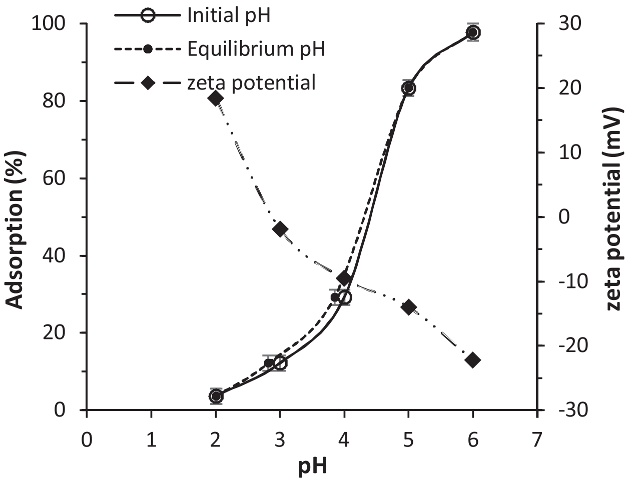

Fig. 6. Effect of pH on La(III) adsorption by modified nanotitania.

processes showed no considerable changes, which can be observed in Fig. 6. The adsorption percentages were found to be low at more acidic pH values and increased with increase in pH. This can be due to competitive adsorption of H_3O^+ and lanthanum ions for the same active adsorption site on the surface of adsorbent. Increasing the pH and thereby lessening of H_3O^+ concentration in solution makes probably the adsorption surface less positive and consequently electrostatic attraction between the lanthanide ions and the surface starker. To investigate this point, zeta potential of the adsorbent was measured in the pH range of 2–6. According to the results (Fig. 6), increasing pH led to more negative zeta potential and surface charge (18.4, −1.91, −9.57, −14, and −22.2 mV at pHs 2, 3, 4, 5, and 6, respectively), which would be probably a reason for the adsorption enhancement of La(III) cations on the adsorbent surface at higher pHs. The amine functional groups could probably take part in metal uptake process through complexation which is pH-dependent and led to the adsorption yield enhancement. The nature of the active sites and sorbent may also change with pH [40]. The maximum adsorption efficiency (93.9%) achieved at pH value of 6.0 which was used for all subsequent experiments.

Lanthanum adsorptions were not considered at pH values higher than 6.0 due to the formation of insoluble metal ion hydroxides such as $La(OH)_3$ [41].

3.4. Effect of adsorbent dose

The effect of adsorbent dose on the removal of La (III) was investigated in the range of 0.05−0.5 g illustrated in Fig. 7. Increasing the adsorbent mass in the range of 0.05−0.2 g led to the increase in adsorption efficiency from 40% to more than 93%, which could be due to an increase in the number of adsorption sites. The adsorption percentage remained closely constant using more than 0.2 g adsorbent; therefore, 0.2 g of the adsorbent dose was selected as the appropriate amount for further adsorption experiments.

3.5. Effect of contact time

The effect of contact time on the adsorption of La (III) onto modified nanotitania from aqueous solutions is shown in Fig. 8. The amount of La(III) adsorbed per unit mass of the adsorbent increased quickly with time. More than 90% of the total metal ions absorption occurred within the first 20 min and slowly reached the saturation at about 90 min and after this period of time no considerable increment was observed in adsorption capacity. So the equilibrium time was set at 90 min for the further experiments. The high adsorption capacity at the beginning of the process could be due to the great number of vacant active sites on the adsorbent surface and also the high concentration of solution.

3.6. Effect of initial concentration and temperature

The initial concentrations of La(III) were varied from 10 to 100 mg L^{-1}. The measured amounts of equilibrium concentrations of La(III) ions after adsorption were lower at high initial concentrations. This trend may be attributed to higher accessibility of lanthanum ions available per unit surface area of adsorbent in the solution leading to increase the probability of surface adsorption and decrease the equilibrium concentration. The measured adsorption capacity at

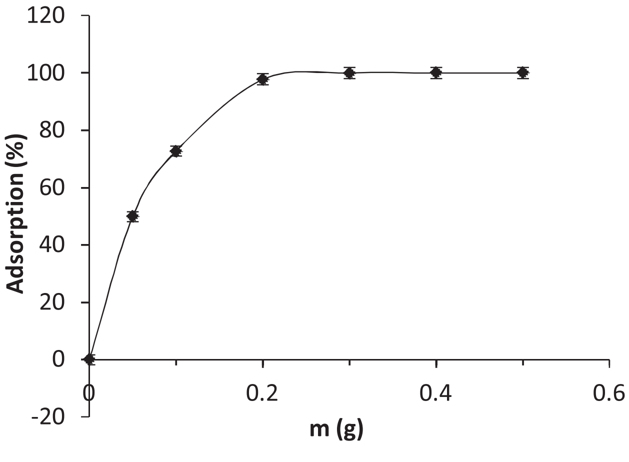

Fig. 7. Effect of adsorbent dose on La(III) adsorption percentage by modified nanotitania.

