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Adsorption behavior studies of Cerium on modified Mesoporous Aluminosilicate

ABSTRACT

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In this paper, the adsorption of cerium on modified Mesoporous aluminosilicate (with Si/Al mole ratio of 10) was studied. The effects of pH, contact time, initial concentration of cerium on adsorption of cerium were investigated. The adsorption capacity was high in the pH range of 4-8 and decreases with decreasing of the pH value. The Langmuir and Freundlich isotherms were applied to represent the adsorption process. Both Langmuir and Freundlich isotherms fit the experimental data quite well. The Langmuir monolayer capacity of the adsorbent was 0.032 mmol.g⁻¹.

Keywords: *Mesoporous; MCM-41; Aluminosilicate; Adsorption studies; Cerium.*

INTRODUCTION

Cerium is one of the cheapest and most abundant rare earths. However, high purity is usually required for its utilization in industry where it is used, for example, for sulfur control in steels, pyrophoric alloys, ceramic, catalyst support, and polishing powders, etc. Cerium is accompanied by other rare earth elements in its minerals, as well as in the spent nuclear fuel [1]. Radioisotopes of cerium are marked products of nuclear fission and hence, they are a common constituent of liquid radioactive wastes arising from nuclear power operations [2]. Many methods have been used to remove the heavy metals from effluents namely oxidation, membrane filtration, coagulation, adsorption, ion exchange, and precipitation, but few of them were accepted due to cost, low efficiency, inapplicability to a wide variety of pollutants. Unfortunately there is a very limited report for removal of cerium ions from aqueous solutions [3,4]. MCM-41 is a mesoporous silicate featuring hexagonally packed arrays of one-dimensional, cylindrical pores, with a uniform pore distribution, large specific surface area and large pore volume [5,6].

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The characteristic of such mesoporous silicates suggest their potential use in the fields of adsorption, catalysis and nanotechnology due to the large specific surface area and regular porosity [7,8]. The modification of the mesoporous materials by various functional groups has received much attention in adsorption and separation science [9-12]. 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 cerium on modified mesoporous aluminosilicate (with Si/Al mole ratio of 10) have been reported. The time effect, pH effect, adsorption isotherm and sorption capacity have also been studied in detail.

EXPERIMENTAL

Reagents

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

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 [13]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [14]. 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 water shaker bath model CH-4311 (Infors AG) was used in determination of distribution coefficients.

Preparation of mesoporous aluminosilicate

Mesoporous aluminosilicate (with Si/Al mole ratio of 10, Al10MCM-41) was prepared as reported earlier [15]. In a typical synthesis, 0.6 g CTAB was dissolved in 23 g of demineralized water, the mixture was stirred for 15 min (140 rpm) after that 3 g of sodium silicate was added to the mixture and it was further stirred for 30 min. The pH of mixture was adjusted to 9 by adding sulfuric acid (2 M). Then solution of $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ containing 0.45 g in 50 mL demineralized water was added dropwise and stirring was continued for 4 h. A bulky white gelatinous precipitate was formed. The resulting gel was transferred to a teflon vessel and was left for 24 h at room temperature. Then the product was filtered, washed thoroughly with demineralized water and then dried at 50°C for 12 h. The material was calcined at 540°C for 6 h. The calcined material was digested in 0.1M HNO_3 for 24 h and then washed demineralized water. A sample only with silica in the framework was also prepared under the same conditions; it was denoted as MCM-41.

Procedure for adsorption studies

Adsorption studies of the cerium ion on the Al10MCM-41 adsorbent were carried out using batch method. In this procedure, 50 mg of adsorbent material was added to 10 mL buffered solution of 5-100 mg L^{-1} ions. The pH of the solution was adjusted with sodium acetate/nitric acid pH 2-6 and $\text{K}_2\text{HPO}_4/\text{HCl}$ 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 cerium ion was determined by ICP. The percentage of cerium ions that was adsorbed on the adsorbent (%uptake) was determined by comparing its concentrations before and after adsorption (C_i (mg L^{-1}) and C_f (mg L^{-1})) respectively.

