

Removal of Cerium from Aqueous Solutions by Amino Phosphate Modified Nano TiO₂: Kinetic, and Equilibrium Studies

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ABSTRACT

Adsorption of Ce(III) from aqueous solution by amino phosphate modified nano TiO₂ was investigated. Effects of pH of solution, adsorbent dose, contact time, initial metal concentration and temperature were examined. Experimental data were fitted well by the pseudo second order model. Adsorption was well described by Freundlich isotherm model with a maximum adsorption capacity of 25 mg/g. According to the obtained thermodynamic parameters, the adsorption was a spontaneous and endothermic process. Effect of interfering cations was studied. Distribution coefficient value for Ce(III) was higher than La(III). Regeneration of adsorbent was performed using HNO₃ with efficiency greater than 84%.

1. Introduction

Cerium is one of the most abundant of the lanthanides and is usually accompanied by other rare earth elements in its mineral. As an element, cerium is neither created nor destroyed within the body. Once absorbed into the body, cerium tends to accumulate primarily in the bone, liver, heart, and lung [1]. Cerium was observed to be localized in the cell, concentrated and precipitated in an insoluble form in association with phosphorus [2]. Chromosomal breaks [3] and intensifying the cardiac effects of magnesium deficiency [4] could be induced by cerium in forms of nitrate and chloride respectively.

For cerium compounds that are soluble

in water, Ce(III) would likely have a pKa close to La(III) (8.5) [5], which indicates that the hydrated Ce(III) ion ([Ce(H₂O)_n]³⁺) will remain in solution at environmental pHs (4-9). Applying cerium compounds in different industries like pharmaceutical [6], metallurgical [7], synthesis of scintillation counters [8], and other various applications lead to discharge of effluent from them to the environment, which makes it necessary to separate these metal ions from aqueous solutions.

Various conventional methods such as chemical precipitation [12], ion exchange [13], floatation [14], coagulation [15], membrane processes [12,16], solvent

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extraction [17] and adsorption [18-21] have been developed to separate heavy metals from aqueous solutions. Adsorption as the most popular approach to remove heavy metals showed many advantages such as easy operation, high efficiency, low cost and production of less sludge volume [22]. Several kinds of materials including activated carbons [23], carbon nanotubes [24], zeolites [25,26], chitosan [27], clays [28,29] and agricultural wastes [30] have been investigated to remove metal cations from aqueous solutions. Nano metal oxides are classified as the promising adsorbents for this purpose [31-33]. In particular, nano TiO₂ is a good candidate for environmental applications due to its physical and chemical stability, non-toxicity, low cost and the resistance to corrosion [34]. A number of nano TiO₂ composites such as TiO₂/montmorillonite [35], TiO₂/fly ash [36], TiO₂/B₂O₃ [37], TiO₂/MCM-41 [38], titania/silica nano-hybrid [39] and titania/dendrimer composites [40] have also been investigated in recent years. Surface functionalization of nano materials is one of the promising methods to improve the adsorption capacity [41-43].

Cerium occur naturally in an array of minerals in the environment including oxides and phosphates showing Ce(III) tendency to phosphate groups. Accordingly it was supposed Ce(III) could be better adsorbed on the surface of nano TiO₂ after phosphate modification. Hence, the surface of nano TiO₂ was modified using 2-aminoethyl dihydrogen phosphate, which was fully characterized using various spectroscopic analysis methods [44] and this novel adsorbent was used to investigate the adsorption of Ce(III). The

effects of some important parameters such as pH of solution, the adsorbent dose, contact time, initial concentration of Ce(III) ions and temperature were studied. The adsorption rates were 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 isotherms. The thermodynamic parameters were evaluated from the adsorption measurements at different temperatures. Effect of interfering cations on the adsorption of Ce(III) was investigated and finally, the reusability of the modified nano TiO₂ was also determined.

2. Experimental

2.1. Materials

TiO₂ nano powder (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 cerium nitrate (Ce(NO₃)₃·6H₂O, 98.5%) purchased from Merck were used to prepare Ce(III) solutions with needed concentrations in deionized water. Other chemicals such as lanthanum nitrate (La(NO₃)₃·6H₂O, 99%), calcium nitrate (Ca(NO₃)₂·4H₂O, 99%), magnesium nitrate (Mg(NO₃)₂·6H₂O, 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 process. 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).

2.2. Methods

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 HNO₃ 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

Surface modification and full characterization of amino phosphate functionalized nano TiO₂ were described in our previous work [44]. Briefly, 2-aminoethyl dihydrogen phosphate (0.141 g, 0.001 mol) was dissolved in 100 mL distilled water. Nano TiO₂ (0.799 g, 0.01 mol) was added and the mixture stirred for 24 h at room temperature. Then the mixture was centrifuged for 30 min at 6000 rpm. The resulted powders were eluted in a Soxhlet extractor with distilled water for 12 h and afterward dried in an oven at 100°C for 12 h.

