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Adsorption Behavior of Lanthanum on Modified Nanoporous Aluminosilicates

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Abstract

In this paper, nanoporous MCM-41 has been modified by incorporation of aluminum ion as a rapid, simple and inexpensive method for modification. The adsorbent is characterized using powder X-ray diffraction and nitrogen adsorption-desorption isotherm data. The distribution coefficient of lanthanum ion on the nanoporous aluminosilicates has been enhanced with the increase of the aluminum in the framework of the adsorbent. Adsorption behavior of lanthanum on the Al10MCM-41 adsorbent has been studied and the Langmuir, Freundlich and Redlich-Peterson isotherms were applied to represent the adsorption process. Langmuir isotherm fits the experimental data quite well. The effects of pH and shaking time have also been studied by batch method. The adsorption capacity is very high in the pH range of 3-8 and decreases with decreasing of the pH value. The adsorption of lanthanum onto Al10MCM-41 follows pseudo-second-order kinetics.

Keywords: Adsorption behavior; Aluminosilicate; Lanthanum; Nanoporous.

1. Introduction

Lanthanum has special attention due to its technological importance because of increasing demands for advanced new materials [1]. Current applications of lanthanum as a pure element or in association with other compounds are in super alloys, catalysts, and special ceramics [2].

Many conventional methods exist for separation and/or removing heavy metals, radionuclides and lanthanides from aqueous solution [3]. Those include adsorption, ion exchange, coagulation, floatation, hyper-

filtration, chemical precipitation, and reverse osmosis.

MCM-41 is a nanoporous silicate featuring hexagonally packed arrays of one-dimensional, cylindrical pores, with a uniform pore distribution, large specific surface area and large pore volume [4, 5]. The characteristics of the MCM-41 suggest their potential use in the fields of adsorption, catalysis and nanotechnology due to the large specific surface area and regular porosity [6, 7]. The modification of the nanoporous materials by various functional groups has received much

attention in adsorption and separation science [8-11]. The modification of MCM-41 by organic modifier is an expensive method, but modification by inorganic metal ions is rapid, simple and inexpensive method.

In this paper, the adsorption studies of lanthanum on modified nanoporous aluminosilicate are reported. The adsorption isotherm, adsorption kinetics, capacity and pH effect have been studied in detail. The equilibrium adsorption data are analyzed by using Langmuir, Freundlich and Redlich-Peterson isotherms.

2. Experimental

2.1. Reagents

All the chemicals used were of analytical grade from Merck, except cetyltrimethylammonium bromide (CTAB) which was supplied by Aldrich (U.K.).

2.2. Apparatus

A Philips X'pert powder diffractometer system with Cu-K α ($\lambda=1.541 \text{ \AA}$) radiation was used for X-ray studies. XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) at a scan rate of 0.02° (2θ)/sec. Nitrogen adsorption studies were made with a Quantachrome NOVA 2200e instrument. Nitrogen adsorption and desorption isotherm of the adsorbent was determined at 77 K and specific surface area was determined by applying the BET equation to the isotherm [12]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [13]. pH measurements were made with a Schott CG841 pH-meter (Germany). Quantitative determination of inorganic ions was made using an inductively coupled plasma-optical emission spectrometer (ICP-OES) of Varian Liberty 150-Axial. A waterbath shaker model CH-4311 (Infors AG)

was used in determination of distribution coefficients.

2.3. Preparation of nanoporous aluminosilicate

Nanoporous aluminosilicates were prepared as reported earlier [14]. Out of Al10MCM-41, Al20MCM-41, Al40MCM-41 and Al80MCM-41 due to favorable adsorption behavior, Al10MCM-41 is chosen for present studies.

2.4. Procedure for adsorption studies

Adsorption studies of the lanthanum ions on the Al10MCM-41 adsorbent was carried out using batch method. In this procedure, 50 mg of adsorbent material was added to a 25 mL buffered solution of 5-100 mg/L ions. The pH of the solution was adjusted with sodium acetate/nitric acid pH 2-6 and K₂HPO₄/HCl for pH 6-8. The suspension was stirred for preselected period of time using a water shaker bath. Then it was filtered and the amount of lanthanum ion was determined by ICP. The percentage of lanthanum ions that was adsorbed on the adsorbent (%uptake) was determined by comparing its concentrations before and after adsorption (C_i (mg/L) and C_f (mg/L)) respectively.

$$\%uptake = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

The distribution ratio (K_d) of lanthanum between the adsorbent and aqueous solution (mL/g) was also determined by following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m} \quad (2)$$

Where V is the volume of the initial solution and m is the mass of adsorbent material.