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

The equilibrium adsorption (q_e , mmol g^{-1}) was also determined by following equation:

$$q_e = (C_i - C_f) \times \frac{V}{m} \quad (1b)$$

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

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 10 mL of the buffer solution containing 20 mg L⁻¹ of cerium ions at various pHs for 3 h.

Kinetic study

In a typical kinetics test, 50 mg of the adsorbent was added to 10 mL of 20 mg L⁻¹ of cerium solution at selected pH (6.7). The suspension was agitated for different periods of time (from 10 min to 14h) using water shaker bath.

Adsorption isotherm

In several batch experiments, 50 mg of the Al10MCM-41 adsorbent were equilibrated with varying concentrations of cerium ions (initial concentration range from 5 to 100 mg L⁻¹) at selected pH (6.7). The suspensions were agitated for 3 h using a water bath shaker. Then, the supernatant solutions were removed and filtered. The concentrations of cerium ion (F , μM) in solution were determined with ICP and the amounts of adsorbed cerium on adsorbent (B , mmol g⁻¹) were calculated from these values.

RESULTS AND DISCUSSION

Characterization of adsorbent

- **XRD analysis**

The XRD patterns of the calcined MCM-41 and Al10MCM-41 are presented in Figure 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 mesoporous MCM-41[5,6]. This result is characteristic of hexagonal pore structure. The slight increase in d-spacing and unit cell parameters of Al-MCM-41 compared to its pure silica analog (Table 1) suggests the presence of aluminium in the framework. The increase in unit cell parameter on Al incorporation is probably due to the replacement of shorter Si–O bonds by longer Al–O bonds in the structure [15].

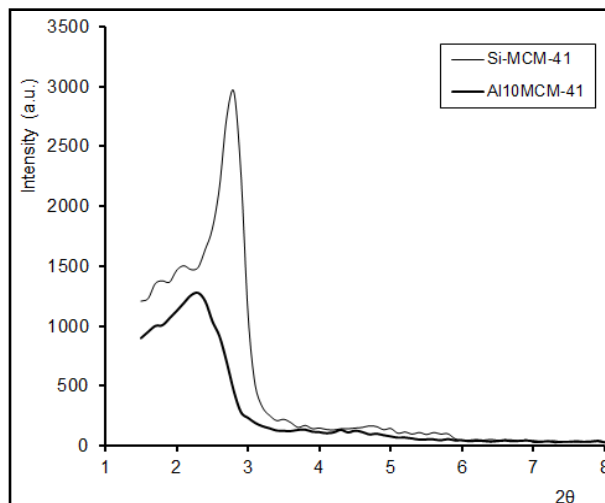


Fig. 1. XRD patterns of the calcined MCM-41 and Al10MCM-41

Table 1. Physical characteristics of MCM-41 and Al10MCM-41

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	792	24.4
MCM-41	31.8	36.7	0.74	1120	21.7

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

- **Nitrogen adsorption isotherms**

The nitrogen adsorption isotherms and corresponding pore size distribution of the MCM-41 and Al10MCM-41 are given in Figure 2a & 2b. N₂ adsorption-desorption isotherms for MCM-41 and Al10MCM-41 showed irreversible type IV adsorption isotherms as defined by IUPAC (Figure 2a). The overall shape of the adsorption-desorption isotherms remained unchanged, and the pronounced steps of capillary condensation in primary mesopores were evident, indicating that the ordering of the MCM-41 support was not affected by the modification. Table-1 shows the specific surface area, pore volume and pore size of the samples.

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Adsorption studies

As reported in our previous work, the distribution coefficient of cerium ions on the mesoporous aluminosilicates (with Si/Al mole ratio of 10, 20, 40 and 80) is increased with increasing amount of aluminum in the framework of the adsorbent [16]. It is maybe due to the fact that, in mesoporous aluminosilicate, the framework exhibits negative charges as a consequence of the incorporation of trivalent aluminum atoms instead of tetravalent silicon. Therefore mesoporous aluminosilicate can act as an inorganic cation exchanger.