2.4. Preparation of Ninhydrin Solution

2,2-Dihydroxyindane-1,3-dione (0.2 g, 0.001 mol) was dissolved in a solution of ethyl acetate (1 mL), ethanol (3 mL), heptane (0.04 mL) and acetic acid (0.12 mL) [45]. It was also possible to prepare the solution without acetic acid. The difference was observed in different colors. Ninhydrin solution with acetic acid leads

to hell violet color, while the absence of acetic acid in ninhydrin solution results in dark violet color, if the test is positive.

2.5. Batch adsorption experiments

Stock solutions of Ce(III) were prepared by dissolving appropriate amounts of Ce(NO₃)₃·6H₂O in deionized water, and the initial concentrations (C₀) were adjusted to 50 mg L⁻¹ for each experiment. A mass of 0.2 g modified nano TiO₂ was added into a flask containing 30 ml Ce(III) solution at room temperature and shaken for 90 min. Afterward the solutions were centrifuged at 6000 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 Ce (III) concentrations in a range of 10–400 mg L⁻¹ at different temperatures (25, 35 and 45°C). The simultaneous adsorption of Ce(III) and La(III) ions and the interfering effects of calcium and magnesium ions on Ce(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 nano titana 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 Eq. (1) and Eq. (2), respectively:

$$\% \text{ Ad} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{v}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium metal ion concentration in mg L⁻¹, respectively.

v is the aqueous solution volume in mL and m is the mass of adsorbent in mg. The average absolute value of relative error, AARE, was used to compare the predicted results with the experimental data. A smaller AARE value indicates a better curve fitting. It is defined as follows:

$$\text{AARE} = \frac{1}{\text{NDP}} \times \sum_{i=1}^{\text{NDP}} \frac{|\text{Predicted value} - \text{Experimental value}|}{\text{Experimental value}} \quad (3)$$

in which, NDP is the number of data points.

The distribution coefficient (K_d) of metal ions between the aqueous phase and the solid phase can be directly obtained using Eq. (4) [46]:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{v}{m} \quad (4)$$

where C_0 (mg/ L) and C_e (mg/ L) are the initial and equilibrium cerium concentrations, v/m describes 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 Ce(III) ions over La(III) ions was investigated by batch procedure and determined by the ratio of the two distribution coefficients, K_d Ce(III) and K_d La(III), which are referred to as the selectivity factors as follow:

$$\alpha = \frac{K_d \text{ Ce(III)}}{K_d \text{ La(III)}} \quad (5)$$

2.6. Regeneration experiments

In order to evaluate the regeneration capacity of amino phosphate modified nano TiO₂, desorption experiments were performed using HNO₃ (0.01, 0.05 and 0.1 mol/L) as the desorbing agent. Adsorption experiments for Ce(III) solutions were done by the procedure described previously (30 mL, 50 mg/L, 25°C, optimum pH and adsorbent dose, 90 min). Afterward, modified nano TiO₂ was centrifuged, agitated with HNO₃, washed several times with distilled water, dried at 40°C and reused for next adsorption. The adsorption–desorption processes were repeated for five cycles.

3. Results and discussion

3.1. Adsorbent characterization

The surface modified nano TiO₂ was characterized utilizing various characterization methods. HRTEM and SEM images showed well dispersed, fairly homogeneous nano particles with spherical shape (Fig. 1). No considerable agglomeration was observed.

According to the BET analysis result, surface area of nano TiO₂ was slightly increased (5–7%) compared to the untreated nano TiO₂. Using CHN, TGA and BET analyses results, the amount of amino phosphate groups on the surface was estimated about 3.17 wt% and the number of coupling agent on the surface was calculated to be ca. 2.43 molecules per nm². The existence of ethylamine (–CH₂–CH₂–NH₂) into nano TiO₂ matrix was demonstrated via observation of two sharp bands centered at 2933 and 2901 cm⁻¹ in the ATR-FT IR spectrum (Fig. 2) related to symmetric and asymmetric stretching vibration of methylene groups,

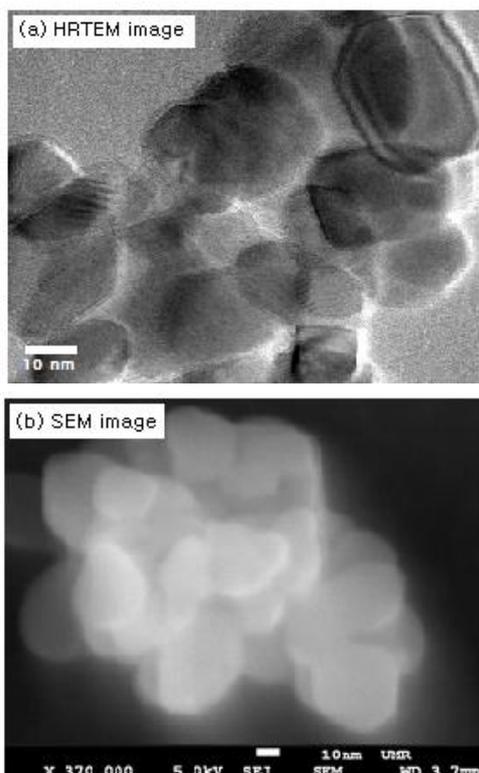


Figure 1. (a) HRTEM and (b) SEM images of amino phosphate modified nano TiO₂.

together with positive ninhydrin test (Fig. 3).

