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Adsorption behavior of cadmium on modified mesoporous aluminosilicates

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Abstract

In this study, mesoporous 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 cadmium ion on the mesoporous aluminosilicates has been enhanced with the increase of the aluminum in the framework of the adsorbent. Adsorption behavior of cadmium on the Al10MCM-41 and Al20MCM-41 adsorbents has been studied and experimental adsorption isotherm is successfully described by Langmuir model. The maximum adsorption cadmium capacity was 11.5 mg g⁻¹. The effects of pH and adsorption kinetics have also been studied by batch method and the result shows pH of solution hasn't any effect on cadmium adsorption.

Keywords: Mesoporous; Aluminosilicate; Adsorption behavior; Cadmium.

1. Introduction

Intramolecular proton-transfer The heavy metal pollution represents a significant environmental problem arising from its toxic effects and accumulation throughout the food chain. The removal and recovery of heavy metals from wastewater is significant in the protection of the environment and human health [1].

Cadmium is widely used and extremely toxic in relatively low dosages, is one of the principal heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells [2]. The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms. Eventually, the toxic element will get transferred to humans via the food chain. Human beings have reported nausea and vomiting at a level of 15 mg/L of cadmium, with no adverse effects at 0.05 mg/L [3].

The conventional methods used for metal removal include chemical precipitation [4], ion-exchange [5], membrane filtration [6] activated carbon adsorption [7], etc. However these treatment methods become less effective and more expensive when situations involving high volumes and low metal concentrations are encountered [8]. The application of membrane processes and activated carbon are also restricted because they are cost intensive.

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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 [9,10]. 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 [11-13]. The modification of the mesoporous materials by various functional groups has received much attention in adsorption and separation science [14-17]. 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 cadmium on modified mesoporous aluminosilicate are reported. The adsorption isotherm, capacity and pH effect have also 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 [18]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [19]. 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 mesoporous aluminosilicate

Mesoporous aluminosilicates were prepared as reported earlier [20]. Out of Al10MCM-41, Al20MCM-41, Al40MCM-41 and Al80MCM-41 due to favorable adsorption behavior, Al10MCM-41 is choose for present studies.

2.4. Procedure for adsorption studies

Adsorption studies of the cadmium ions on the Al10MCM-41 adsorbent were carried out using batch method. In this procedure, 50 mg of absorbent material was added to a 25 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 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 cadmium ion was determined by ICP. The percentage of cadmium 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.

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

The distribution ratio (K_d) of cadmium between the adsorbent and aqueous solution (mL g^{-1}) was also determined by following equation:

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

Where V is the volume of the initial solution and mL 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 A110MCM-41 adsorbent was equilibrated with 25 mL of the buffer solution containing 20 mg L^{-1} of cadmium 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^{-1} of cadmium 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 A110MCM-41 adsorbent was equilibrated with varying concentrations of cadmium ions (initial concentration range from 5 to 100 mg L^{-1}) 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 cadmium ion (F, μM) in solution were determined with ICP and the amounts of adsorbed cadmium on adsorbent (B, mmol g^{-1}) 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, A110MCM-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 mesoporous MCM-41 [9, 10]. This result is characteristic of hexagonal pore structure.

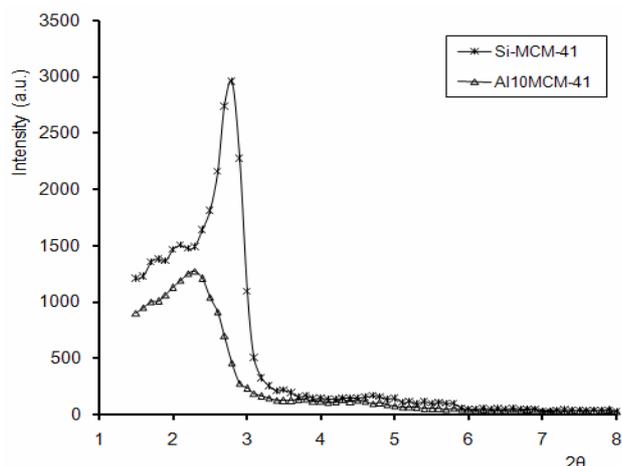


Fig. 1. XRD patterns of the calcined MCM-41, Al10MCM-41.

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. N₂ 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 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.