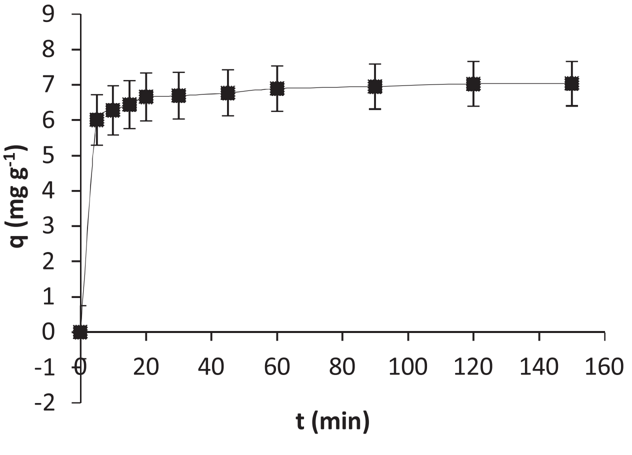

Fig. 8. Effect of contact time on La(III) adsorption capacity by modified nanotitania.

25℃ was enhanced from 1.48 to 10.18 mg g^{-1} with increasing initial concentration from 10 to 100 mg L^{-1}. This could be due to an increase in the initial concentration of lanthanum ions providing a larger driving force to overcome the total mass transfer resistance of the lanthanum ions between the liquid and solid phases, so resulting in higher collision between adsorbates and surface of adsorbent [42].

The observed improvement of the adsorption capacities with increasing temperature could be related to increased mobility of lanthanum ions and their tendency to be adsorbed from the aqueous solution. Moreover, it was also found that the adsorption of La(III) ions onto the modified nanotitania was an endothermic process (Fig. 9).

3.7. Adsorption kinetics

Kinetic studies of adsorption process provide important information about the mechanism and the rate-limiting step. In order to investigate the adsorption kinetics, three kinetic models including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were applied to the experimental data. The pseudo-first-order kinetic model that so-called Lagergren equation considers is that the adsorption rate is proportional to the number of free sites [43,44]. The rate constant of adsorption can be determined using Eq. (5):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{5}$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at any time, t (min), respectively.

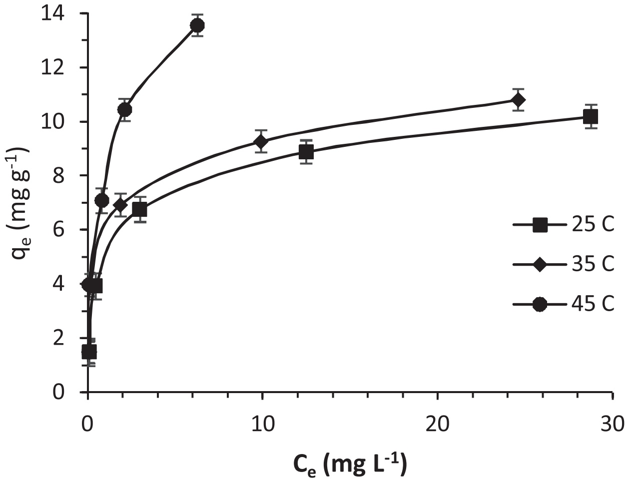

Fig. 9. Effect of initial concentration and temperature on La(III) adsorption by modified nanotitania.

After integration and applying boundary conditions, we have:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{6}$$

where k_1 (min^{-1}) is the pseudo-first-order rate constant for adsorption and can be obtained from Eq. (5) using the MATLAB software.

The pseudo-second-order kinetic model is based on the assumption that the adsorption rate is related to the square of the number of unoccupied sites [43,45]. It can be expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

The pseudo-second-order equation and its linear form are given in Eqs. (8) and (9), respectively:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant for adsorption and can be determined from Eqs. (7) and (8) using the MATLAB software and plotting t/q_t vs. t, respectively. Chemical reaction may be considered as the rate-limiting step for pseudo-first-order and pseudo-second-order kinetic models.

The intra-particle diffusion kinetic model assumes that diffusion phenomenon is the rate-controlling step [45,46]. This kinetic model is described by the Eq. (10):

$$q_t = k_{id} t^{0.5} + C \tag{10}$$

where k_{id} (mg g^{-1} min$^{-0.5}$) is the intra-particle diffusion rate constant and C (mg g^{-1}) is the boundary layer thickness. The value of C is proportional to the boundary layer effect on the adsorption process and can be calculated from Eq. (9) by plotting q_t against $t^{0.5}$. If this plot produces a single straight line passing through the origin (C = 0), then intra-particle diffusion only controls the adsorption process. But, if the plot yields multi-linear portions, then two or more steps like external diffusion, pore diffusion, surface diffusion, and adsorption onto the pore surface influence the adsorption process. The kinetic parameters of the described models were calculated for La(III) adsorption onto modified nanotitania. The results are presented in Table 2 and the fitting curves are shown in ESM 5, 6, and 7.