³¹P MAS NMR spectroscopy was utilized for further study of modified nano TiO₂ and showed a distinct downfield shift for ³¹P signal at δ 2.11 ppm compared with the pure capping agent (δ 0.17 ppm) due to P–O–Ti bond formation (Fig. 4).

¹³C CP MAS NMR spectrum 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. Considerable upfield shift of ¹³C signal of O–C was a proof for amino phosphate group bonding with nano TiO₂ through phosphate groups. The phosphate groups interact with the surface via quite strong covalent interaction, while according to the analyses results, the surface amine groups remained uncoordinated (positive ninhydrin test) [44].

3.2. Effect of surface modification

The results of comparative tests performed for Ce (III) adsorption on the untreated nano titania and the treated one with 2-aminoethyl dihydrogen phosphate showed that surface modification led to the increase of adsorption percentage from 48% to more than 98% (about 50% adsorption enhancement). Apparently the described surface modification plays an important role in adsorption behavior. The considerably enhanced adsorption of Ce(III) onto treated nano titania compared

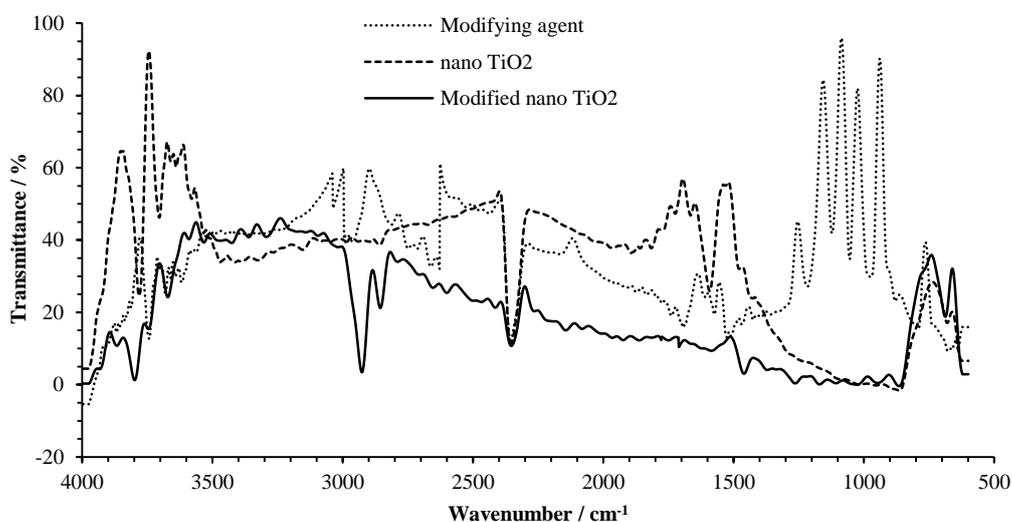


Figure 2. ATR-FT IR spectrum of modified nano TiO₂.

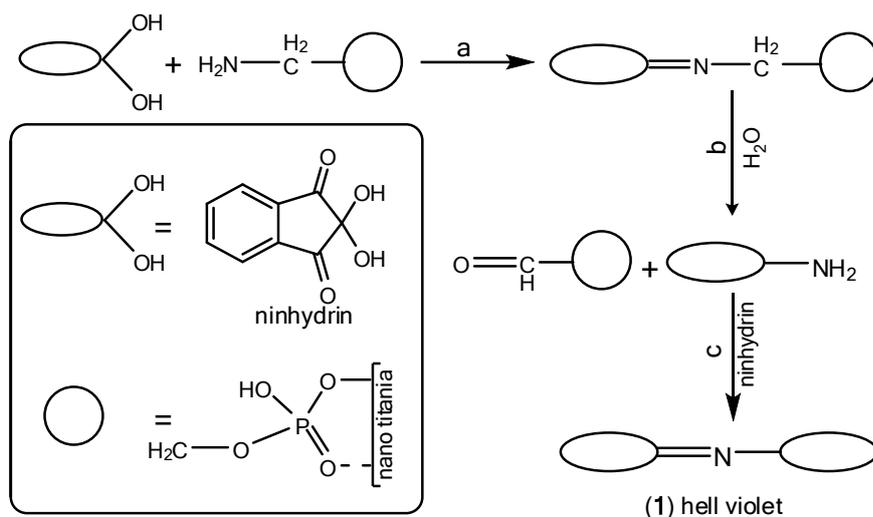


Figure 3. The reaction between ninhydrin and free amino groups on the surface leads to the formation of compound 1 showing hell violet color.