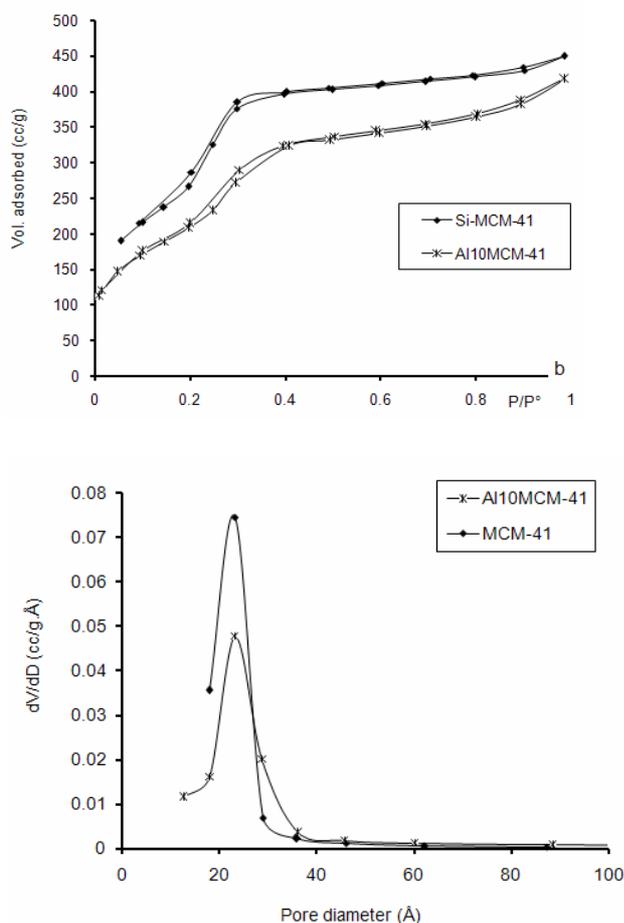


Fig. 2. (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution for calcined MCM-41, Al10MCM-41.

3.2. Adsorption studies

The distribution coefficient of cadmium ion on the mesoporous aluminosilicates is increased with increasing amount of aluminum in the framework of the adsorbent. 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 [20].

Table 1

Physical characteristics of MCM-41 and Al10MCM-41.

Adsorbent	XRD d100 (Å)	Unit cell parameter ^b (a_0) (Å)	Pore volume (cc g ⁻¹)	BET surface area (m ² g ⁻¹)	Av. pore diameter (Å)
Al10MCM-41	38.3	42.3	0.73	792	24.4
MCM-41	31.8	37.4	0.74	1120	21.7

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

3.2.1. Effect of pH

The speciation diagram of cadmium in solution shows that Cd²⁺ is only species dominant upto pH 8 [21]. The adsorption of cadmium was studied in the pH range of 2-7. As seen in Fig. 3, the adsorptions of cadmium don't vary with the pH of solution. The adsorption percent of cadmium is very high (>98%) in the pH range of 2-7. it is maybe due to the fact that, after incorporation of aluminum, mesoporous aluminosilicate can act as an inorganic cation exchanger.

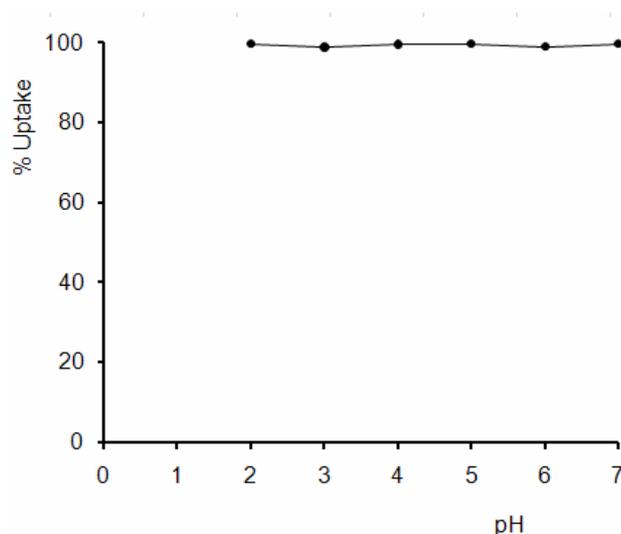


Fig. 3. Effect of pH on adsorption of Cd onto the Al10MCM-41 adsorbent.

3.2.2. Kinetic study

The adsorption kinetics experiments were carried out at an initial Cd concentration of 20 mg L⁻¹ and at natural pH (7.0). The adsorption kinetic results are shown in Fig. 4. It is observed that the adsorption equilibrium is attained fast in about 10 min which is efficient time comparing with other adsorbent [22,23]. The fast adsorption rate suggests that the silanol groups are readily available and easily accessible probably because the uniform mesoporous channels of the A110MCM-41 adsorbent facilitate the Cd ions transportation in the process.

