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Adsorption Behavior of Molybdenum on Modified Mesoporous Zirconium Silicates

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In this study, mesoporous MCM-41 has been modified by the incorporation of zirconium 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 molybdenum ion on the mesoporous zirconium silicates has been enhanced with the increase of the zirconium in the framework of the adsorbent. The adsorption behavior of molybdenum on the Zr10MCM-41 adsorbent has been studied and the experimental adsorption isotherm is successfully described by the Langmuir model. The effect of pH and adsorption kinetics have also been studied by batch method. The adsorption capacity is very high in the pH range of 2–3 and decreases with increasing of the pH value.

Keywords adsorption behavior; mesoporous; molybdenum; zirconium silicate

INTRODUCTION

Molybdenum is regarded as one of the vital strategic element in modern technology. It is used in the industrial sector, medicine, and as a necessary element for the human body and plants (1–3). Molybdenum is a characteristic element associated with airborne particulates originating from oil combustion. These airborne particulates enter into surface water through rainfall as molybdenum is found to be present ($0.1\ \mu gL^{-1}$) in river and lake water samples (4). High levels of molybdenum can interfere with the body's uptake of copper, producing copper deficiency. Molybdenum prevents plasma proteins from binding to copper, and it also increases the amount of copper that is excreted in urine (5). Therefore the separation and the removal of this element from wastes and water streams is necessary.

Molybdenum-99 (^{99}Mo) is the most important radionuclides used in nuclear medicine practice. ^{99}Mo is produced mainly by nuclear fission of ^{235}U. Extraction and purification of ^{99}Mo is very difficult. On the other hand, reactive waste from the production of ^{99}Mo must be managed in such a way that the protection of people and the environment is ensured, both now and in the future. A literature survey reveals that the solvent extraction method is usually used for extraction of Mo(VI) from aqueous media (6–12). The inability of the quantitative stripping of Mo(VI) from the extractants, the consumption of relatively large amount of organic solvents, and inorganic acids are the disadvantages of this method.

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 (13,14). 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 (15,16). The modification of the mesoporous materials by various functional groups has received much attention in adsorption and separation science (17–20). Ganjali et al. have reported the synthesis of aminofunctionalized mesoporous molecular sieves (AMMS) and its use in the separation and purification of molybdenum (VI) from fission products of uranium (3). The modification of MCM-41 by an organic modifier is an expensive method, but modification by inorganic metal ions is a rapid, simple, and inexpensive method.

In this paper, the adsorption studies of molybdenum on modified mesoporous zirconium silicate are reported. The adsorption isotherm, adsorption kinetics, capacity, and pH effect have also been studied in detail. The equilibrium adsorption data are analyzed by using Freundlich and Langmuir isotherms.

EXPERIMENTAL

Reagents

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

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Apparatus

A Philips X'pert powder diffractometer system with Cu-Kα($\lambda = 1.541$ Å) 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. The nitrogen adsorption and the desorption isotherm of the adsorbent was determined at 77 K and the specific surface area was determined by applying the BET equation to the isotherm (21). The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula (22). 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 the determination of distribution coefficients.

Preparation of Mesoporous Zirconium Silicate

Mesoporous zirconium silicates were prepared as reported earlier (23). Out of Zr10MCM-41, Zr20MCM-41, Zr40MCM-41, and Zr80MCM-41 due to favorable adsorption behavior, Zr10MCM-41 is chosen for the present studies.

Procedure for Adsorption Studies

The adsorption studies of the molybdenum ion on the Zr10MCM-41 adsorbents 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 μg mL^{-1} molybdenum ion. The pH of the solution was adjusted with sodium acetate/nitric acid pH 2–6 and K_2HPO_4/HCl for pH 6–8. The suspension was stirred for a preselected period of time using a water shaker bath. Then it was filtered and the amount of the molybdenum ion was determined by ICP. The percentage of molybdenum ion that was adsorbed on the adsorbent (% uptake) was determined by comparing its concentrations before and after adsorption (C_i (μg mL^{-1}) and C_f (μg mL^{-1})) respectively.

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

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

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

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

Effect of pH

The effect of the solution pH on the adsorption behavior was determined at a constant temperature of 25°C. In batch experiments, 50 mg of Zr10MCM-41 adsorbent was equilibrated with 25 mL of the buffer solution containing 20 μg mL^{-1} of molybdenum 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 μg mL^{-1} of the molybdenum solution at pH = 3. The suspension was agitated for different periods of time (from 5 to 270 min) using water-bath shaker.

Adsorption Isotherm

In several batch experiments, 50 mg portions of the Zr10MCM-41 adsorbent were equilibrated with varying concentrations of molybdenum ion (initial concentration range from 5 to 100 μg mL^{-1}) at pH 3. The suspensions were agitated for 1 h using a water bath shaker. Then, the supernatant solutions were removed and filtered. The concentrations of molybdenum ion (F, μM) in solution were determined with ICP and the amounts of the adsorbed molybdenum on the adsorbent (B, μmol g^{-1}) were calculated from these values.