2.5.1. Effect of pH

The effect of solution pH on the adsorption behavior was determined at a constant temperature of 25 °C. In batch experiments, 50 mg of Al10MCM-41 adsorbent was equilibrated with 25 mL of the buffer solution containing 20 mg/L of lanthanum ions at various pHs for 3 h.

2.5.2. Kinetic study

In a typical kinetics test, 50 mg of the adsorbent was added to 20 mL of 20 mg/L of lanthanum solutions at selected pH. The suspension was agitated for different periods of time (from 10 to 300 min) using waterbath shaker.

2.5.3. Adsorption isotherm

In several batch experiments, 50 mg portions of the Al10MCM-41 adsorbent was equilibrated with varying concentrations of lanthanum ions (initial concentration range from 5 to 100 mg/L) at selected pH. The suspensions were agitated for 3 h using a water bath shaker. Then, the supernatant solutions were removed and filtered. The concentrations of lanthanum ion (F, $\mu\text{mol/L}$) in solution were determined with ICP and the amounts of adsorbed lanthanum on adsorbent (B, mmol/g) were calculated from these values.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. XRD analysis

The XRD patterns of the calcined MCM-41, Al10MCM-41 is presented in Fig. 1. The XRD patterns of samples show a strong diffraction at 2θ smaller than 3° along with presence of small peaks that confirms the formation of nanoporous MCM-41 [4, 5]. This result is characteristic of hexagonal pore structure.

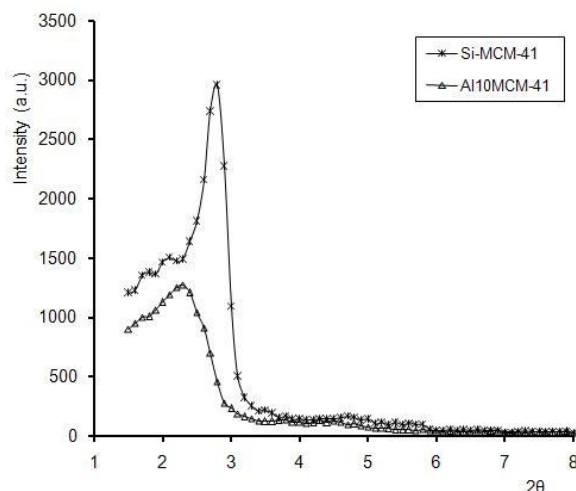


Fig. 1. XRD patterns of the calcined MCM-41 and Al10MCM-41.

3.1.2. Nitrogen sorption isotherms

The nitrogen adsorption isotherms and corresponding pore size distribution of the MCM-41, Al10MCM-41 are given in Fig. 2. N_2 adsorption-desorption isotherms for MCM-41, Al10MCM-41 showed irreversible type IV adsorption isotherms as defined by IUPAC (Fig. 2). The overall shape of the adsorption/desorption isotherms remained unchanged, and the pronounced steps of capillary condensation in primary nanopores were evident, indicating that the ordering of the MCM-41 support was not affected by the modification. Table 2 shows the specific surface area, pore volume and pore size of the samples.

3.2. Adsorption studies

The distribution coefficient of lanthanum ion on the nanoporous aluminosilicates is increased with increasing amount of aluminum in the framework of the adsorbent. It is maybe due to the fact that, in nanoporous aluminosilicate, the framework exhibits negative charges as a consequence of the incorporation of trivalent aluminum atoms instead of tetravalent silicon. Therefore nanoporous aluminosilicate can act as an inorganic cation exchanger [14]. www.SID.ir