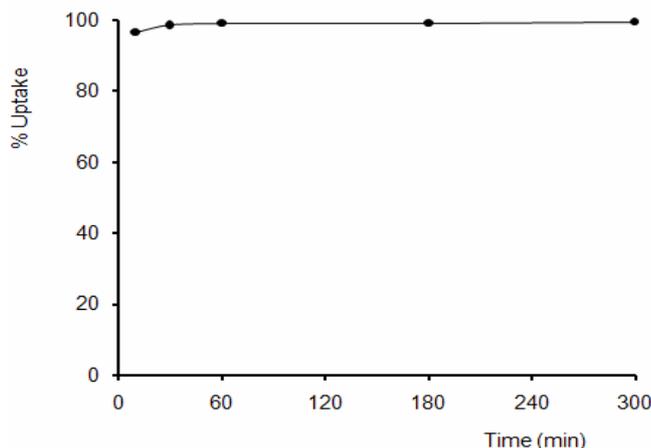


Fig. 4. Effect of contact time on adsorption of Cd onto the A110MCM-41 adsorbent at 25 °C and C₀=20 µg mL⁻¹.

3.2.3. Adsorption isotherm

The adsorption isotherm is plotted in Fig. 5. The isotherm belongs to the L-type of the classification proposed by Giles [24]. 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 (mmol g⁻¹) is amount of analyte bound to adsorbent, F (µM) is equilibrium concentration of adsorbate in solution. q_{max} is maximum adsorption capacity (mmol g⁻¹) 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. 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 R² summarized in Table 2 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 [25]:

$$B = \frac{K_{rp} F}{1 + P_e F^g} \quad (3b)$$

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

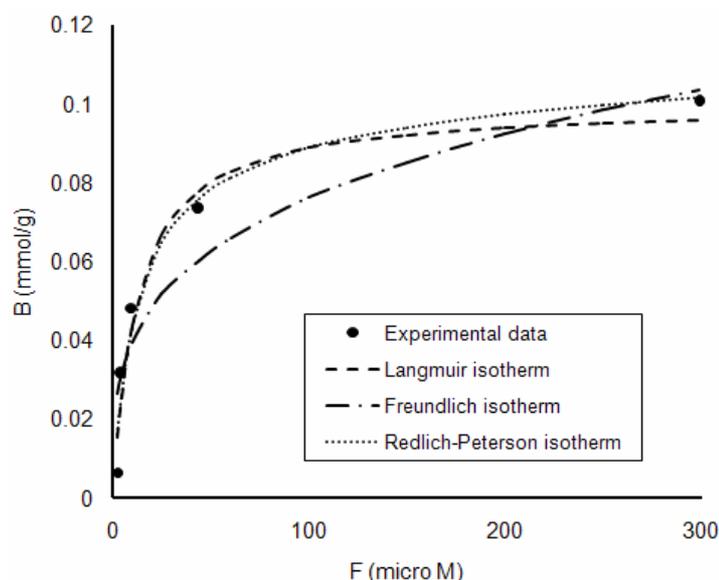


Fig. 5. Experimental adsorption data (points) and Langmuir, freundlich and Redlich-Peterson isotherms fit (lines).

When the exponent $g=1$, the Langmuir equation results, given by (2a). 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 $g=1$ [26].

Table 2 shows that K_{rp} and $P_e < 1$ and $g=0.94$. Therefore the Redlich-Peterson isotherm also confirms that the Langmuir equation provides a better fitting than the Freundlich one.

Table 2 also shows that adsorption cadmium capacity was 0.1 mmol g^{-1} (11.5 mg g^{-1}) which is a higher adsorption capacity compared with those of other adsorbents such as montmorillonite and illite (6.6 and 6.6 mg g^{-1} respectively) due to high surface area of mesoporous aluminosilicate against zeolites [27].

Table 2

Fitting parameters of adsorption model isotherms.

Fitting parameters				
Langmuir	R^2	$K_l (\text{L mmol}^{-1})$	$q_{\max} (\text{mmol g}^{-1})$	
	0.97	0.08	0.10	
Freundlich	R^2	$K_f (\text{mmol g}^{-1} \mu\text{M}^{-1})$	m	
	0.88	0.02	0.28	
Redlich-Peterson	R^2	$K_{rp} (\text{L g}^{-1})$	$P_e (\text{L mg}^{-(1-1/K_{rp})})$	g
	0.97	0.01	0.12	0.94

4. Conclusions

Mesoporous aluminosilicate (Al10MCM-41) with Si/Al mole ratio 10 has been successfully synthesized by a nonthermal route and is a promising adsorbent for Cd 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 mesoporous aluminosilicate endow the adsorbent with an improved adsorption ability of 11.5 mg g⁻¹ and fast kinetics of less than 10 min for Cd.

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