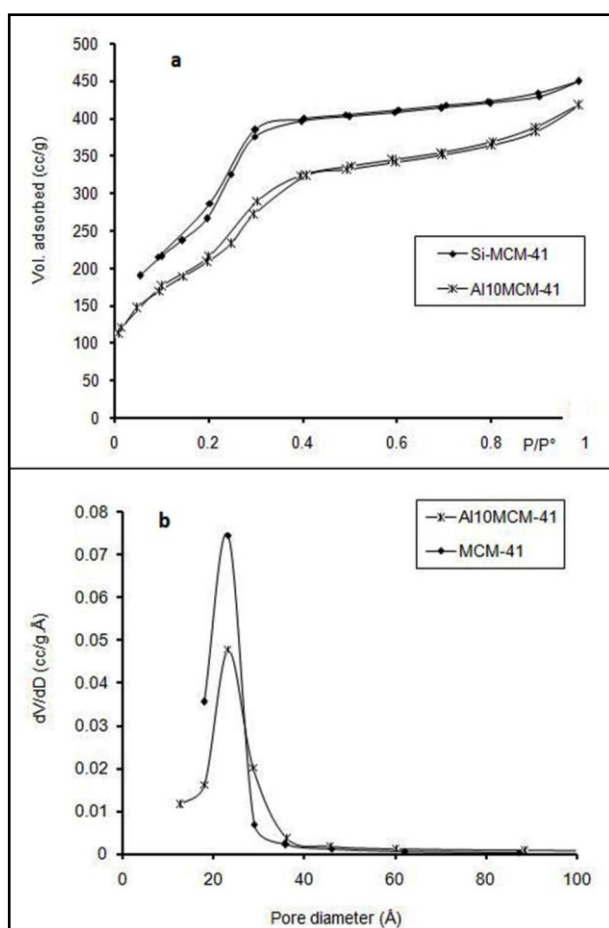


Fig. 2. (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution for calcined MCM-41 and Al10MCM-41

- **Effect of pH**

Based on hydrolysis constants of cerium, up to pH 5, no hydrolysis takes place and all the cerium would be present as Ce^{3+} ions [17]. The adsorption of cerium was studied in the pH range of

2-8. As seen in Figure 3, the adsorption of cerium is high (about 70%), even, in pH=2.0. It is maybe due to the fact that, after incorporation of aluminum, mesoporous aluminosilicate can act as an inorganic cation exchanger. The adsorption of cerium 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 MCM-41 were as SiOH_2^+ . So, in pH=2.0, it was found that Ce(III) showed little adsorption toward MCM-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 Ce^{3+} gradually hydrolyzed to $\text{Ce}(\text{OH})^{2+}$ by connecting with OH^- . Since $\text{Ce}(\text{OH})^{2+}$ was a complexible species with the neutral Si-OH, so, Ce(III) showed the adsorption towards MCM-41 adsorbent with an increase in pH value. On other hand, the acidity of Al-MCM-41 increases with increase in Al incorporation into the MCM-41 framework [18]. Therefore with increasing acidic site in the framework, ion exchange capacity will increase. The next experiments in this study were carried out at natural pH (6.7).

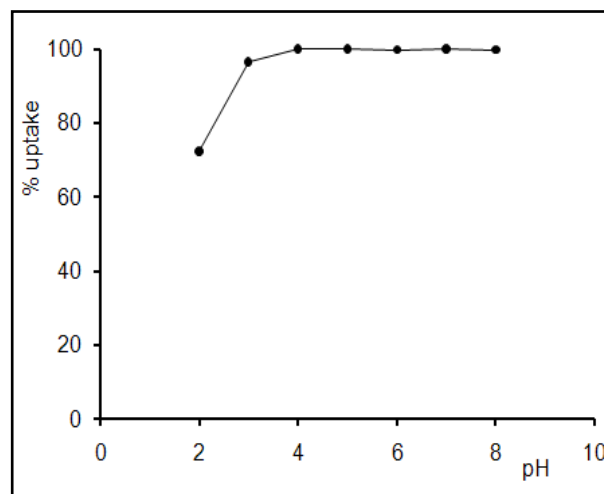


Fig. 3. Effect of pH on adsorption of Ce onto the Al10MCM-41 adsorbent

- **Kinetic study**

The adsorption kinetics experiments were carried out at an initial Ce concentration of 20 mg L^{-1} and at natural pH (6.7). The adsorption kinetic results are shown in Figure 4. It is observed that the adsorption equilibrium is attained fast in about 1 h.

