



ORIGINAL ARTICLE

Study of isotherm and kinetic models of lanthanum adsorption on activated carbon loaded with recently synthesized Schiff's base



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Batch method

Abstract A new effective adsorbent was developed for a selective extraction and determination of lanthanum from aqueous media by use of inductively coupled plasma-optical emission spectrometry. The new adsorbent was based on activated carbon modified with Schiff's base derived from diethylenetriamine and 3,4-dihydroxybenzaldehyde (AC-DETADHBA). Isotherm and kinetic models were systematically investigated to evaluate the analytical potential of the AC-DETADHBA phase toward La(III) by employing a batch adsorption technique. Surface properties of AC-DETADHBA were characterized by Fourier transform infrared spectrometry. The maximum static adsorption capacity was determined to be 144.80 mg g⁻¹ at pH 6, providing that the adsorption capacity of La(III) was improved by 61.79% with the AC-DETADHBA phase as compared to the carboxylic acid derivative of activated carbon after only 1 h contact time. Adsorption isotherm results demonstrated that the adsorption process was mainly monolayer on a homogeneous adsorbent surface, confirming the validity of Langmuir adsorption isotherm model. Data obtained from kinetic models study indicated that the adsorption of La(III) onto the AC-DETADHBA phase obeyed a pseudo second-order kinetic model. In addition, results of thermodynamic investigation also revealed that the adsorption mechanism of AC-DETADHBA toward La(III) is a general spontaneous process and favorable. The effect of several coexisting metal ions displayed that the recovery of La(III) was not affected by the medium composition containing either individual or mixed

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metals. Finally, the newly proposed method gave satisfactory results for the determination of La(III) in environmental water samples.

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1. Introduction

Rare earth elements (REEs) are of continual interest because of their unique properties, such as the production of superconductors, super-magnets and geochemical natures. REEs are important elements not only in industrial applications but also in energy and environmental applications (Li and Hu, 2010). Lanthanum, one of lanthanide elements, has attracted increasing interests in its unique physical and chemical properties because of increasing demands for advanced new materials (Kondo and Kamio, 2002; Rao and Biju, 2000). Lanthanum is found in rare earth minerals such as cerite, monazite, allanite and bastnasite. Monazite and bastnasite minerals are principal ores that contain up to 25% and 38% lanthanum, respectively. Approximately 25% lanthanum is found in mischmetals used in making lighter flints. Lanthanum is also used for the manufacture of specialized lenses because lanthanum compounds bring about special optical qualities in glass. Moreover, lanthanum compounds containing fluorine or oxygen are used in making carbon arc lamps for the motion picture industry. Lanthanum salts are included in the zeolite catalysts used in petroleum refining due to its stabilizing action on the zeolite at high temperatures (Awwad et al., 2010).

In general, it is very important to find appropriate methods that meet a quality control for the determination of metal ions. However, direct determination of metal ions using analytical methods at ultra-trace concentration is insufficient due to their low concentrations and the high concentration of interfering matrix components in most real samples. Thus, an effective separation procedure is usually required prior to the sensitive, accurate and interference-free determination of metal ions. There are a wide range of treatment techniques for the separation of trace REEs, such as precipitation (Souza et al., 2011), solvent extraction (Tong et al., 2009), adsorption (Sun et al., 2008) and ion-exchange (Hershey and Keliher, 1989), etc. Although the solvent extraction has been widely used due to the effective extraction ability and separation selectivity, the large amount of organic solution strongly destroys the environment and harms human health. Among various methods, adsorption technique is doubtlessly 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 adsorbents are used as adsorption materials including inorganic oxides (Rauf et al., 1993; Hang et al., 2003; Quan et al., 2004; Liang et al., 2007), zeolites (Pasinli et al., 2005), silica (Mashhadizadeh et al., 2008; Zhang et al., 2007; Liang and Fa, 2005), various resins (Sun et al., 2008; Jia et al., 2008; Lee et al., 2009; Kim et al., 2006; Ansari et al., 2006; Jain et al., 2001; Jelinek et al., 2007; Dave et al., 2010), biological adsorbents (Diniz and Volesky, 2005; Li et al., 2002; Shan et al., 2002) and activated carbon (Jankowski et al., 2005; Marwani et al., 2012a,b).

Activated carbon (AC) has been proven to be an effective adsorbent for the separation of a wide variety of pollutants from aqueous or gaseous media. AC has also been widely used

in deodorization, purification of drinking water, treatment of waste water and the adsorption and separation of various organic and inorganic chemicals (Yin et al., 2007). AC is a porous material with exceptionally high surface area (ranges from 500 to 1500 m² g⁻¹), large pore volume and well-developed internal microporosity and wide spectrum of surface functional groups. In addition, a chemical modification of AC offers flexibility in their specific physical and chemical properties and enhances their affinity for inorganic and/or organic species present in waters. These properties include their specific surface area, pore-size distribution, pore volume and the presence of different types of surface functional groups (Rivera-Utrilla et al., 2011). In general, the most successful solid phase extractors for trace metal ions are those immobilized basically by sulfur and nitrogen containing compounds (Soliman et al., 2004). For example, Schiff's base, mainly nitrogen containing compound, is a classical ligand that can be used as modifier in AC. Schiff's bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis and as polymer stabilizers (Dhar and Taploo, 1982).