The coefficient of correlation for pseudo-second-order kinetic model ($R^2 > 0.99$) was higher than the pseudo-first-order and intra-particle diffusion kinetic models (Fig. 10).

Moreover, the calculated adsorption capacity (q_e) from pseudo-second-order kinetic model is close the experimental data. According to these results, it could be explained that the pseudo-second-order kinetic model successfully described the kinetics of lanthanum ions adsorption onto the modified nanotitania.

3.8. Adsorption isotherms

The equilibrium adsorption isotherm describes the interactive behavior between the adsorbate and adsorbent, and is necessary in the design of new adsorption systems. In this study, the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were used to fit the experimental data for La(III) adsorption. These models were analyzed at three different temperatures including 25, 35, and 45˚C. The Langmuir isotherm model assumes that all adsorption sites are energetically identical and adsorption occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed species [47,48]. This model can be expressed by Eq. (11):

Table 2
Kinetic parameters for La(III) adsorption by modified nanotitania

q_{exp} (mg g^{-1})	6.8529	
Non-linear pseudo-first-order model		
k_1 (min^{-1})	q (mg g^{-1})	R^2
0.3656	6.4560	0.980
Non-linear pseudo-second-order model		
k_2 (g mg^{-1} min^{-1})	q (mg g^{-1})	R^2
0.0923	6.890	0.9914
Linear pseudo-second-order model		
k_2 (g mg^{-1} min^{-1})	q (mg g^{-1})	R^2
0.0633	6.9013	0.9998
Linear intra-particle diffusion model		
k_{id} (mg g^{-1} min$^{-0.5}$)	C (mg g^{-1})	R^2
0.1155	5.5672	0.9087

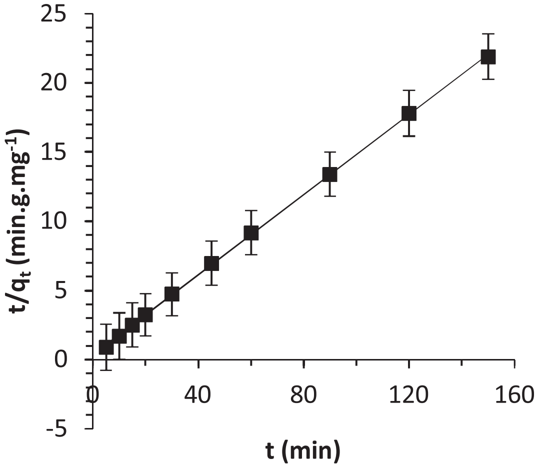

Fig. 10. Linear pseudo-second-order kinetic fitting curve for La(III) adsorption by modified nanotitania.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{11}$$

where q_e (mg g^{-1}) is the amount of solute adsorbed per mass unit adsorbent and C_e (mg L^{-1}) is the equilibrium concentration of the metal ions. q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants related to monolayer capacity and energy of adsorption, respectively. One of the crucial parameters of Langmuir isotherm model is the separation factor (R_L) that indicates the favorability of adsorption reaction. The adsorption is considered to be (i) favorable when $0 < R_L < 1$, (ii) irreversible when $R_L = 0$, (iii) linear when $R_L = 1$, and (iv) unfavorable when $R_L > 1$. This dimensionless parameter is calculated using Eq. (12):

$$R_L = \frac{1}{1 + K_L C_o} \tag{12}$$

where C_o (mg L^{-1}) is the initial concentration of metal ions.

The Freundlich isotherm model is valid for multilayer adsorption process with a non-uniform distribution of heat of adsorption on heterogeneous surfaces [49]. This empirical equation is given as Eq. (13):

$$q_e = K_F C_e^n \tag{13}$$

where K_F (mg g^{-1} × (L mg^{-1})^n) is Freundlich constant related to the adsorption capacity. The parameter n is Freundlich constant which represents the degree of dependence of the adsorption on the equilibrium concentration.

The Dubinin–Radushkevich isotherm [12] is described by Eq. (14):

$$q_\mathrm{e} = q_\mathrm{DR} \exp(-k\varepsilon^2) \tag{14}$$

The Dubinin–Radushkevich constants q_DR (mmol g^{-1}) and K_DR (mol^2 J^{-2}) are related to the adsorption capacity and adsorption energy, respectively. The Polanyi potential (ε) is defined by Eq. (15):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_\mathrm{e}}\right) \tag{15}$$

where R (8.314 J mol^{-1} K^{-1}) and T (K) are the gas universal constant and the absolute temperature, respectively.