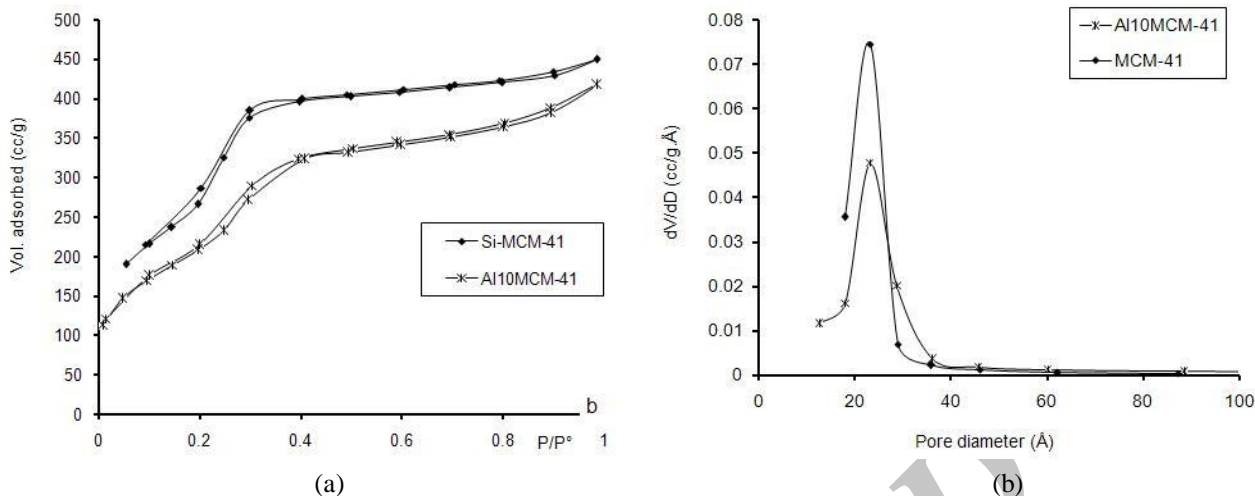


Fig. 2. (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution for calcined MCM-41 and Al10MCM-41.

Table 1. Distribution coefficients of lanthanum ion on the mesoporous aluminosilicates.

Adsorbent	MCM-41	Al180MCM-41	Al40MCM-41	Al20MCM-41	Al10MCM-41
Si/Al mole ratio (found)	-	80 (37.2)	40 (32.0)	20 (19.7)	10 (16.4)
K_d value (mL/g) for La	41	226	1120	3800	11875

Table 2. Physical characteristics of MCM-41 and Al10MCM-41 adsorbents

Adsorbent	XRD d_{100} (Å)	Unit cell parameter ^a (a_0) (Å)	Pore volume (cc/g)	BET surface area (m ² /g)	Average pore diameter (Å)
Al10MCM-41	38.3	42.3	0.73	762	24.4
MCM-41	31.8	42.5	0.74	1120	21.7

a. Calculated from the equation $a_0 = 2d_{100} / \sqrt{3}$.

3.2.1. Effect of pH

Based on hydrolysis constants of lanthanum, up to pH 6, no hydrolysis takes place and all the lanthanum would be present as La^{3+} ions [15]. The adsorption of lanthanum was studied in the pH range of 2-8. As seen in Fig. 3, the adsorption of lanthanum is high (about 70%), even, in pH=2.0. It is maybe due to the fact that, after incorporation of aluminum, nanoporous aluminosilicate can act as an inorganic cation exchanger. The adsorption of lanthanum increased until to about 100% with increasing pH of solution. It is maybe due to the fact that, in this acidic region, silanol groups onto pores of Al10MCM-41 were as SiOH_2^+ . So, in pH=2.0, it was found that La showed little adsorption toward Al10MCM-41.

After $\text{pH} \geq 2$ with an increase in basicity of the aqueous solution, Si-OH_2^+ as a cation gradually converted to a neutral Si-OH by reacting with OH^- . While La^{3+} gradually hydrolyzed to La(OH)^{2+} by connecting with OH^- . Since La(OH)^{2+} was a complexible species with the neutral Si-OH , so, La(III) showed the adsorption towards Al10MCM-41 adsorbent with an increase in pH value. The next experiments in this study were carried out at natural pH (6.8)

3.2.2. Kinetic study

The adsorption kinetics experiments were carried out at an initial La concentration of 20 mg/L and at natural pH (6.8). The adsorption kinetic results are shown in Figs 4 & 5

observed that the adsorption equilibrium is attained fast in about 10 min (for 91% adsorption). The fast adsorption rate suggests that the silanol groups are readily available and easily accessible probably because the uniform nanoporous channels of the A110MCM-41 adsorbent facilitate the La ions transportation in the process.