Adsorption capacity of La(III) with different solid phase extractors was previously reported by other studies. For instance, La(III) uptake capacity was found to be 5.35 mg g⁻¹ (Tong et al., 2011) by multiwalled carbon nanotube modified with tannic acid, 120 mg g⁻¹ (Chen, 2010) by Bamboo charcoal, 175 mg g⁻¹ (Awwad et al., 2010) by rice husk, and 111.1 mg g⁻¹ (Diniz and Volesky, 2005) by Sargassum biomass. The existence of different types of adsorbents for the extraction of La(III) strongly supports the increasing interest in its unique physical and chemical properties.

In accordance, the aim of this study was to explore the analytical potential of the newly modified AC phase toward a selective adsorption and determination of La(III) prior to its determination by inductively coupled plasma-optical emission spectrometry. The newly modified AC phase was based on a chemical modification of new Schiff's base ligand, derived from diethylenetriamine and 3,4-dihydroxybenzaldehyde, on the surface of oxidized AC (AC-DETADHBA). Fourier transform infrared (FT-IR) spectroscopic measurements confirmed the formation of the new chemically modified phase (AC-DETADHBA). The effect of pH on the selectivity of AC-DETADHBA toward different metal ions [Cd(II), Cr(III), Fe(II), Fe(III), La(III) and Zn(II)] was also investigated in order to study the effectiveness of AC-DETADHBA on the adsorption of selected metal ions. The selectivity of AC-DETADHBA toward La(III) was the most based on the pH study. Other parameters influencing the maximum uptake of La(III) on the AC-DETADHBA phase were also studied under batch techniques. The thermodynamic behavior of La(III) adsorption on the AC-DETADHBA phase was investigated. Desorption study for the regeneration of adsorbent was also achieved using hydrochloric acid solution. The effect of several coexisting metal ions suggested that the extraction of La(III) was not affected by the medium composition containing either individual or mixed metals.

The newly proposed method, ultimately, provided reasonable results for the determination of La(III) in real water samples.

2. Experimental

2.1. Chemicals and reagents

Powdered activated carbon, nitric acid, hydrochloric acid, ethanol (Et-OH), dimethylformamide (DMF), dichloromethane, *N,N'*-dicyclohexylcarbodiimide (DCC), diethylenetriamine (DETA), and 3,4-dihydroxybenzaldehyde (DHBA) were obtained from Sigma–Aldrich (Milwaukee, WI, USA). Stock standard solutions of Cd(II), Cr(III), Fe(II), Fe(III), La(III) and Zn(II) were also purchased from Sigma–Aldrich. All reagents used were of analytical and spectral purity grade. Doubly distilled deionized water was also used throughout experimental studies.

2.2. Preparation of the new solid phase extractor based on AC

2.2.1. Purification of AC

AC powder was first purified with 10% (v/v) hydrochloric acid solution for 24 h to remove adsorbed impurities and metal ions. Then, it was filtered, washed with 18.2 M Ω -cm distilled deionized water and oven dried at 80 °C for 5 h.

2.2.2. Preparation of carboxylic acid derivative of AC (AC-COOH)

10 g of purified AC was suspended in 300 mL of 32.5% (v/v) nitric acid solution under stirring and heating for 5 h at 60 °C. The mixture was filtered, thoroughly rinsed with 18.2 M Ω -cm distilled deionized water to neutral and oven dried at 80 °C for 8 h.

2.2.3. Synthesis of new phase (AC-DETADHBA)

One equivalent of DETA undergoes Schiff's base condensation reaction with two equivalents of DHBA in 150 ml DMF. The reaction mixture was refluxed for 2 h. The resultant Schiff's base product (DETADHBA) was left to cool, filtered, washed with DMF, Et-OH and diethyl ether and dried under vacuum at 80 °C for 5 h. Then, 1.0 g DETADHBA was weighed and completely dissolved by warming in 50 ml DMF. To this solution, 5.0 g AC-COOH was mixed with 3 g DCC dissolved in 100 mL DMF. The reaction mixture was stirred at 60 °C for 12 h. The newly modified AC-DETADHBA phase was filtered and washed with 50 mL DMF, Et-OH on three portions and diethyl ether. The AC-DETADHBA phase was then allowed to dry in an oven at 80 °C for 5 h. The synthetic route of AC-DETADHBA is displayed in [Scheme 1](#).

2.2.4. Determination of the surface coverage value of the AC-DETADHBA phase

An amount of 100 mg of the newly modified AC-DETADHBA phase was weighed in a dry porcelain crucible and was gradually heated into a furnace from 50 to 700 °C. The ignited phase was then kept at this temperature for 1 h. The remaining AC-DETADHBA phase was left to cool in a desiccator and weighed to determine the mass of desorbed DETADHBA. The weight loss of Schiff's base product, DETADHBA, was determined by the difference in sample masses before and after

the process of thermal desorption. The concentration of DETADHBA on the surface of AC-COOH was determined to be 0.51 mmol g⁻¹ based on thermal desorption method.