RESULTS AND DISCUSSION

Characterization of Adsorbent

XRD Analysis

The XRD patterns of the MCM-41 (calcined) and Zr10MCM-41 (calcined) are presented in Fig. 1. The XRD patterns of samples show a strong diffraction at

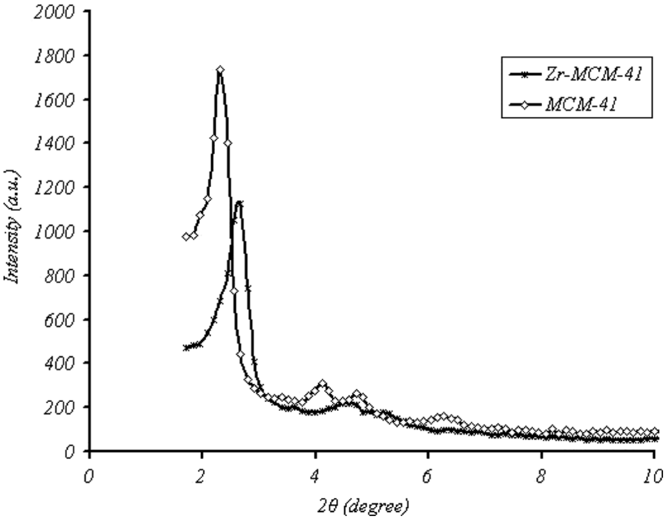
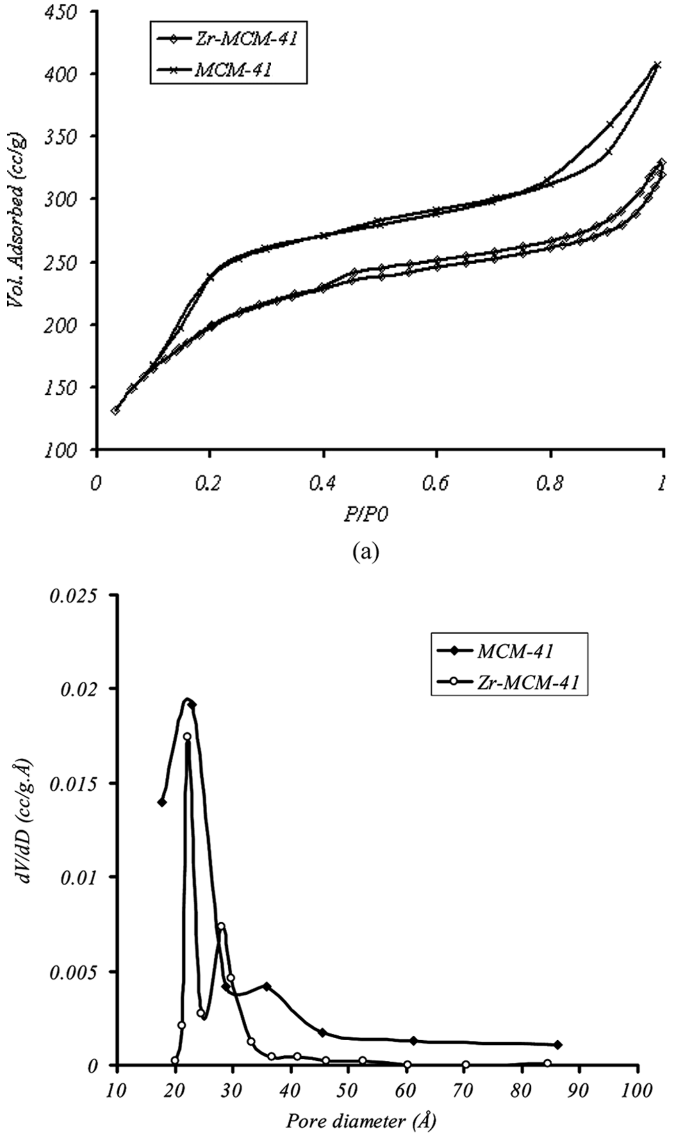


FIG. 1. XRD patterns of the MCM-41 (calcined) and Zr10MCM-41 (calcined).



(a)

(b)

FIG. 2. (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution for MCM-41 and Zr10MCM-41.

2θ smaller than 3° along with the presence of small peaks that confirms the formation of mesoporous MCM-41 (13–14). This result is characteristic of the hexagonal pore structure.

Nitrogen Sorption Isotherms

The nitrogen adsorption isotherms and corresponding pore size distribution of the MCM-41 and Zr10MCM-41 are given in Fig. 2. N_2 adsorption-desorption isotherms for MCM-41 and Zr10MCM-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 2 shows the specific surface area, the pore volume, and the pore size of the samples.