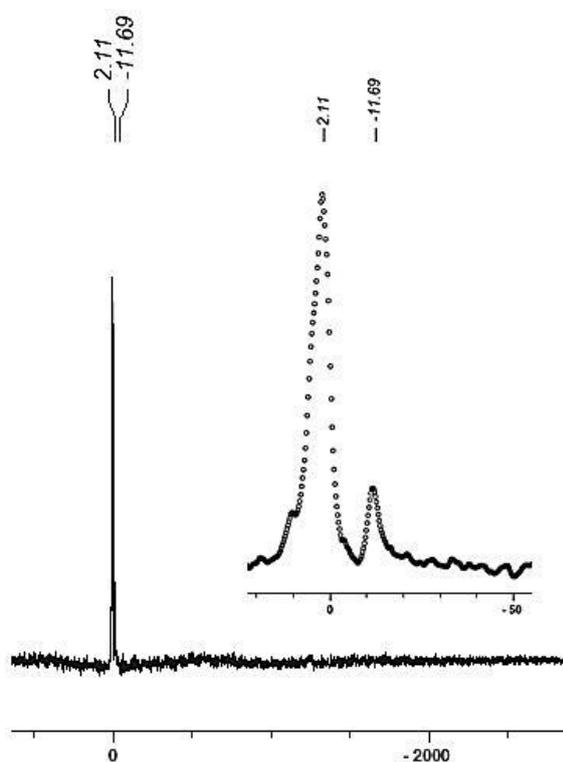


Figure 4. ³¹P MAS NMR spectrum of modified nano TiO₂.

with untreated one could be due to the ability of amine and phosphate groups to form complexes with Ce(III). Du *et al.* performed molecular dynamic (MD) simulation of the structures and properties of cerium containing glasses and showed that the cerium ions were preferentially

surrounded by phosphate oxygen polyhedral [47], which could be a sign of tendency of cerium to phosphate. Such coordination is probably the reason for the enhanced adsorption of Ce(III) on the surface of amino phosphate modified nano TiO₂.

3.3. Effect of pH

The initial pH value is one of the most affecting parameters in the adsorption process due to pH dependency of the various complexation reactions or electrostatic interactions at the surface [48]. 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 should be determined. The initial pH values of the solutions were varied in the range of 2–6 to examine the pH effect on the adsorption of Ce(III) ions (Fig. 5). The adsorption percentages increased with an increase in pH. This could be due to competitive adsorption of H₃O⁺ and cerium ions for the same active adsorption site on the surface

of adsorbent. Increasing the pH and thereby decreasing the H_3O^+ concentration in solution makes the adsorption surface less positive and consequently electrostatic attraction between the cerium ions and the surface starker occurs. The amine functional groups could probably take part in metal uptake process through complexation which is pH-dependent and leads to the adsorption yield enhancement. The nature of the active sites and sorbent may also change with pH [49]. For Ce(III) ions, the maximum adsorption efficiency (97.8%) was achieved at pH value of 6.0 which was used for all subsequent experiments.

Cerium adsorptions were not considered at pH values higher than 6.0 due to the formation of insoluble metal ion hydroxides such as $Ce(OH)_3$ [50].

3.4. Effect of adsorbent dose

The effect of adsorbent dose on the removal of Ce(III) was examined in the range of 0.05–0.5 g illustrated in Fig. 6. Increasing the adsorbent mass in the range of 0.05–0.2 g led to the increase of adsorption efficiency from 40% to more than 93%, which could be the result of an increase in the number of adsorption sites. Adsorption percentage showed no further increase using more than 0.2 g adsorbent,

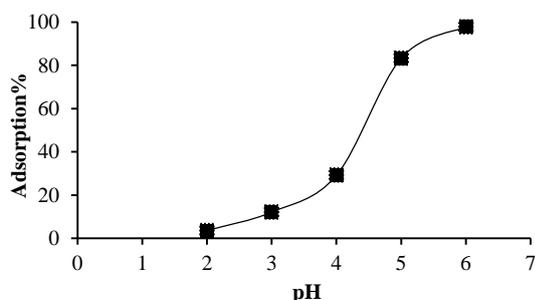


Figure 5. Effect of pH on Ce(III) adsorption by modified nano TiO_2 .

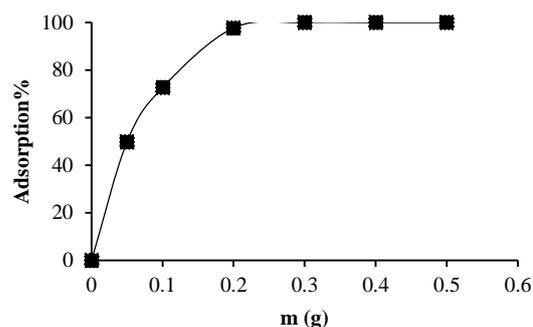


Figure 6. Effect of adsorbent dose on Ce(III) adsorption percentage by modified nano TiO_2 .

therefore, 0.2 g of the adsorbent dose was selected as the appropriate amount for additional adsorption experiments.