2.3. Adsorption method procedure

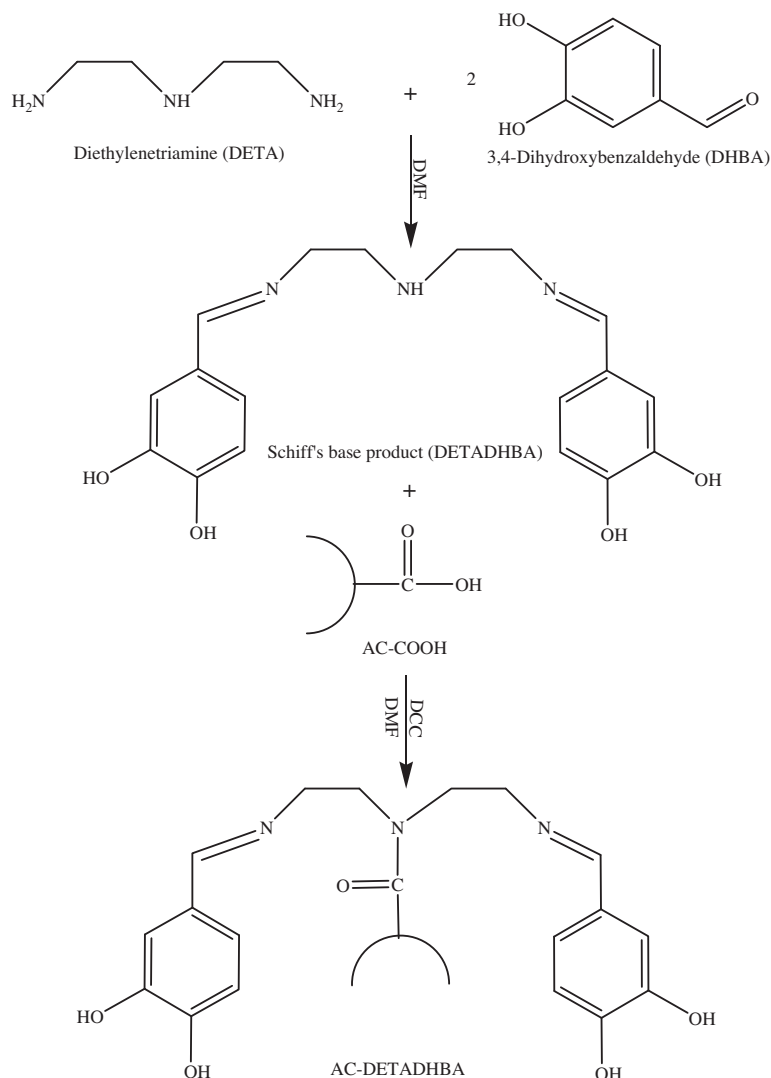
All stock solutions of Cd(II), Cr(III), Fe(II), Fe(III), La(III) and Zn(II) were prepared in 18.2 M Ω -cm distilled deionized water and stored in the dark at 4 °C. Standard solutions of 5 mg L⁻¹ of each metal ion were prepared and adjusted to pH values ranging from 1.0–7.0 with appropriate buffer solutions, HCl/KCl buffer for pH (1.0 and 2.0), acetate buffer for pH (3.0–6.0) and Na₂HPO₄/H₃PO₄ buffer for pH 7.0. Then, all these standard solutions were individually mixed with 25 mg AC-DETADHBA in order to study the effect of pH on the selectivity of the AC-DETADHBA adsorption toward selected metal ions. These mixtures were mechanically shaken for 1 h at room temperature using a mechanical shaker. The AC-DETADHBA was then removed by filtration, and the concentration of La(III) in the aqueous solution was determined by inductively coupled plasma-optical emission spectrometer. For the study of adsorption capacity of La(III) under batch conditions, standard solutions of 10, 50, 70, 100, 150, 200, 250, 300, 350 and 400 mg L⁻¹ were prepared as above, adjusted to the optimum pH value of 6.0 with acetate buffer and individually mixed with 25 mg AC-DETADHBA. In addition, the effect of contact time on La(III) uptake capacity was performed under the same batch conditions but at different equilibrium periods (1, 5, 10, 20, 30, 40, 50 and 60 min). For thermodynamic investigation, a standard solution of 5 mg L⁻¹ La(III) was prepared, adjusted to the pH value of 6.0 as above and mixed with 25 mg AC-DETADHBA. Thermodynamic study of the adsorption of AC-DETADHBA toward La(III) was also performed under the same batch conditions but at different temperatures (298, 313 and 338 K).

2.4. Desorption method procedure

The reversibility of adsorption of 25 mg AC-DETADHBA for La(III) was investigated by desorption study at different concentrations (5 and 10 mg L⁻¹) of La(III). Once the equilibrium was reached, the saturated AC-DETADHBA with La(III) was removed from the solution and transferred to 25 mL of (0.05–0.15 mol L⁻¹) HCl solution. The mixture was mechanically shaken for 2 h at 150 rpm and room temperature using a mechanical shaker. The AC-DETADHBA adsorbent was then removed by centrifugation, and the concentration of La(III) in the aqueous solution was determined by inductively coupled plasma-optical emission spectrometer.

2.5. Instrumentation

FT-IR spectra were acquired before and after modification of the AC phase on a Shimadzu IR 470 spectrophotometer in the range of 4000–600 cm⁻¹. A pH meter (InoLab® pH 7200, IL, USA) was employed for the pH measurements with absolute accuracy limits at pH measurements being defined by NIST buffers. A Perkin Elmer inductively coupled plasma-optical emission spectrometer (ICP-OES) model Optima 4100 DV, USA was used for the determination of metal ions. The ICP-OES instrument was optimized daily before measurement



Scheme 1 Synthetic route of AC-DETADHBA phase.

and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min⁻¹; auxiliary gas (Ar) flow, 0.2 L min⁻¹; nebulizer gas (Ar) flow, 0.8 L min⁻¹; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min⁻¹; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. Concentrations of selected metal ions were determined at wavelengths of 214.44 nm for Cd(II), 267.00 nm for Cr(III), 238.20 nm for Fe(II) and Fe(III), 348.90 nm for La(III) and 206.20 nm for Zn(II).