E (kJ mol^{-1}) is one of the other parameters of (D–R) equation which defines the free energy change of transferring one mole of solute to the surface of the adsorbent from infinity in the solution. The type of the adsorption process can be specified by E value according to Eq. (16):

$$E = \frac{1}{\sqrt{-2K}} \tag{16}$$

The E value less than 8 kJ mol^{-1}, indicates that the physical adsorption becomes a dominant mechanism.

The estimated parameters of the isotherm models were reported in Table 3. Higher correlation coefficient showed that Langmuir model described the experimental data better than Freundlich and Dubinin–Radushkevich models, which may be due to the homogeneous distribution of active sites on the nanoadsorbent (Fig. 11).

Also the values of R_L were all between 0 and 1, indicating that the adsorption was favorable. The values of K_L increased as the temperature increased showing the enhancement of adsorption at higher temperatures. The Langmuir maximum adsorption capacity increased from 10.34 to 14.33 mg g^{-1} with a rise in temperature from 25 to 45°C for La(III) ions. These results reflected the endothermic nature of the adsorption process.

The maximum adsorption capacity of La(III) on the modified nanotitania was comparable with some other adsorbent investigated, showing the effectiveness of amino phosphate modification process to improve the adsorption capacity (Table 4).

3.9. Thermodynamic studies of the adsorption

Thermodynamic parameters for the adsorption such as Gibbs free energy change (ΔG°, kJ mol^{-1}), enthalpy change (ΔH°, kJ mol^{-1}), and entropy change (ΔS°, kJ mol^{-1} K^{-1}) were determined using the following Van't Hoff thermodynamic equations [49]:

Table 3
Isotherm parameters for La(III) adsorption by modified nanotitania

	Langmuir isotherm			
Temp. (°C)	q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
25	10.34	0.9080	0.0113–0.1021	0.997
35	10.90	1.2754	0.0081–0.0749	0.997
45	14.33	1.9497	0.0053–0.0503	0.99
	Freundlich isotherm			
	K_F (mg^{1-n} L^n g^{-1})	n		R^2
25	3.961	0.3273		0.939
35	4.717	0.3007		0.850
45	7.345	0.3944		0.886
	Dubinin–Radushkevich isotherm			
	q_DR (mmol g^{-1})	$K_\mathrm{D–R}$ (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
25	0.0843	0.0061	9.027	0.993
35	0.0900	0.0050	9.942	0.897
45	0.1388	0.0049	9.997	0.905

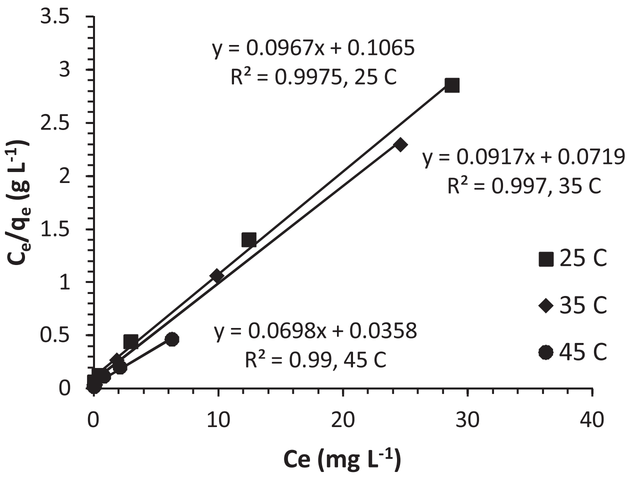

Fig. 11. Langmuir isotherm fitting curve for La(III) adsorption by modified nanotitania.

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{17}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{18}$$

where K_L (L mol^{-1}) is the Langmuir constant. The values of ΔH° and ΔS° can be obtained from the slope and intercept of the linear plots of $\ln(K_L)$ vs. reciprocal temperature, T^{-1}, respectively (Fig. 12). The results are shown in Table 5. The positive value of ΔH° confirmed the endothermic nature of La(III) adsorption ions on the adsorbent surface. Accordingly, some other phenomena of chemical nature like La(III) complexation with phosphate or amine functional groups on the surface could be probably involved in the adsorption process. In addition, the calculated positive value of ΔS° indicated the increasing randomness at solid–liquid interface during the adsorption of lanthanum ions on the surface. The Gibbs free energy change is the basic criterion of spontaneity. The increasing negative values of ΔG° at higher temperatures suggested the adsorption to be a feasible and spontaneous process, which led to better adsorption at higher temperatures.