3.5. Effect of contact time

The effect of contact time on the adsorption of Ce(III) onto modified nano TiO_2 from aqueous solutions is shown in Fig. 7. The amount of Ce(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 Ce(III) were varied from 10 to 400 mg/L. The measured amounts of adsorbed Ce(III) ions per unit mass of adsorbent were higher at high concentrations (Fig. 8). This uptrend may be attributed to greater

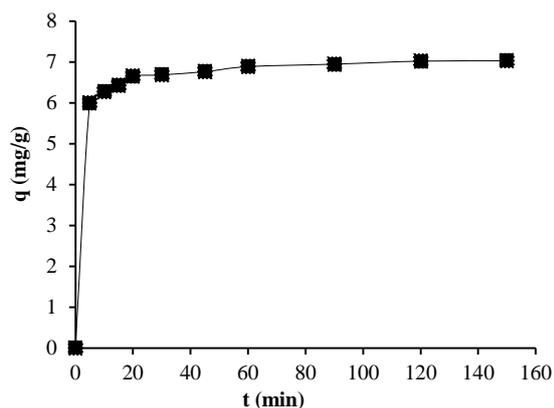


Figure 7. Effect of contact time on Ce(III) adsorption capacity by modified nano TiO₂.

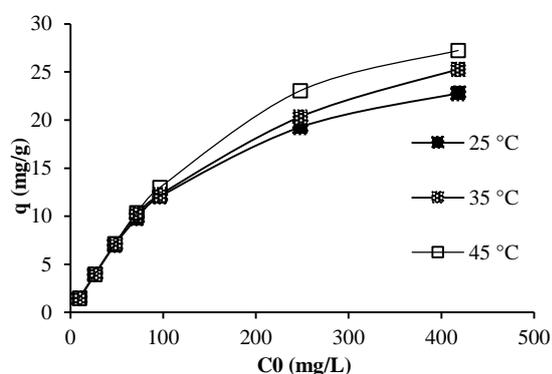


Figure 8. Effect of initial concentration and temperature on Ce(III) adsorption by modified nano TiO₂.

accessibility of cerium ions available per unit surface area of adsorbent in the solution leading to increased probability of surface adsorption. The measured adsorption capacity at 25°C was enhanced from 1.48 mg/g to 22.79 mg/g. This could be due to an increase in the initial concentration of cerium ions providing a larger driving force to overcome the total mass transfer resistance of the cerium ions between the liquid and solid phases, thus resulting in higher collision between adsorbates and surface of adsorbent [51].

The adsorption capacities were improved with increasing temperature, which could be related to increased mobility of cerium ions and their tendency to be adsorbed from the aqueous solution.

Moreover, it was also found that the adsorption of Ce(III) ions onto the modified nano TiO₂ was an endothermic process.

3.7. Adsorption kinetics

Kinetic studies of adsorption process provide important information about the mechanism and the rate limiting step [52]. Three kinetic models including pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to the experimental data in order to investigate the adsorption kinetic. The pseudo-first-order kinetic model, the so-called Lagergren equation, takes into consideration that the adsorption rate is proportional to the number of free sites [53,54]. The rate constant of adsorption can be determined using Eq. (6):

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (6)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium at any time, t (min), respectively. After integration and applying boundary conditions, we have:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

where k_1 (min⁻¹) is the pseudo first-order rate constant for adsorption and can be obtained from Eq. (6) 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 [53,55]. It can be expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

The pseudo-second-order equation and its linear form are given in Eq. (9) and (10), respectively:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where k_2 (g/mg.min) is the pseudo second-order rate constant for adsorption and can be determined from Eq. (8) and (9) using the MATLAB software and plotting t/q_t versus 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 [54,55]. This kinetic model is described by the Eq. (11):

$$q_t = K_{id} t^{0.5} + C \quad (11)$$

where k_{id} (mg/g.min^{0.5}) is the intra-particle diffusion rate constant and C (mg/g) 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. (10) 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 Ce(III) adsorption onto modified nano TiO₂ and the results are presented in Table 1. The average absolute value of relative error (AARE%) and the correlation coefficient (R^2) of models were used to evaluate the quality of fit. The coefficient of correlation for the linear and non-linear pseudo-second-order kinetic models ($R^2 >$

0.99) was higher than the pseudo-first-order and intra-particle diffusion kinetic models and also the obtained values of AARE% for the pseudo-second-order kinetic model were lower in comparison with two other kinetic models. Moreover, the calculated adsorption capacity (q_e) from pseudo-second-order kinetic model is close to the experimental data. According to these results, it could be explained by the fact that the pseudo-second-order kinetic model successfully described the kinetics of cerium ions adsorption onto the modified nano TiO₂, suggesting that the rate-limiting step was chemical adsorption rather than diffusion.

