

Adsorption Studies of Lead on Modified Mesoporous Al-MCM-41

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ABSTRACT

In this paper, the sorption of lead on modified mesoporous aluminosilicate was studied. The effect of pH, contact time, initial concentration of lead on sorption was investigated. The distribution coefficient of lead ion on the mesoporous aluminosilicates has been enhanced with the increase of the aluminum in the framework of the adsorbent. Adsorption behavior of lead on the Al₂₀MCM-41 adsorbents has been studied and the Langmuir and Freundlich isotherms were applied to represent the adsorption process. The Langmuir equation provides a better fitting than the Freundlich one. The Langmuir monolayer capacity of the sorbent was 14.6 mg.g⁻¹. The adsorption capacity is very high in the pH range of 3-7 and decreases with decreasing of the pH value.

Keywords: mesoporous materials; aluminosilicate; adsorption behavior; lead

INTRODUCTION

The heavy metal pollution represents a significant environmental problem arising from its toxic effects and accumulation throughout the food chain.¹ The excessive use of the metal cations is increasing their amounts in the aquatic systems. Heavy metals are among the most important pollutants in waters. They are non-degradable and, therefore, continue to accumulate in body waters.^{2,3} Because of their toxic properties and the tendency for bio-accumulation in the food chain, it is necessary to reduce the concentration levels of heavy metals in waters.

The conventional methods precipitation, ion exchange and adsorption have been frequently practiced for the removal of heavy metals from water.⁴⁻⁷

Lead (Pb) is also one of the potentially toxic trace metal whose physiochemical cycle has been substantially affected by human activities. Lead is highly toxic when its concentration exceeds the threshold limit value (15 ppb) in

drinking water. The environmental chemistry of Pb has probably stimulated more scientific interest than all other metallic elements combined.^{8,9} The major source of Pb exposure by the general population is drinking water.⁴ The entrance of Pb ion at elevated levels into the blood causes anemia, paralysis, coma, kidney dysfunctions, brain damage, bone diseases, skin and lung cancer, convulsion and even death. High blood lead levels are associated with delayed puberty in girls and lead is also harmful for women's ability to reproduce. It is, therefore, necessary to reduce the level of Pb in effluent before it is discharged into the body water.

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.^{10,11} 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.^{12,13} The modification

of the mesoporous materials by various functional groups has received much attention in adsorption and separation science.¹⁴⁻¹⁹ The modification of MCM-41 by organic modifier is an expensive method, but modification by inorganic metal ions is rapid, simple and inexpensive method.

Oshima and coworkers have been reported sorption of Pb and Cd onto MCM-41 in presence of acetylacetone.²⁰

In this paper, the adsorption studies of lead on modified mesoporous aluminosilicate as a novel adsorbent are reported. The pH and time effect, adsorption isotherm and capacity have also been studied in detail. The equilibrium adsorption data are analyzed by using Langmuir, Freundlich models.

EXPERIMENTAL

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

Preparation of mesoporous aluminosilicate: Mesoporous aluminosilicates were prepared as reported earlier.²¹ 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 sulphuric acid (2 M). Then for preparing four materials with different ratios of Si/Al solutions of $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ containing 0.45, 0.22, 0.11 and 0.06 g in 50 mL demineralized water for mole ratios 10, 20, 40 and 80 respectively were added dropwise to obtain the particular material. The 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. A small portion of this material was calcined at 540 °C for 6 h. The material was digested in 0.1M HNO_3 for 24 h and then washed demineralized water.

The samples prepared were labeled as follows: $\text{Al}_x\text{MCM-41}$ where x indicated the Si/Al molar ratio and MCM-41 (Mobile crystalline Material) indicated hexagonal ordered mesoporous silicate. In order to study the effect of addition of aluminum in these types of materials, a sample only with silica in the framework was also prepared under the same conditions and it was

marked as MCM-41. Out of $\text{Al}_{10}\text{MCM-41}$, $\text{Al}_{20}\text{MCM-41}$, $\text{Al}_{40}\text{MCM-41}$ and $\text{Al}_{80}\text{MCM-41}$ due to favorable adsorption behavior, $\text{Al}_{20}\text{MCM-41}$ is chosen for present studies.

Characterization: A Philips X'pert powder diffractometer system with $\text{Cu-K}\alpha$ ($\lambda=1.541 \text{ \AA}$) radiation was used for X-ray studies. XRD analysis was performed from 1.5° (2 θ) to 10.0° (2 θ) at a scan rate of 0.02° (2 θ)/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.²² The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula.²³ 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.