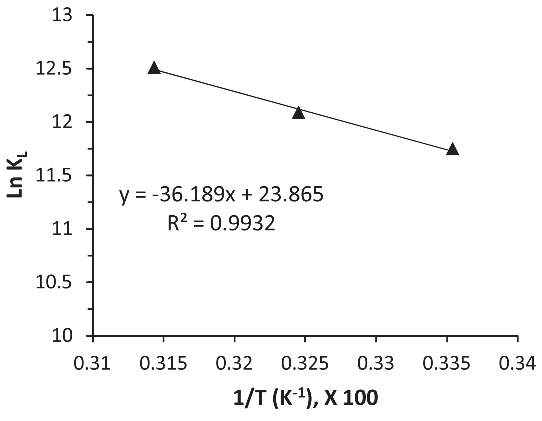

Fig. 12. The Vant Hoff's plots for thermodynamic parameters of La(III) adsorption by modified nanotitania.

3.10. Effect of interfering cations on the adsorption of La(III)

The influence of Ca and Mg cations, which are found commonly in aqueous solutions, was investigated on the adsorption of lanthanum ions in mono- and multi-metal reaction systems in a range of 50–150 mg L^{-1}. No significant change was observed in the adsorption percentage of lanthanum ions in the presence of Ca and Mg cations (Fig. 13).

3.11. Investigation on the simultaneous removal of La(III) and Ce(III)

Distribution coefficient (K_d) can be used as a useful parameter for comparing the adsorptive capacity of a sorbent for different ions under the same experimental conditions and is defined as the ratio of the metal ion concentration in the solid phase to that in the equilibrium solution after a specified reaction time. It

Table 4
Comparison of adsorption capacity of modified nanotitania and other adsorbents for La(III) adsorption

Adsorbent	q_m (mg g^{-1})	Refs.
Barium carbonate	16	[50]
XAD-4 impregnated with Aliquat-336 resin	11.49	[51]
Magnesium silicate functionalized with dibenzo-18-Crown-6	11.45	[52]
Carbon nanoparticles	0.52	[53]
Hydroxyapatite	0.25	[54]
Modified nanotitania (optimized condition)	**14.33**	Present study

Notes: The bold value 14.33 shows the adsorption capacity of modified nanotitania in our work and compare it with other adsorbents, reported in literatures.

Table 5
Thermodynamic parameters for La(III) adsorption by modified nanotitania

ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
		298 K	308 K	318 K
0.3009	0.1984	−58.8561	−60.8403	−62.8244

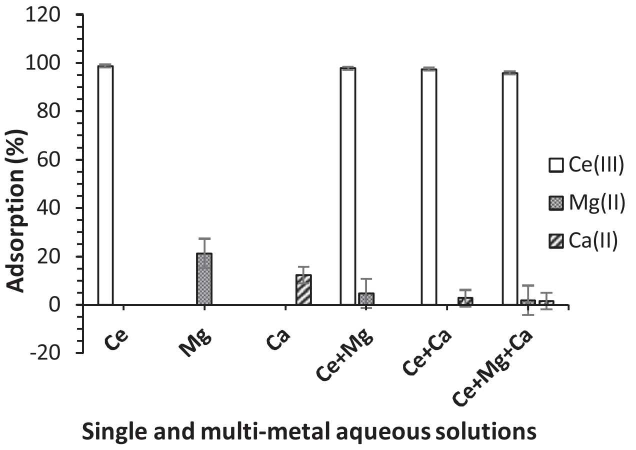

Fig. 13. Effect of Ca and Mg ions on La(III) adsorption by modified nanotitania.

has been showed that lower and higher K_d values indicated lower and higher affinity of metal cations for retention onto solid adsorbent, leading to higher and lower metal availability in the solution, respectively [54].

Adsorption of La(III) in the presence of Ce(III) as the adjacent element was also performed to investigate the possibility of simultaneous removal of La(III) and Ce(III) as lanthanides in bimetallic systems. Three adsorption experiments were performed, in which concentration of La(III) was 50 mg L^{-1}, whereas concentration of Ce(III) was adjusted to 30, 50, and 70 mg L^{-1}. The adsorption efficiency for La(III) reduced to about 86, 78, and 76%, respectively (Table 6).

The results showed that increasing Ce(III) concentration led to lower K_d value for La(III) ions. Decreasing trend of La(III) adsorption in the presence of Ce(III) compared to the single component system of Ln(III) (more than 97%) could be due to competition of the metal ions for the adsorption sites. The similarity in chemical properties and the ionic radiuses of La(III) and Ce(III) (1.216 and 1.196 Å [55], respectively) could be regarded as the reason for competition. However, adsorption percentage and K_d value for La(III) was always acceptable, even when Ce(III) concentration was more than La(III).