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

Table 1
Kinetic parameters for Ce(III) adsorption by modified nano TiO₂.

q (mg/g)		7.0323	
Non-Linear pseudo first-order model			
k_1 (1/min)	q (mg/g)	R^2	AARE%
0.4059	6.774	0.989	2.7635
Non-Linear pseudo second-order model			
k_2 (g/mg.min)	q (mg/g)	R^2	AARE%
0.1223	7.104	0.9964	1.5875
Linear pseudo second-order model			
k_2 (g/mg.min)	q (mg/g)	R^2	AARE%
0.0936	7.0922	0.9999	1.5618
Linear intra-particle diffusion model			
k	C (mg/g)	R^2	AARE%
0.0916	6.0643	0.8351	1.6569

the experimental data for Ce(III) adsorption. These models were analyzed at three different temperatures including 25, 35 and 45°C by non-linear regression using the MATLAB software. 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 [57,58]. This model can be expressed by Eq (12):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (12)$$

where q_e (mg/g) is the amount of solute adsorbed per mass unit adsorbent and C_e (mg/L) is

the equilibrium concentration of the metal ions. q_m (mg/g) and K_L (L/mg) 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. (13):

$$R_L = \frac{1}{1 + K_L C_0} \quad (13)$$

where C_0 (mg/L) 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 [52]. This empirical equation is given as Eq. (14):

$$q_e = K_F C_e^n \quad (14)$$

where K_F ($\text{mg/g} \times (\text{L/mg})^n$) 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.

Table 2

The isotherm parameters for Ce(III) adsorption by modified nano TiO₂.

Temp. (°C)	Langmuir isotherm				
	q_m (mg/ g)	K_L (L/mg)	R_L	R^2	%AARE
25	21.39	0.1323	0.018-0.432	0.874	40.781
35	22.38	0.1973	0.012-0.338	0.849	45.028
45	25.00	0.2194	0.011-0.315	0.869	46.452
	Freundlich isotherm				%AARE
	$K_F(\text{mg}^{1-n}\text{L}^n/\text{g})$	n	R^2		
25	6.350	0.2303	0.994		15.043
35	6.988	0.2304	0.992		16.269
45	8.059	0.2255	0.993		17.532
	Dubinin–Radushkevich isotherm				
	q_{DR} (mmol/g)	$K_{D-R}(\text{mol}^2 \text{ K/J})$	E (KJ/ mol)	R^2	%AARE
25	0.1517	0.0126	6.287	0.896	38.708
35	0.1637	0.0103	6.954	0.885	42.079
45	0.1856	0.0095	7.239	0.897	43.567

The Dubinin–Radushkevich isotherm [59] is described by Eq. (15):

$$q_e = q_{DR} \exp(-K_{DR} \varepsilon^2) \quad (15)$$

The Dubinin–Radushkevich constants q_{DR} (mmol/g) 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. (16):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (16)$$

where R (8.314 J/ mol. K) and T (K) are the gas universal constant and the absolute temperature, respectively.

E (kJ/mol) 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. (17):

$$E = \frac{1}{\sqrt{-2KDR}} \quad (17)$$

The E value less than 8 kJ/mol, indicates that the physical adsorption becomes a dominant mechanism. If $8 < E$ (kJ/mol) < 16 , the chemical adsorption occurs.

The estimated parameters of the isotherm models were reported in Table 2. Higher correlation coefficients and lower average absolute values of relative error showed that Freundlich model described the experimental data better than Langmuir and Dubinin–Radushkevich models, which may be due to the heterogeneous distribution of active sites on the nano adsorbent. As can be noticed, the n value between 0 and 1 showed the favorable nature of adsorption for cerium ions. 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 21.4 to 25 mg/g with a rise in temperature from 25 to 45°C for Ce(III) ions. These results reflected the endothermic nature of the adsorption process. The mean free energy between 1 and 8 kJ/mol revealed that the adsorption processes of cerium ions were carried out by physical adsorption mechanism. The maximum adsorption capacities of Ce(III) on the modified nano TiO_2 increased compared to untreated one and was comparable with some other investigated adsorbents, showing the effectiveness of amino phosphate modification process to improve the adsorption capacity (Table 3).

3.9. Thermodynamic studies of the adsorption

Thermodynamic parameters for the adsorption such as Gibbs free energy change (ΔG° , kJ/mol), enthalpy change (ΔH° , kJ/mol) and entropy change (ΔS° , kJ/mol.K) were determined using the following Van't Hoff thermodynamic equations [60]:

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19)$$

where K_L (mol/L) is the Langmuir constant. The values of ΔH° and ΔS° can be obtained from the slope and intercept of the linear plots of $\ln(K_L)$ versus reciprocal temperature, T^{-1} , respectively (Fig. 9). The results are shown in Table 4. The positive values of ΔH° confirmed the endothermic nature of adsorption processes for cerium ions on the adsorbent. In addition, the calculated positive values of ΔS° indicated the increasing

Table 3

Comparison of adsorption capacity (mg/g) of modified nano TiO₂ adsorbent for Ce(III) adsorption with unmodified nano TiO₂.