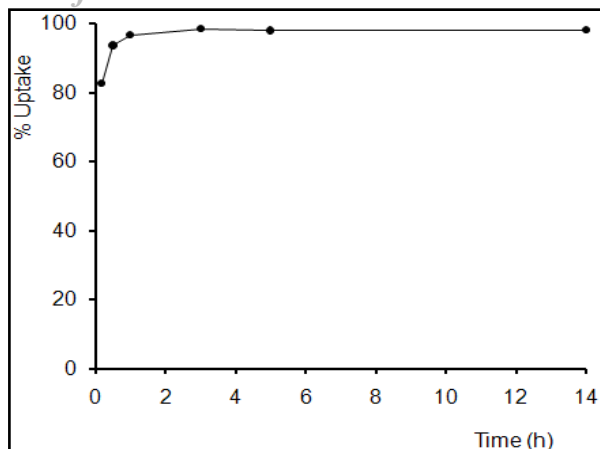


Fig. 4. Effect of contact time of sorbate on adsorption of Ce onto the Al10MCM-41 adsorbent at 25 °C and $C_0=20 \text{ mg L}^{-1}$.

• **Adsorption isotherm**

The adsorption isotherm is plotted in Figure 5. The isotherm belongs to the L-type of the classification proposed by Giles [19]. 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;

$$B = \frac{K_l(q_{max})F}{1 + K_l F} \quad (2a)$$

Where $B \text{ (mmol.g}^{-1}\text{)}$ is amount of analyte bound to adsorbent, $F \text{ (}\mu\text{M)}$ is equilibrium concentration of adsorbate in solution. q_{max} is maximum adsorption capacity $\text{(mmol.g}^{-1}\text{)}$ 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 Figure 5, 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 2). For comparative purposes the experimental data have been fitted to the well-known Freundlich equation:

$$B = K_f F^m \quad (2b)$$

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 2 it may be calculated that both equations fit reasonably well the experimental data. The Langmuir monolayer capacity of the sorbent was $0.032 \text{ mmol.g}^{-1}$.

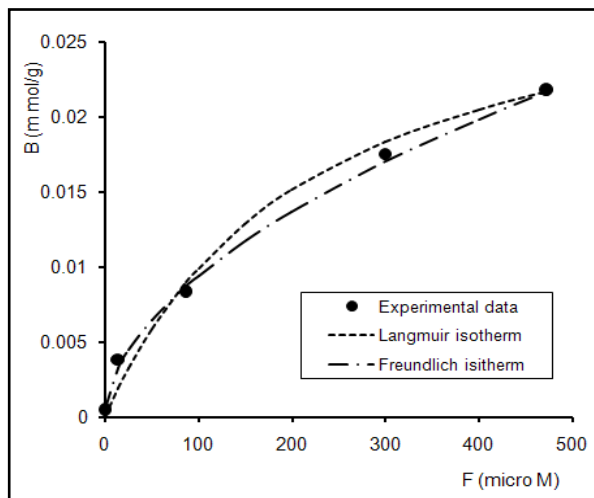


Fig. 5. Experimental adsorption data (points) and Langmuir and Freundlich isotherms fit (lines).

Table 2. Fitting parameters of adsorption model isotherms

	Fitting parameters		
Langmuir	R^2 0.984	$K_l \text{ (L mmol}^{-1}\text{)}$ 0.004	$q_{max} \text{ (mmol g}^{-1}\text{)}$ 0.032
Freundlich	R^2 0.998	$K_f \text{ (mmol g}^{-1}\text{ }\mu\text{M}^{-1}\text{)}$ 0.0008	m 0.538

CONCLUSIONS

Mesoporous aluminosilicate (Al10MCM-41) with Si/Al mole ratio of 10 has been successfully synthesized by a non-thermal route and is a promising adsorbent for Ce removal from aqueous solutions. The modification of MCM-41 by aluminum ion is rapid, simple and inexpensive method in comparison with the modification by organic modifiers.

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