3.12. Desorption and regeneration studies

Desorption, a phenomenon whereby the adsorbate (e.g. heavy metal ion) is released from the adsorbent surface, is important to evaluate the economic justification for regeneration and reuse of the adsorbent. In other words, the success of adsorption process depends on the possibility of recovering metal ions, reusing the adsorbent and thus desorption efficiency especially in industrial application to remove heavy metal from wastewater. According to the results corresponding to the desorption experiments, 0.1 mol L^{-1} HNO_3 was more effective than 0.01 and 0.05 mol L^{-1} HNO_3. It seemed that increase in H_3O^+ concentration led to more competition for the active sites where the metal ions hosted on the adsorbent. For amino phosphate functionalized nanotitania adsorbent, adsorption capacity of La(III) ions decreased from 6.85 to 5.8 mg g^{-1} after five cycles of adsorption–desorption using optimum concentration of HNO_3. No significant loss in adsorption performance after frequent use was observed indicating modified nanotitiania as a promising adsorbent for La(III) removal (Fig. 14).

Table 6
K_d values for La(III) in the presence of Ce(III)

Entry	La + Ce (mg L^{-1}), respectively	Ad (%), La	K_d (mL g^{-1}), La	α (La/Ce)
1	50, 0.0	93.88	–	–
2	50, 30	86.20	6,147	1.59
3	50, 50	78.54	549.12	0.99
4	50, 70	76.10	477.73	0.98

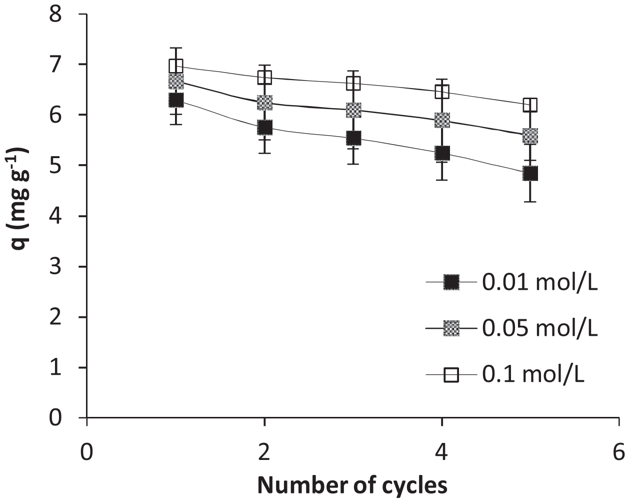

Fig. 14. Five cycles of La(III) adsorption–desorption processes using HNO_3 with different concentrations.

4. Conclusion

The surface of nanotitania powder was modified using 2-aminoethyl dihydrogen phosphate. Organic amino phosphate groups bonded covalently to the nanotitania surface and amino groups remained free. The modified nanotitania was utilized to remove La (III) from aqueous solutions. The considerably enhanced adsorption of La(III) onto treated nanotitania comparing with untreated one could be due to the ability of $–NH_2$ and partly –OH groups of phosphate on the nanotitania surface to coordinate to La(III). The effect of important parameters was investigated. The results indicated that the adsorption was strongly dependent on pH and the optimum pH was 6.0. The kinetic and equilibrium data were exactly described by the pseudo-second-order and Freundlich models for lanthanum. According to the Langmuir model, Maximum adsorption uptakes was obtained as 25.74 for La(III). In addition, from the equilibrium parameter (R_L) values, it was concluded that modified nanotitania was useful for La(III) adsorption from aqueous solutions. The surface modification led to the enhancement of the adsorption capacity for La(III) ions. Thermodynamic parameters showed that the adsorption process was spontaneous and endothermic in nature. The presence of cations commomly present in aqueous solutions such as Ca and Mg ions had no significant effect on the adsorption of La(III). 0.1 mol L^{-1} HNO_3 was considered as an efficient agent for desorption studies and the results revealed no appreciable loss in efficiency over the studied five adsorption–desorption cycles. The presence of Ce(III) with increasing concentration from 30 to 70 mg L^{-1} led to decreasing La(III) adsorption from 84 to 76%. Due to high adsorption percentage, and low-cost, it is concluded that the use of amino phosphate-modified nano TiO_2 as an appropriate adsorbent is promising for the removal of lanthanide elements especially La(III) and Ce(III) from contaminated sites.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2016.1177734.

References

[1] C. Turra, E.A.N. Fernandes, M.A. Bacchi, Evaluation on rare earth elements of Brazilian agricultural supplies, J. Environ. Chem. Ecotoxicol. 3 (2011) 86–92.

[2] D. Das, C.J.S. Varshini, N. Das, Recovery of lanthanum(III) from aqueous solution using biosorbents of plant and animal origin: Batch and column studies, Miner. Eng. 69 (2014) 40–56.

[3] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.

[4] I.H. Lee, Y.C. Kuan, J.M. Chern, Equilibrium and kinetics of heavy metal ion exchange, J. Chin. Inst. Chem. Eng. 38 (2007) 71–84.