Adsorbent	q _m (mg/g)	References
Pinus brutia leaf powder	17.24	[57]
Unmodified nano TiO ₂	12.08	Present study
Modified nano TiO ₂	21.39	Present study

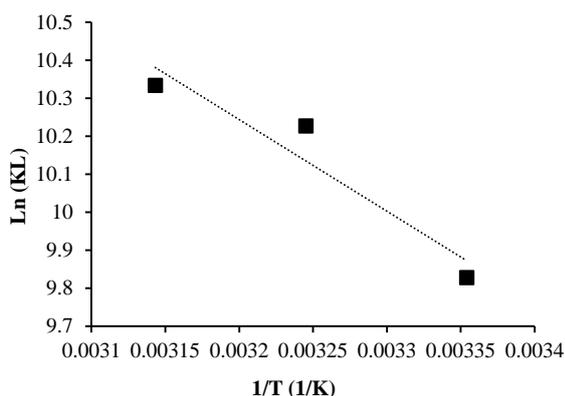


Figure 9. The Van't Hoff's plots for thermodynamic parameters of Ce(III) adsorption by modified nano TiO₂.

randomness at solid-liquid interface during the adsorption of cerium ions on the modified nano TiO₂s surface. The Gibbs free energy change is the basic criterion of spontaneity. The increasing negative values of ΔG° suggested the adsorption to be a feasible and spontaneous process, which led to better adsorption at higher temperatures.

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

The influence of Ca and Mg ions, which are commonly found in aqueous solution, was investigated on the adsorption of Ce(III) in mono and multi-metal reaction systems in a range of 50-150 mg/L. As can be seen in Fig. 10, no significant change was observed in the adsorption

percentage and adsorption capacity for Ce(III) in the presence of Ca and Mg ions.

3.11. Investigation on the distribution and selectivity coefficient

Distribution coefficient (K_d) is a useful parameter for comparing the adsorptive capacity of different sorbents for any particular ion or 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 [62]. It has been shown 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 [61].

According to the distribution coefficients values in this study, the K_d value for Ce(III) ions in single metal solution is more than La(III) ions (6571.96 and 2299.83 mL/g, respectively) and the resultant α value is 2.86, showing that Ce(III) ions were retained stronger than La(III) ions. Simultaneous adsorption of Ce(III) and La(III) was also performed to

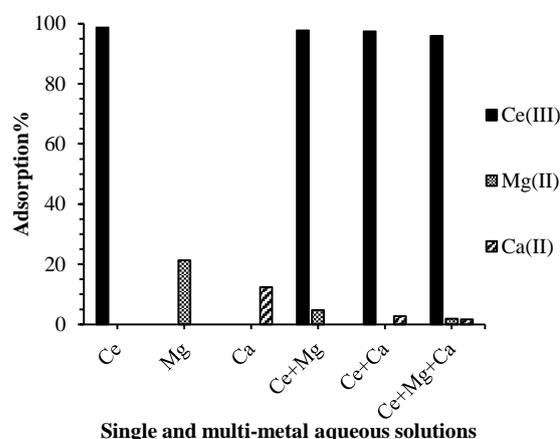


Figure 10. Effect of Ca and Mg ions on Ce(III) adsorption on modified nano TiO₂.

investigate the tendency of modified nano titania for Ce(III) in the presence of competitor ion, La(III). Three adsorption experiments were performed, in which concentration of Ce(III) was 50 mg/L, whereas concentration of La(III) was adjusted 30, 50 and 70 mg/L. The results showed that increasing La(III) concentration led to lower K_d value for Ce(III) ions. In this way, as the concentration of La(III) was increased from 30 to 50 and 70 mg/L, selectivity coefficient (α) for Ce(III) against La(III) was decreased (Table 5). However, adsorption percentage and K_d value for Ce(III) was always high, even when La(III) concentration was more than Ce(III).

Lanthanide elements are difficult to separate due to their close physical and chemical similarities. However, the exhibited sorption preference of amino phosphate modified nano TiO₂ for Ce(III) against La(III) was almost 1.37-2.86 times as many as La(III). Lanthanide elements have a great affinity for most functional groups in organic matter including phosphate groups. It has also been shown that the decrease in ionic radius of lanthanide elements is associated with an

increasing tendency to form complexes, and this is the basis for fractional extraction of lanthanide ions with tributylphosphate [62]. Due to the lanthanide contraction, ionic radius of Ce(III) is slightly smaller than that of La(III), which could probably facilitate the complex formation of Ce(III) with modifying agent on the surface of nano titania and amplify the adsorption of Ce(III) compared to 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 HNO₃ was more effective than 0.01 and 0.05 mol/L HNO₃. It seemed that increase of H₃O⁺ concentration led to more competition for the active sites where the metal ions hosted on the adsorbent. For amino phosphate functionalized nano TiO₂ adsorbent, adsorption capacity of Ce(III) ions decreased from 7.03 to 6.2 mg/g after five cycles of adsorption-desorption (using optimum concentration of HNO₃), respectively. No significant loss in adsorption performance after frequent use was observed indicating modified nano titania as a promising adsorbent for Ce(III) removal.