3. Results and discussion

3.1. FT-IR characterization

FT-IR spectrum of the AC-DETADHBA phase confirms the chemical binding of Schiff's base product DETADHBA to AC-COOH surface (Fig. 1). The spectral data in Fig. 1 show

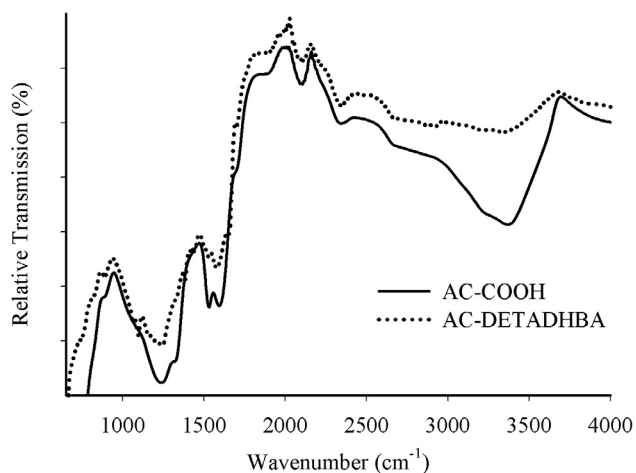


Figure 1 FT-IR spectra of AC-COOH and AC-DETADHBA.

new characteristic vibration bands at 1400 and 1661 cm⁻¹, not present in the FT-IR spectrum of AC-COOH, correspond

to aromatic γ (C=C) and azomethane γ (C=CN) groups, respectively, indicating the formation of Schiff's base product. In addition, there are new peaks appeared in the FT-IR spectrum of AC-DETADHBA which can be assigned by their characteristic absorbance ν (cm^{-1}) as follows: 1116 cm^{-1} (C–O single); 1461 (C–N); 3102–3612 (O–H).

3.2. Effect of pH

Extraction of metal ions from aqueous media by adsorption is usually pH dependent because pH affects the surface charge of adsorbents, the degree of ionization and species of adsorbate (Zhang et al., 2008). In this study, the effect of pH on the adsorption of different metal ions, including Cd(II), Cr(III), Fe(II), Fe(III), La(III) and Zn(II), by the newly modified AC-DETADHBA phase was investigated. A concentration of 5 mg L^{-1} of each metal ion was chosen, and pH values of sample solutions were adjusted to a range from 1.0 to 7.0 with corresponding buffer solutions. All standard solutions were individually mixed with 25 mg AC-DETADHBA. The percentage extraction of each metal ion was calculated based on a difference between the initial (C_o) and final (C_f) concentrations before and after filtration with AC-DETADHBA, respectively, as follows:

$$\% \text{ Extraction} = \frac{C_o - C_f}{C_f} \times 100 \quad (1)$$

It can be clearly observed from Fig. 2 that the % extraction is strongly dependent on the pH value of selected metal ions. Fig. 2 depicts that there is an increase in the % extraction of all metal ions included in this study, except for La(III), followed by a subsequent decrease with an increase of the pH value. For La(III), it is interesting to note that there is a continual increase in the % extraction with an increase of the pH value from 1.0 up to 7.0. A close examination of Fig. 2 indicates that the maximum % extraction (99.60%) is reached and obtained with La(III). Moreover, the selectivity of the AC-DETADHBA phase toward La(III) was the most among all metal ions at a high pH value.

The pH of zero point charge (pH_{zpc}) value of AC-DETADHBA adsorbent was measured to be two by the use of

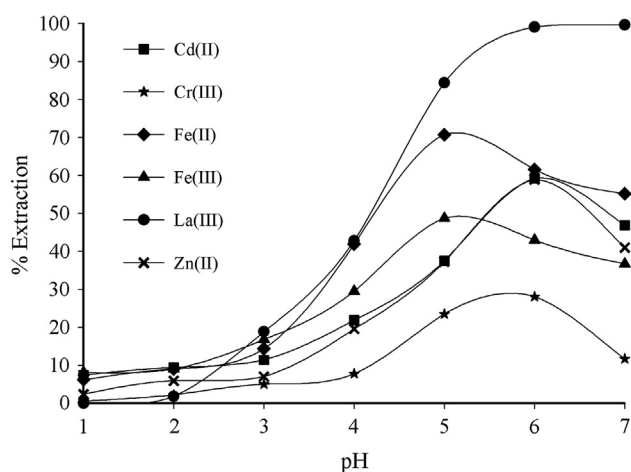


Figure 2 Effect of pH on the adsorption of 5 mg L^{-1} Cd(II), Cr(III), Fe(II), Fe(III), La(III) and Zn(II) on 25 mg AC-DETADHBA phase at 25 °C.