[5] H. Polat, D. Erdogan, Heavy metal removal from waste waters by ion flotation, J. Hazard. Mater. 148 (2007) 267–273.

[6] V.V. Goncharuk, B.Y. Kornilovich, V.M. Pavlenko, M.I. Babak, G.N. Pshinko, B.V. Pysmennyi, I.A. Kovalchuk, V.G. Safonova, Water treatment and demineralization technology—Removal of uranium compounds from natural and waste waters, J. Water Chem. Technol. 23 (2001) 44–50.

[7] H.A. Qdais, H. Moussa, Removal of heavy metals from wastewater by membrane processes: A comparative study, Desalination 164 (2004) 105–110.

[8] F. Ferella, M. Prisciandaro, I.D. De Michelis, F. Veglio, Removal of heavy metals by surfactant enhanced ultrafiltration from wastewaters, Desalination 207 (2007) 125–133.

[9] J.S. Kim, C.H. Lee, S.H. Han, M.Y. Suh, Studies on complexation and solvent extraction of lanthanides in the presence of diaza-18-crown-6-di-isopropionic acid, Talanta 45 (1997) 437–444.

[10] D. Mohan, S. Chander, Single component and multi-component adsorption of metal ions by activated carbons, Colloids Surf. A: Physicochem. Eng. Aspects 177 (2001) 183–196.

[11] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[12] N. Ünlü, M. Ersoz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, J. Hazard. Mater. 136 (2006) 272–280.

[13] S.S. Gupta, K.G. Bhattacharyya, Kinetics of adsorption of metal ions on inorganic materials: A review, Adv. Colloid Interface Sci. 162 (2011) 39–58.

[14] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse fly ash—A low cost adsorbent, Ind. Eng. Chem. Res. 42 (2003) 6619–6624.

[15] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresour. Technol. 76 (2001) 63–65.

[16] A. Stafiej, K. Pyrzynska, Adsorption of heavy metal ions with carbon nanotubes, Sep. Purif. Technol. 58 (2007) 49–52.

[17] B. Subotić, J. Bronić, Removal of cerium(III) species from solutions using granulated zeolites, J. Radioanal. Nucl. Chem. Art. 102 (1986) 465–481.

[18] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[19] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu (II) ions onto chitosan, J. Colloid Interface Sci. 255 (2002) 64–74.

[20] R. Celis, M.C. HermosÍn, J. Cornejo, Heavy metal adsorption by functionalized clays, Environ. Sci. Technol. 34 (2000) 4593–4599.

[21] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, Miner. Eng. 19 (2006) 463–470.

[22] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—A review, Bioresour. Technol. 99 (2008) 6017–6027.

[23] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: A review, J. Hazard. Mater. 211–212 (2012) 317–331.

[24] X. Wang, Y. Guo, L. Yang, M. Han, J. Zhao, X. Cheng, Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment, J. Environ. Anal. Toxicol. 2 (2012) 1–7.

[25] S. Bhattacharya, I. Saha, A. Mukhopadhayay, D. Chattopadhyay, U. Chand Ghosh, D. Chatterjee, Role of nanotechnology in water treatment and purification: Potential applications and implications, Int. J. Chem. Sci. Technol. 3 (2013) 59–64.

[26] D. Nabi, I. Aslam, I.A. Qazi, Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal, J. Environ. Sci. 21 (2009) 402–408.

[27] B. Dou, V. Dupont, W. Pan, B. Chen, Removal of aqueous toxic Hg(II) by synthesized TiO_2 nanoparticles and TiO_2/montmorillonite, Chem. Eng. J. 166 (2011) 631–638.

[28] M. Visa, A. Duta, TiO_2/fly ash novel substrate for simultaneous removal of heavy metals and surfactants, Chem. Eng. J. 223 (2013) 860–868.

[29] B. Al-Rashdi, C. Tizaoui, N. Hilal, Copper removal from aqueous solutions using nano-scale diboron trioxide/titanium dioxide (B_2O_3/TiO_2) adsorbent, Chem. Eng. J. 183 (2012) 294–302.

[30] K. Parida, K.G. Mishra, S.K. Dash, Adsorption of toxic metal ion Cr(VI) from aqueous state by TiO_2/MCM-41: Equilibrium and kinetic studies, J. Hazard. Mater. 241–242 (2012) 395–403.

[31] N.M. Mahmoodi, F. Najafi, Synthesis, amine functionalization and dye removal ability of titania/silica nano-hybrid, Microporous Mesoporous Mater. 156 (2012) 153–160.

[32] M.A. Barakat, M.H. Ramadan, M.A. Alghamdi, S.S. Algarny, H.L. Woodcock, J.N. Kuhn, Remediation of Cu(II), Ni(II), and Cr(III) ions from simulated wastewater by dendrimer/titania composites, J. Environ. Manage. 117 (2013) 50–57.