In order to clarify the adsorption kinetics of lanthanum onto A110MCM-41, Lagergren's pseudo-first-order and pseudo-second-order kinetic models were applied to experimental data. The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

Where q_t and q_e (mg/g) are the amount of metal ions adsorbed at t (min) and equilibrium respectively, and K_1 is the rate constant of the equation (min^{-1}). The adsorption rate constant (K_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t . The plots of $\ln(q_e - q_t)$ versus t for the Lagergren-first-order model does not fit a pseudo-first-order kinetic model and the R^2 value for this model is low (0.904) for the lanthanum adsorption by A110MCM-41. Experimental data were also applied to the pseudo-second-order kinetic mode which is given in the following form

$$t / q_t = 1/(K_2 q_e^2) + (1/q_e)t \quad (4)$$

Where K_2 (g/mg.min) is the rate constant of the second-order equation, q_e is the amount of adsorption equilibrium (mg/g) and q_t (mg/g) the amount of adsorption time t (min). The linear plots of t/q_e versus t for pseudo-second-order model for the adsorption of lanthanum onto A110MCM-41 at 25 °C are shown in Fig. 5. The rate constants (K_2), correlation coefficient of the plots together with the q_e value is given in Table 3. These results suggest that the adsorption of lanthanum onto A110MCM-41 follows well the pseudo-second-order kinetics.

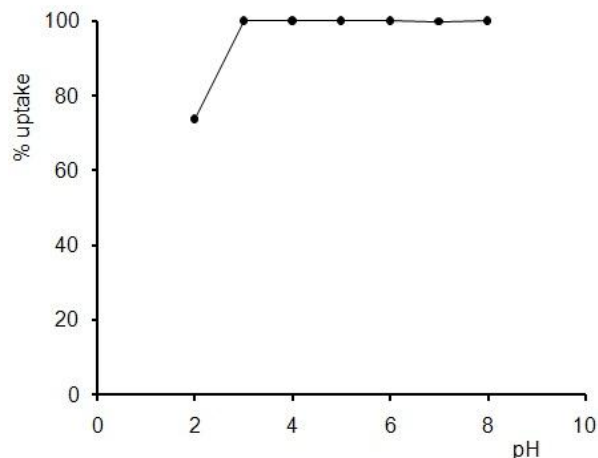


Fig. 3. Effect of pH on adsorption of La onto the A110MCM-41 adsorbent.

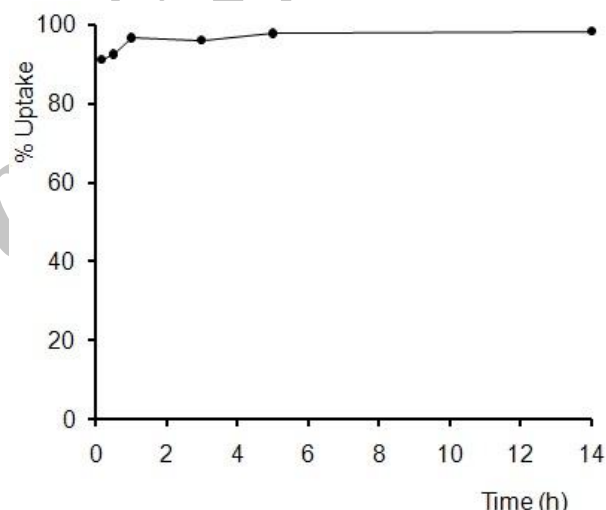


Fig. 4. Effect of contact time on adsorption of La onto the A110MCM-41 adsorbent at 25 °C and $C_0=20 \mu\text{g/mL}$.

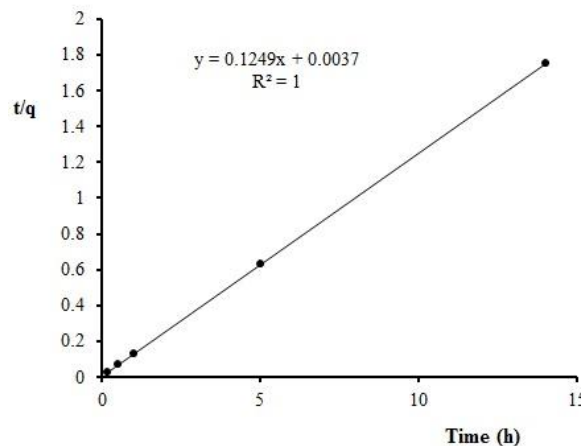


Fig. 5. Pseudo-second-order adsorption kinetic of La onto the A110MCM-41 adsorbent.