potentiometric titration. The oxidized activated carbon (AC-COOH) contains acidic carbon–oxygen surface groups that ionized in solution to produce H^+ ions in the liquid phase, leaving the carbon surface with a negative charge. It can be also clearly noticed that La(III) ions are inhibited in the acidic medium due to the presence of H^+ ions competing with the La(III) ions for the adsorption sites of AC-DETADHBA phase (Fig. 2). In fact, the negative charge of the carbon surface depends on the amount of the acidic-surface groups present on the carbon surface and the pH of the solution. At higher pH values than $\text{pH}_{\text{zpc}} = 2$, the electrostatic attractive interaction between the negatively charged sites preponderantly produced on the surface of AC-DETADHBA and the positively-charged cations, La(III), was enhanced. In addition, incorporated donor atoms (O and N) presented in the Schiff's base product, DETADHBA, of the AC-DETADHBA adsorbent were capable to bind La(III) easily. Based on the above results, La(III) was selected among other metal ions for the study of other parameters controlling its maximum uptake on AC-DETADHBA under batch conditions and at the optimum pH value of 6.0. The optimum pH value of 6.0 was selected instead of 7.0 for the adsorption of La(III) by the AC-DETADHBA phase to avoid the formation of suspended gelatinous lanthanide hydroxides with buffer solutions at pH values beyond 6.0.

3.3. Determination of adsorption capacity

The capacity of the adsorbent is an important factor because it determines how much sorbent is required for a quantitative adsorption of specific amount of metal ion from solution (Madrakian et al., 2006). It is the maximum metal quantity taken up by 1 g of the solid phase and given by mg metal g^{-1} . In this study, the La(III) uptake capacity was investigated by varying amounts of La(III) and individually mixing them with 25 mg of AC-DETADHBA at pH 6.0 under batch procedure. Adsorption capacity can be calculated using Eq. (2) as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where q_e refers to the adsorbed La(III) by the AC-DETADHBA phase (mg g^{-1}), C_o and C_e are the initial and equilibrium concentrations of La(III) ion in solution (mg L^{-1}), respectively, V is the volume (L), and m is the weight of the AC-DETADHBA phase (g). To study the adsorption efficiency of the modified AC-DETADHBA phase toward La(III), the adsorption capacity was conducted twice, once with AC-COOH and once with AC-DETADHBA as shown in Fig. 3. From adsorption isotherm study, the adsorption capacity of AC-DETADHBA for La(III) was determined to be 144.80 mg g^{-1} (Fig. 3), which is comparable to those previously reported the adsorption capacity of La(III) with other adsorbents [120.00 mg g^{-1} (Chen, 2010), 154.70 mg g^{-1} (Vijayaraghavan et al., 2010) and 175.40 mg g^{-1} (Awwad et al., 2010)]. The adsorption capacity of La(III) on the AC-COOH was also determined to be 89.50 mg g^{-1} under the same batch conditions as well as that of La(III) with the AC-DETADHBA phase (Fig. 3). These results indicated that the adsorption capacity for La(III) was improved by 61.79%

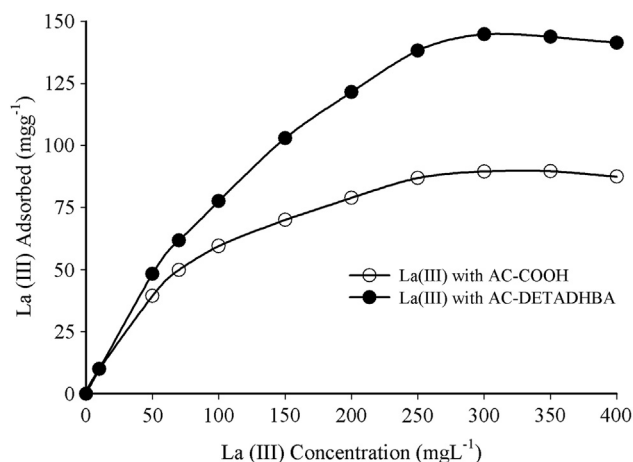


Figure 3 Adsorption profile of La(III) on 25 mg AC-COOH and AC-DETADHBA in relation to the concentration at pH 6.0 and 25 °C.

with the newly modified AC-DETADHBA phase as compared to AC-COOH.

3.4. Adsorption isotherm models

The distribution of metal ions between the liquid phase and adsorbent can generally be expressed by one or more of a series of adsorption isotherm models. They evaluate the nature of adsorption process. Langmuir and Freundlich adsorption isotherm models (Mckay, 1984; Ho et al., 1996) were used to interpret equilibrium isotherm data. The experimental data were well correlated to Langmuir equation. The Langmuir isotherm model is based upon an assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Langmuir classical adsorption isotherm can be expressed by the following equation (Langmuir, 1916):

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b \quad (3)$$

where C_e is the unadsorbed metal ion in the filtrate (mg mL^{-1}) when adsorption equilibrium is attained, and q_e represents the adsorbed metal ion by the adsorbate (mg g^{-1}). The symbols Q_o and b refer to Langmuir constants for the AC-DETADHBA phase. Q_o is related to the maximum La(III) adsorption capacity (mg g^{-1}), and b indicates the nature of adsorption and the shape of isotherm (L mg^{-1}). These constants can be calculated from a linear plot of C_e/q_e against C_e with a slope and intercept equal to $1/Q_o$ and $1/Q_o b$, respectively. In addition, essential characteristics of the Langmuir adsorption isotherm model can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as follows:

$$R_L = \frac{1}{(1 + bC_o)} \quad (4)$$

The R_L value indicates the type of the isotherm, and R_L values between 0 and 1 represent a favorable adsorption (Mckay et al., 1982).