[33] S.H. Huang, D.-H. Chen, Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent, J. Hazard. Mater. 163 (2009) 174–179.

[34] A.R. Mahdavian, M.A.S. Mirrahimi, Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through surface modification, Chem. Eng. J. 159 (2010) 264–271.

[35] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: A review, Sci. Total Environ. 424 (2012) 1–10.

[36] E. Iravani, S.A. Allahyari, Z. Shojaei, M. Torab-Mostaedi, Surface modification and spectroscopic characterization of TiO_2 nanoparticles with 2-aminoethyl dihydrogen phosphate, J. Braz. Chem. Soc. 26 (2015) 1608–1616.

[37] T. Paunikallio, M. Suvanto, T.T. Pakkanen, Viscose fiber/polyamide 12 composites: Novel gas-phase method for the modification of cellulose fibers with an aminosilane coupling agent, J. Appl. Polym. Sci. 102 (2006) 4478–4483.

[38] H. Sepehrian, R. Cheraghali, P. Rezaei, H.A. Abdi, Adsorption behavior of lanthanum on modified nanoporous aluminosilicates, Int. J. Ind. Chem. 2 (2011) 235–241.

[39] Z. Ghasemi, A. Seif, T.S. Ahmadi, B. Zargar, F. Rashidi, G.M. Rouzbahani, Thermodynamic and kinetic studies for the adsorption of Hg(II) by nano-TiO_2 from aqueous solution, Adv. Powder Technol. 23 (2012) 148–156.

[40] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. 105 (2003) 121–142.

[41] S. Chegrouche, A. Mellah, S. Telmoune, Removal of lanthanum from aqueous solutions by natural bentonite, Water Res. 31 (1997) 1733–1737.

[42] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies, J. Hazard. Mater. 138 (2006) 142–151.

[43] N. Chiron, R. Guilet, E. Deydier, Adsorption of Cu(II) and Pb(II) onto a grafted silica: Isotherms and kinetic models, Water Res. 37 (2003) 3079–3086.

[44] E. Da'na, N. De Silva, A. Sayari, Adsorption of copper on amine-functionalized SBA-15 prepared by co-condensation: Kinetics properties, Chem. Eng. J. 166 (2011) 454–459.

[45] S. Debnath, U.C. Ghosh, Nanostructured hydrous titanium(IV) oxide: Synthesis, characterization and Ni(II) adsorption behavior, Chem. Eng. J. 152 (2009) 480–491.

[46] S. Debnath, U.C. Ghosh, Equilibrium modeling of single and binary adsorption of Cd(II) and Cu(II) onto

agglomerated nano structured titanium(IV) oxide, Desalination 273 (2011) 330–342.

[47] S. Yang, J. Li, D. Shao, J. Hu, X. Wang, Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA, J. Hazard. Mater. 166 (2009) 109–116.

[48] S. Abbasizadeh, A.R. Keshtkar, M.A. Mousavian, Sorption of heavy metal ions from aqueous solution by a novel cast PVA/TiO_2 nanohybrid adsorbent functionalized with amine groups, J. Ind. Eng. Chem. 20 (2014) 1656–1664.

[49] G.D. Vuković, A.D. Marinković, M. Čolić, M.Đ. Ristić, R. Aleksić, A.A. Perić-Grujić, P.S. Uskoković, Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes, Chem. Eng. J. 157 (2010) 238–248.

[50] E.A. Elsofany, Removal of lanthanum and gadolinium from nitrate medium using Aliquat-336 impregnated onto Amberlite XAD-4, J. Hazard. Mater. 153 (2008) 948–954.

[51] A. Gabor, C.M. Davidescu, A. Negrea, M. Ciopec, P. Negrea, Use of magnesium silicate functionalized with dibenzo-18-crown-6 for environmental protection, Chem. Bull. "POLITEHNICA" Univ. 58 (2013) 10–12.

[52] A.M. Younis, A.V. Kolesnikov, A.V. Desyatov, Efficient removal of La(III) and Nd(III) from aqueous solutions using carbon nanoparticles, Am. J. Anal. Chem. 5 (2014) 1273–1284.

[53] F. Granados-Correa, J. Vilchis-Granados, M. Jiménez-Reyes, L.A. Quiroz-Granados, Adsorption behaviour of La(III) and Eu(III) ions from aqueous solutions by hydroxyapatite: Kinetic, isotherm, and thermodynamic studies, J. Chem. (2013) 1–9.

[54] S.M. Shaheen, A.S. Derbalah, F.S. Moghanm, Removal of heavy metals from aqueous solution by zeolite in competitive sorption system, Int. J. Environ. Sci. Dev. 3 (2012) 362–367.

[55] Available from: <http://abulafia.mt.ic.ac.uk/shannon/ptable.php> (last accessed 2 March 2016).