Procedure for adsorption studies: Adsorption studies of the lead ions on the $\text{Al}_{20}\text{MCM-41}$ 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^{-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 lead ion was determined by ICP. The percentage of lead 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 distribution ratio (K_d) of lead 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 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 Al20MCM41 adsorbent was equilibrated with 25 mL of the buffer solution containing 20 mg.L⁻¹ of lead ions at various pHs for 3 h.

Kinetic study: In a typical kinetics test, 50 mg of the adsorbent was added to 20 mL of 20 mg.L⁻¹ of lead solutions at selected pH. The suspension was agitated for different periods of time (from 10 to 300 min) using waterbath shaker.

Adsorption isotherm: In several batch experiments, 50 mg portions of the Al20MCM41 adsorbent was equilibrated with varying concentrations of lead 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 lead ion (F, μM) in solution were determined with ICP and the amounts of adsorbed lead on adsorbent (B, mmol.g⁻¹) were calculated from these values.

RESULTS AND DISCUSSION

XRD analysis: The XRD patterns of the calcined MCM-41, Al20MCM41 is presented in Fig. 1. The XRD pattern of Al20MCM41 show a strong diffraction at 2θ smaller than 3° along with presence of small peaks as showed by MCM-41.^{10,11} This result is characteristic of hexagonal pore structure and has been indicated that the

Al20MCM41 structure was not changed by the modification significantly.

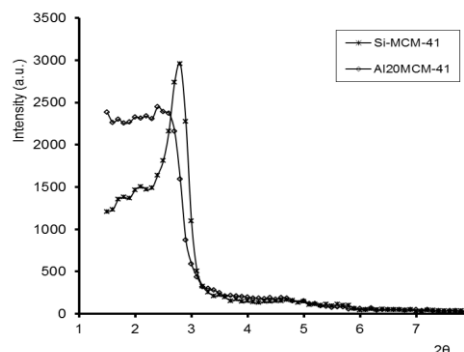


Figure 1 XRD patterns of the calcined MCM-41, Al20MCM-41.

Nitrogen sorption isotherms: N₂ adsorption-desorption isotherms for MCM-41, Al20MCM41 showed irreversible type IV adsorption isotherms as defined by IUPAC. 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 II shows the specific surface area, pore volume and pore size of the samples.

Table I Distribution coefficients of lead ion on the mesoporous aluminosilicates.

Adsorbent	MCM-41	Al80MCM-41	Al40MCM-41	Al20MCM-41	Al10MCM41
Si/Al mole ratio (found)	-	80 (37.2)	40 (32.0)	20 (19.7)	10 (16.4)
K_d value (mL/g)	72	26	50	763	381

Table II Physical characteristics of MCM-41 and Al20MCM-41

Adsorbent	XRD d100 [Å]	Unit cell parameter ^a (a_0) [Å]	Pore volume [cc/g]	BET surface area [m ² /g]	Average pore diameter [Å]
Al20MCM-41	35.7	41.3	0.67	834	21.8
MCM-41	31.8	36.8	0.74	1120	21.7

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

Adsorption studies: The distribution coefficient of lead ion on the mesoporous aluminosilicates is increased with increasing amount of aluminum in the framework of the adsorbent (Table I). 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.¹⁸

The distribution coefficient of lead ion on Al10MCM-41 (with Si/Al mole ratio 10)

decreased that it is maybe due to the fact that, its surface area ($792 \text{ m}^2.\text{g}^{-1}$) is lower than the Al20MCM-41 ($834 \text{ m}^2.\text{g}^{-1}$).

Effect of pH: The speciation diagram of lead in solution shows that Pb^{2+} is only species dominant upto pH 7.²⁴ The adsorption of lead was studied in the pH range of 2-7. As seen in Fig. 2, the adsorption of lead don't varied in the pH range of 3-7. The adsorption percent of lead is very high ($>98\%$) in the pH range of 3-7. it is maybe due to the fact that, after incorporation of aluminum, mesoporous aluminosilicate can act as an inorganic cation exchanger. Also it is maybe due to the fact that, in this acidic region, silanol groups onto pores were as SiOH_2^+ in $\text{pH} < 3.0$. So, in $\text{pH} < 3.0$, it was found that Pb^{2+} showed little adsorption toward Al20MCM-41. After $\text{pH} \geq 3$ with a 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 Pb^{2+} is only species dominant upto pH 7. So, Pb^{2+} showed the adsorption towards Al20MCM-41 adsorbent with an increase in pH value. The next experiments in this study were carried out at natural pH (6.5)

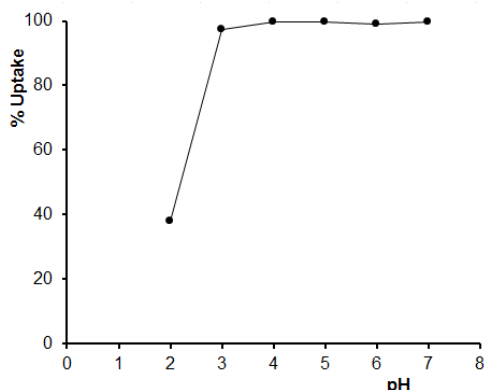


Figure 2 Effect of pH on adsorption of Pb onto the Al20MCM-41 adsorbent.