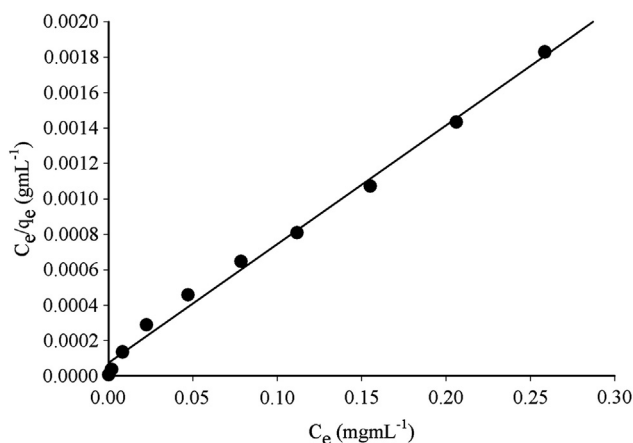


Figure 4 Langmuir adsorption isotherm model of La(III) adsorption on 25 mg AC-DETADHBA at pH 6.0 and 25 °C. Adsorption experiments were obtained at different concentrations (10–400 mg L^{-1}) of La(III) under batch conditions.

A linear plot was obtained from Langmuir isotherm equation based on the least square fit, confirming the validity of Langmuir adsorption isotherm model for the adsorption process (Fig. 4). As a result, adsorption isotherm data strongly supported that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. Calculated Langmuir constants Q_o and b are determined to be 149.25 mg g^{-1} and 0.1 L mg^{-1} , respectively. The correlation coefficient obtained from the Langmuir model is found to be $R^2 = 0.99$ for adsorption of La(III) on AC-DETADHBA, further indicating that the data were well fit with the Langmuir model. The R_L value of La(III) adsorption on the AC-DETADHBA is 0.03, supporting a highly favorable adsorption process based on the Langmuir model.

3.5. Effect of contact time

The effect of shaking time on the % extraction of La(III) is considered to be of significant importance to determine the possible discrimination order in the behavior of the AC-DET-

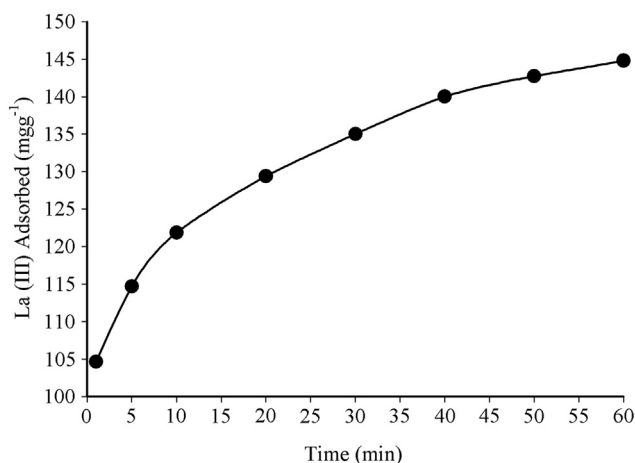


Figure 5 Effect of contact time on the adsorption of La(III) on AC-DETADHBA phase at pH 6.0 and 25 °C.

ADHBA adsorption toward La(III). In this study, different contact times ranging from 1.0 to 60.0 min were studied in order to perform the effect of shaking time on the La(III) adsorption capacity (Fig. 5). Results of the adsorption of La(III) on the AC-DETADHBA phase indicated that the AC-DETADHBA had rapid adsorption kinetics for La(III). As displayed in Fig. 5, over 121 mg g^{-1} La(III) was adsorbed on the AC-DETADHBA phase after only 10 min of the equilibrium periods. The amount of La(III) adsorbed was also raised up to more than 135 mg g^{-1} after 30 min until the maximum adsorption of AC-DETADHBA for La(III) was reached to 144.80 mg g^{-1} after 60 min.

3.6. Kinetic study

The effect of concentration on reaction rates is very important in understanding the reaction mechanism. The adsorption kinetic data of La(III) adsorption on the AC-DETADHBA phase were investigated in terms of pseudo first- and second-order kinetic equations (Rao et al., 2009) in order to quantify the changes in adsorption with time and to evaluate kinetic parameters. Kinetic models were used for goodness of fit for the experimental data using the correlation coefficient (R^2) as a measure of agreement between the experimental data. The pseudo first-order equation is as follows:

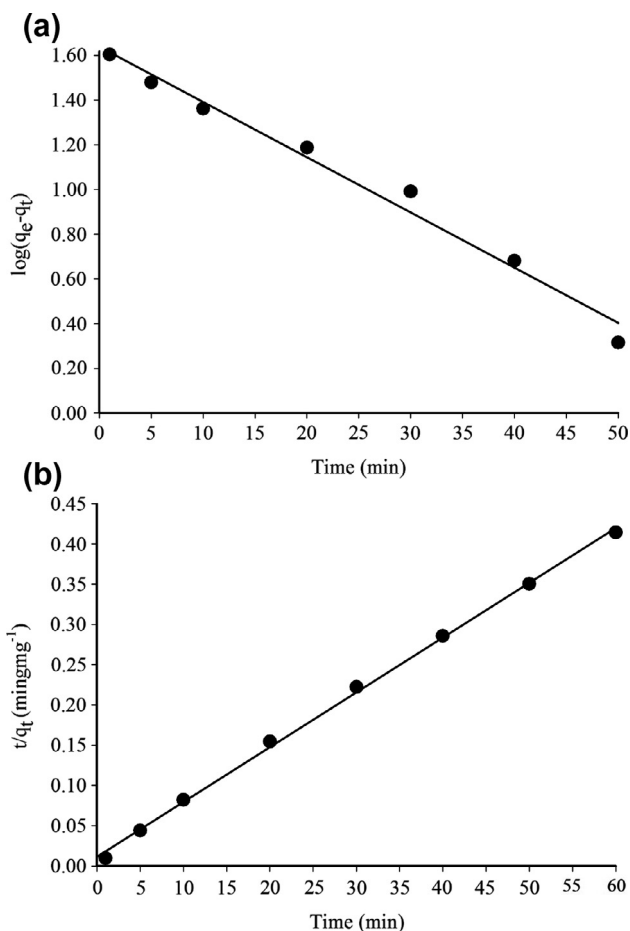


Figure 6 Pseudo (a) first- and (b) second-order adsorption kinetic models of La(III) uptake on 25 mg AC-DETADHBA at pH 6.0 and 25 °C.

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (5)$$

where k_1 (min^{-1}) is the rate constant of the pseudo first-order adsorption, q_t (mg g^{-1}) denotes the amount of adsorption at time t (min), and q_e (mg g^{-1}) is the amount of adsorption at equilibrium. The adsorption rate constant k_1 and adsorption capacity q_e for the AC-DETADHBA phase can be calculated from the slope and intercepts of the plot of $\log(q_e - q_t)$ against t (Fig. 6a).

The adsorption kinetic data of La(III) adsorbed on the AC-DETADHBA phase were also examined in terms of a pseudo second-order adsorption. Pseudo-second order model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate (Ho and McKay, 2000). The pseudo second-order equation can be written as follows:

$$t/q_t = 1/v_o + (1/q_e)t \quad (6)$$

where $v_o = k_2 q_e^2$ is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$), and k_2 ($\text{gmg}^{-1} \text{min}^{-1}$) corresponds to the rate constant of adsorption, q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, and q_t (mg g^{-1}) refers to the amount of metal ion on the surface of the adsorbent at any time t (min). The parameters v_o and q_e can be easily deduced from the intercept and slope, respectively, of a plot of t/q_t versus t (Fig. 6b). It is interesting to note that adsorption kinetic data were well fit with both pseudo first- and second-order kinetic models (Fig. 6a and b). Kinetic parameters were calculated for both pseudo first- and second-order kinetic models (Table 1).

However, it can be clearly observed that the value of q_e (147.06 mg g^{-1}), calculated from the pseudo second-order kinetic equation, is consistent with the results of adsorption isotherms. These results proved that the pseudo second-order model was more reliable and accurate in comparison to the pseudo first-order model and strongly supported the validity of Langmuir adsorption isotherm model.

3.7. Thermodynamic study

The investigation of thermodynamic parameters also provides a deeper mechanistic understanding of the adsorption of AC-DETADHBA for La(III). Therefore, the effect of temperature on the adsorption of 25 mg AC-DETADHBA for 5 mg L^{-1} La(III) was investigated at different temperatures from 298 to 338 K. The distribution adsorption coefficient (K_d) corresponding to the character of a metal ion adsorbed by an adsorbent (mL g^{-1}) can be obtained from the following equation (Han et al., 2005):

$$K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V}{m} \quad (7)$$

Table 1 Calculated kinetic parameters of the pseudo first- and second-order kinetic for La(III) adsorption on AC-DETADHBA phase at pH 6.0 and 25 °C.

| Kinetic isotherm | R^2 | k | q_e (mg g^{-1}) |
|---------------------|--------|-------|------------------------------|
| Pseudo first-order | 0.9831 | 0.057 | 43.60 |
| Pseudo second-order | 0.9986 | 0.004 | 147.06 |

Table 2 Calculated thermodynamic parameters of 5 mg L⁻¹ La(III) adsorption on 25 mg AC-DETADHBA at pH 6.0.

| ΔH° (kJ mol ⁻¹) | ΔS° (J mol ⁻¹ K ⁻¹) | ΔG° (kJ mol ⁻¹) | | |
|---|--|--|-------------|-------------|
| | | $T = 298$ K | $T = 313$ K | $T = 338$ K |
| -55.44 | -92.05 | -28.50 | -25.75 | -24.70 |

where C_i and C_e represent the initial and final concentrations (mg L⁻¹), respectively, V donates the volume of solution (mL), and m is the mass of adsorbent (g). Based on that, thermodynamic parameters of the standard enthalpy change (ΔH° , kJ mol⁻¹) and standard entropy change (ΔS° , J mol⁻¹ K⁻¹) were calculated, as shown in Table 2, from the slopes and intercepts of the linear variation of $\ln K_d$ with the reciprocal of the temperature ($1/T$) as follows:

$$\ln K_d = \Delta S^\circ / R - (\Delta H^\circ / RT) \quad (8)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the temperature in Kelvin. The standard Gibbs free energy change (ΔG° , kJ mol⁻¹), Table 2, was obtained from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

As can be observed from Table 2, calculated thermodynamic parameters were all negative. The negative values of ΔG° provide that the adsorption mechanism of AC-DETADHBA toward La(III) is a general spontaneous process and thermodynamically favorable. The reported negative value of ΔH° provides that the adsorption process of AC-DETADHBA toward La(III) is an exothermic process. The negative ΔS° indicates that the degree of freedom decreases at the solid-liquid interface during the adsorption of La(III) on AC-DETADHBA. These results strongly supported the data obtained from adsorption isotherm experiment and Langmuir adsorption isotherm model.