Table 3. Parameters for adsorption of lanthnum onto A110MCM-41 driven from the pseudo-first and second-order models

pseudo-first-order			pseudo-second-order			
q_e (mg/g)	K_1 (min ⁻¹)	R^2	K_2 (g/mg.min)	h (mg/g.min)	q_e (mg/g)	R^2
1.265	1.213	0.9039	4.216	270.27	8.006	1

3.2.3. Adsorption isotherm

The adsorption isotherm is plotted in Fig. 6. The isotherm belongs to the L-type of the classification proposed by Giles [16]. Among various binding models, Langmuir and Freundlich isotherms have been frequently employed to describe experimental data of adsorption isotherms. The Langmuir adsorption isotherm is mathematically expressed as;

$$B = \frac{K_l(q_{\max})F}{1 + K_l F} \quad (5)$$

Where B (mmol/g) is amount of analyte bound to adsorbent, F (μ mol/L) is equilibrium concentration of adsorbate in solution. q_{\max} is maximum adsorption capacity (mmol/g) and K_l is constant for a given adsorbate and adsorbent at a particular temperature. Here, the experimental isotherm data (F and B) were successfully fitted to the Langmuir isotherm. Langmuir equation is the most common model employed to describe the adsorption process in homogenous systems. As seen in Fig. 6, it is observed that the adsorption data fit the Langmuir equation well and the equation constant values q_{\max} and b, calculated from the experimental data (Table 4). For comparative purposes the experimental data have been fitted to the well-known Freundlich equation:

$$B = K_f F^m \quad (6)$$

K_f and m are constants for a given adsorbate and adsorbent at a particular temperature. From the values of R^2 summarized in Table 4 it may be calculated that the Langmuir equation provides a better fitting than the Freundlich one.

The Redlich-Peterson equation is a combination of Langmuir and Freundlich models. The Redlich-Peterson isotherm as reported the original article is given by [17]:

$$B = \frac{K_{rp}F}{1 + P_e F^g} \quad (7)$$

Where K_{rp} and P_e are the Redlich-Peterson constant and g is the exponent, which lies between 0 and 1.

When the exponent $g=1$, the Langmuir equation results, given by (eq. 5). When the $g=0$, Redlich-Peterson equation transform to Henry's law equation. The Redlich-Peterson isotherm following the Freundlich isotherm for the constants K_{rp} and $P_e \gg 1$ and $g=1$ [18].

Table 4 shows that K_{rp} and $P_e < 1$ and $g=0.95$. Therefore the Redlich-Peterson isotherm also confirms that the Langmuir equation provides a better fitting than the Freundlich one.

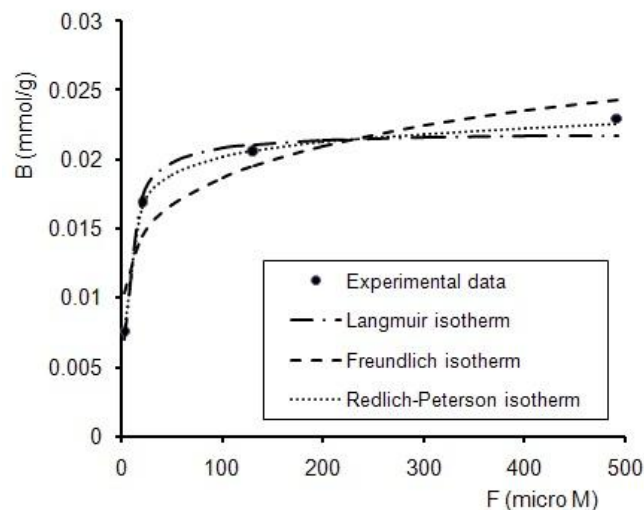


Fig. 6. Experimental adsorption data (points) and Langmuir, Freundlich and Redlich-Peterson isotherms fit (lines).

Table 4. Fitting parameters of adsorption model isotherms.

Fitting parameters				
Langmuir	R^2	K_l (L/mmol)	q_{max} (mmol/g)	
	0.984	0.180	0.022	
Freundlich	R^2	K_f (mmol/g μ M)	m	
	0.883	0.009	0.164	
Redlich-Peterson	R^2	K_{rp} (L/g)	P_e (L mg $^{-(1-1/K_{rp})}$)	g
	0.998	0.005	0.309	0.951

4. Conclusions

Nanoporous aluminosilicate (Al10MCM-41) with Si/Al mole ratio 10 has been successfully synthesized by a non-thermal route and is a promising adsorbent for La removal from aqueous solutions. The modification of MCM-41 by aluminum ion is rapid, simple and inexpensive method compared the modification by organic modifiers. The excellent properties of nanoporous aluminosilicate endow the adsorbent with an improved adsorption ability of 3.1 mg/g and fast kinetics of less than 10 min for La.

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