Table 5

Effect of competitor ion, La(III), on the K_d and α value of Ce(III) adsorption by modified nano TiO₂.

Entry	Ce (mg/L)	La (mg/L)	Ad%	K_d (mL/g)	α (Ce/La)
1	0	50	93.88*	2299.83*	-
2	50	0	97.77	6571.96	2.86**
3	50	30	87.99	6274.5	1.63
4	50	50	84.22	800.8	1.44
5	50	70	81.49	660.34	1.37

*Data marked with * are related to La(III); all the other Ad% and K_d values are related to Ce(III).

**This α value was calculated using K_d values of Ce(III) and La(III) in single component solutions.

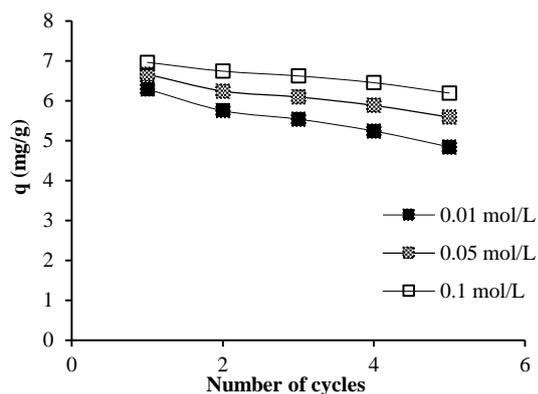


Figure 11. Five cycles of Ce(III) adsorption-desorption processes using HNO₃ with different concentrations.

4. Conclusions

Amino phosphate modified nano TiO₂ was prepared and utilized for adsorption of Ce(III) from aqueous solutions. 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 cerium ions. According to the Langmuir model, Maximum adsorption uptakes were obtained as 25 mg/g for Ce(III). In addition, from the equilibrium parameter (R_L) value, it was concluded that modified nano TiO₂ was useful for these ions adsorption from aqueous solutions. Comparing the q_m values for Ce(III) adsorption using nano TiO₂ and amino functionalized nano TiO₂ showed that the surface modification led to the enhancement of the adsorption capacity for Ce(III) ions. Thermodynamic parameters showed that the adsorption process was spontaneous and endothermic in nature. The presence of cations such as Ca and Mg in the solution had no significant effect on the adsorption of Ce(III). 0.1 mol/L HNO₃ 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. As confirmed in our previous work, amino phosphate groups bonds covalently to the nano titania surface predominantly through bidentate bridging mode and amino groups remain free. The considerably enhanced adsorption of Ce(III) onto treated nano titania compared with untreated one could be due to the ability of -NH₂ and partly -OH groups of phosphate on the nano titania surface to coordinate to Ce(III).

The quantity of distribution coefficient (K_d), the affinity of Ce(III) for retention onto modified nano TiO₂, was higher than La(III). Due to high adsorption percentage, and low cost it is concluded that the use of amino phosphate modified nano TiO₂ as an appropriate adsorbent is promising for the removal of lanthanide elements, especially Ce(III) from contaminated sites.

Nomenclature

AARE%	average absolute value of relative error
C_0	initial metal ion concentration (mg/L)
C_e	equilibrium metal ion concentration
E	free energy change of transferring one mole of solute to the surface of the adsorbent from infinity in the solution (kJ/mol)
K_1	pseudo first-order rate constant (1/min)
K_2	pseudo second-order rate constant (g/mg.min)
K_d	distribution coefficient (mL/g)
K_{DR}	Dubinin-Radushkevich constant related to the adsorption energy (mol ² /J ²)
K_F	Freundlich constant (mg ¹⁻ⁿ L ⁿ /g)
K_{id}	intra-particle diffusion rate constant (mg/g.min ^{-0.5})
K_L	Langmuir constant related to the adsorption energy (L/mg)

m	Adsorbent mass (mg)
q_{DR}	Dubinin–Radushkevich constant related to the adsorption capacity (mmol/g)
q_e	adsorption capacity at equilibrium (mg/g)
q_m	Langmuir constants related to the monolayer capacity (mg/g)
q_t	adsorption capacity at any time (mg/g)
R	gas universal constant (8.314) (J/mol.K)
R_2	correlation coefficient
R_L	separation factor
T	Temperature (K)
v	aqueous solution volume (mL)
α	selectivity factor
ε	Polanyi potential
ΔG°	Gibbs free energy change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
ΔS°	entropy change (kJ/mol)

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