Kinetic study: The adsorption kinetics experiments were carried out at an initial Pb concentration of 20 mg.L^{-1} and at natural pH (6.5). The adsorption kinetic results are shown in Fig. 3. It is observed that the adsorption equilibrium is attained fast in about 10 min. The fast adsorption rate suggests that the ion-exchange sites are readily available and easily accessible probably because the uniform mesoporous channels of the Al20MCM41 adsorbent facilitate the Pb ions transportation in the process.

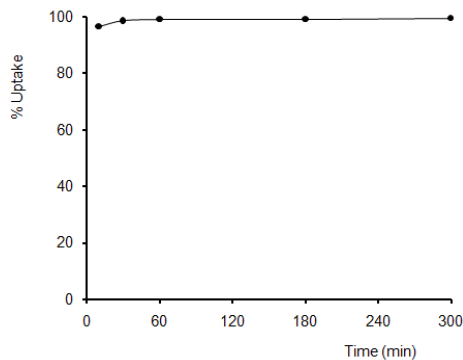


Figure 3 Effect of contact time on adsorption of Pb onto the Al20MCM-41 adsorbent at 25°C and $C_0 = 20 \text{ mg.L}^{-1}$.

Adsorption isotherm: The adsorption isotherm is plotted in Fig.4. 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;

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

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

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_f 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. 4, 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 III). The Langmuir monolayer capacity of the sorbent was 14.6 mg.g^{-1} .

For comparative purposes the experimental data have been fitted to the well-known Freundlich equation:

$$B = K_f F^m \quad (3a)$$

$$\log B = \log K_f + m \log F \quad (3b)$$

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 III it may be calculated that the Langmuir equation provides a better fitting than the Freundlich one.

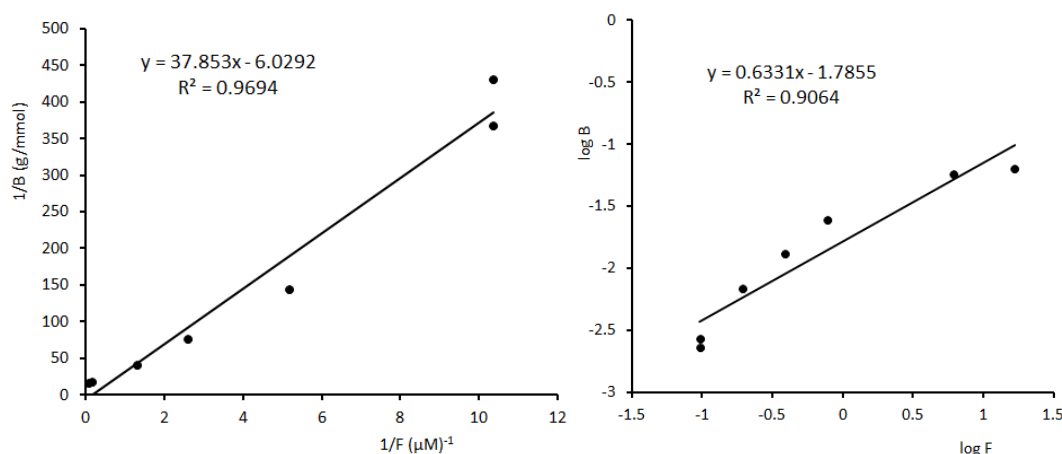


Figure 4 Experimental adsorption data (points) and Langmuir (left), Freundlich (right) isotherms fit (lines).

Table III Fitting parameters of adsorption model isotherms.

Fitting parameters			
Langmuir	R²	K_l (L.mmol⁻¹)	q_{max} (mmol.g⁻¹)
	0.97	0.64	0.07
Freundlich	R²	K_f (mmol.g⁻¹.μM⁻¹)	m
	0.91	0.02	0.41

CONCLUSIONS

Mesoporous aluminosilicate (Al20MCM-41) with Si/Al mole ratio 20 has been successfully synthesized as a simple and low-cost route and is a promising adsorbent for Pb 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 14.6 mg.g⁻¹ and fast kinetics of less than 10 min for Pb.

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