3.8. Desorption study

Desorption study for regeneration of the adsorbent is very important before the practical use of adsorbent for environmental applications to reduce the cost for the replacement of adsorbents in water and wastewater treatment. Therefore, the repeated availability performance of 5 and 10 mg L⁻¹ La(III) adsorption onto 25 mg AC-DETADHBA was evaluated. In this study, desorption of the adsorbed La(III) from the AC-DETADHBA adsorbent was achieved. The percent

Table 3 Percent recovery of La(III) on 25 mg AC-DETADHBA based on desorption study (N = 3) at 25 °C.

| La(III) initial concentration (mg L ⁻¹) | HCl concentration (mol L ⁻¹) | % Recovery |
|--|---|------------|
| 5 | 0.05 | 84.48 |
| | 0.10 | 96.37 |
| | 0.15 | 96.49 |
| | 0.05 | 83.14 |
| 10 | 0.10 | 93.25 |
| | 0.15 | 93.60 |

Table 4 Effect of coexisting ions on the percent extraction of 1 mg L⁻¹ La(III) adsorption on 25 mg AC-DETADHBA at pH 6.0 and 25 °C (N = 3).

| Coexisting ions | Concentration (mg L ⁻¹) | % Extraction of La(III) |
|---|--|----------------------------|
| Na ⁺ , K ⁺ , NH ₄ ⁺ | 2500 | 99.87 |
| Ca ²⁺ , Mg ²⁺ , Ba ²⁺ | 2500 | 98.65 |
| Co ²⁺ | 1200 | 96.99 |
| Cu ²⁺ | 1200 | 97.74 |
| Pb ²⁺ | 1200 | 98.41 |
| Mn ²⁺ | 1300 | 99.86 |
| Au ³⁺ | 1500 | 97.66 |
| Al ³⁺ | 1500 | 97.36 |
| Cl ⁻ , F ⁻ , NO ₃ ⁻ | 500 | 98.55 |
| CO ₃ ²⁻ , SO ₄ ²⁻ | 500 | 99.05 |
| PO ₄ ³⁻ | 300 | 98.28 |

Table 5 Percent extraction of 5, 10 or 50 mg L⁻¹ La(III) spiked in real water samples using 25 mg AC-DETADHBA at pH 6.0 and 25 °C (N = 3).

| La(III) spiked (mg L ⁻¹) | Tap water | Lake water | Seawater |
|--------------------------------------|-----------|------------|----------|
| 5 | 98.54 | 100 | 98.86 |
| 10 | 100 | 100 | 99.65 |
| 50 | 95.76 | 93.48 | 93.24 |

recovery of La(III) increased with an increase in the concentration of HCl from 0.05 to 0.15 mol L⁻¹ and then remained constant, as illustrated in Table 3.

3.9. Performance of method in analytical applications

3.9.1. Effect of coexisting metal ions

The effect of common coexisting ions on the adsorption of La(III) on the AC-DETADHBA phase was investigated. In these experiments, the interference of several cations and anions was studied under optimized batch conditions. Different solutions of 1 mg L⁻¹ of La(III) containing individual or mixed various salts and metal ions matrix were mixed with 25 mg of the newly modified AC-DETADHBA phase. The added interfering ions were treated according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of La(III) to be less than 90%. Results illustrated in Table 4 demonstrated that the presence of major cations and anions had no significant influence on the extraction of La(III) under the selected conditions. Thus, the selectivity of the proposed method is high enough to be applied to the determination of La(III) in environmental samples.

3.9.2. Application of the proposed method

The proposed method was implemented to the determination of La(III) in environmental water samples to confirm the applicability of the method to real environmental samples. Three types of water samples were used for the evaluation of the method, including lake water, seawater and tap water, collected from Jeddah in Saudi Arabia. Water samples were analyzed using the standard addition method under the same

batch conditions as above. The % extraction of different amounts of La(III) was calculated, as displayed in Table 5. As can be noted the extraction of La(III) in spiked water samples was satisfactory for trace analysis and apparently demonstrated that the method is reliable, feasible and suitable for analyzing real samples.

4. Conclusion

The proposed method based on Schiff's base (DETADHBA) immobilized on activated carbon as an adsorbent was simple and rapid for selective separation and determination of La(III) in different water samples. The newly modified AC-DETADHBA phase not only had the efficiency toward a selective adsorption of La(III) but also provided high uptake capacity of La(III). Results obtained from adsorption isotherm models indicated that Langmuir adsorption isotherm model best described the metal adsorption process. Kinetic isotherm results demonstrated that the adsorption of La(III) on the AC-DETADHBA phase obeyed a pseudo second-order kinetic reaction. The adsorption mechanism of AC-DETADHBA toward La(III) is a general spontaneous process and thermodynamically favorable, and the adsorption process is found to be exothermic in nature. The AC-DETADHBA adsorbent and AC related materials would be useful for the economic treatment of real water samples, as confirmed by desorption study. Further, most common coexisting anions and cations did not interfere with La(III) under optimum conditions. This method is an effective approach in providing a selective separation and determination of La(III) from the complex matrices including environmental water samples. Finally, the findings of the present study may have significant implications for different applications.

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