Adsorption Studies

The distribution coefficient of molybdenum ion on the mesoporous zirconium silicates is increased with an increasing amount of zirconium in the framework of the adsorbent (Table 1). It is because the incorporation of zirconium in the framework of MCM-41 results in an increase of the number of Brönsted and to a lower extent Lewis acid sites (24).

Effect of pH

In the absence of the chelating agent, the molybdenum species are affected by the pH of the medium. The molybdenum ions often form non-ionic or anionic species at various pHs (25). The adsorption of molybdenum was studied in the pH range of 2–8. As seen in Fig. 3, the adsorption of molybdenum varied significantly with the pH of solution. The observed molybdenum adsorption patterns can be explained by the electric charges on the adsorbent surface and on the molybdenum species. It is reported that $Mo_8O_{24}^{4-}$ predominates below pH 2 whereas $Mo_7O_{24}^{6-}$ exits as the dominant species between pH 2 and 6. MoO_4^{2-} and $Mo_7O_{24}^{6-}$ occur in the pH 6 to 8 range; MoO_4^{2-} predominates above pH 8 (26). As expected, the silanol groups on the pores of the adsorbent convert to cationic form (Si-OH_2^{2+}) at lower pH and it adsorbs the anionic species of molybdenum as a cation-exchanger. But at higher pH, the silanol groups convert to the anion-exchanger and cannot adsorb the anionic species of molybdenum. The next set of experiments in this study were carried out at pH = 3.

TABLE 1
Distribution coefficients of molybdenum ion on the mesoporous zirconium silicates

Adsorbent	MCM-41	Zr80MCM-41	Zr40MCM-41	Zr20MCM-41	Zr10MCM-41
Si/Zr mole ratio (found)	–	80 (26.3)	40 (13.7)	20 (7.3)	10 (3.7)
K_d value (mL/g)	52	92	364	6325	>10000

TABLE 2
Physical characteristics of MCM-41 and Zr10MCM-41

Adsorbent	XRD d_{100} (Å)	Unit cell parameter^b (a_o) (Å)	Pore volume (cc/g)	BET surface area (m^2/g)	Average pore diameter (Å)
Zrl0MCM-41	33.4	38.5	0.51	788	17.8
MCM-41	36.8	42.5	0.63	876	17.9

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

Kinetic Study

The adsorption kinetics experiments were carried out at an initial Mo concentration of 20 µg mL^{-1} and pH = 3. The adsorption kinetic results are shown in Fig. 4. It is observed that the adsorption equilibrium is attained fast in about 30 min which is efficient time compared with the other adsorbent (27,28). The fast adsorption rate suggests that the silanol groups are readily available and easily accessible probably because the uniform mesoporous channels of the Zr10MCM-41 adsorbent facilitate the Mo ions transportation in the process. Further investigation is still needed to understand the interaction between the adsorbate and the active sites.

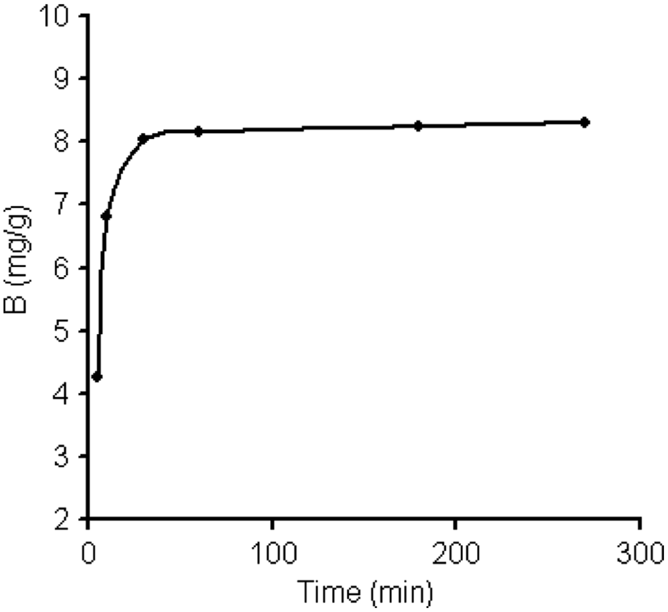


FIG. 4. Effect of contact time of sorbate on adsorption of Mo onto the Zr10MCM-41 adsorbent at 25°C, pH = 3 and $C_0 = 20\,\mu g\,mL^{-1}$.

Adsorption Isotherm

The adsorption isotherm is plotted in Fig. 5. The isotherm belongs to the L-type of the classification proposed by Giles (29). Among various binding models, the Langmuir and Freundlich isotherms have been frequently employed to describe experimental data of adsorption isotherms. The Langmuir adsorption isotherm is mathematically expressed as;

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

Where B (µmol g^{-1}) is amount of analyte bound to adsorbent, F (µM) is equilibrium concentration of adsorbate in solution. q_{max} is maximum adsorption capacity (µmol g^{-1})

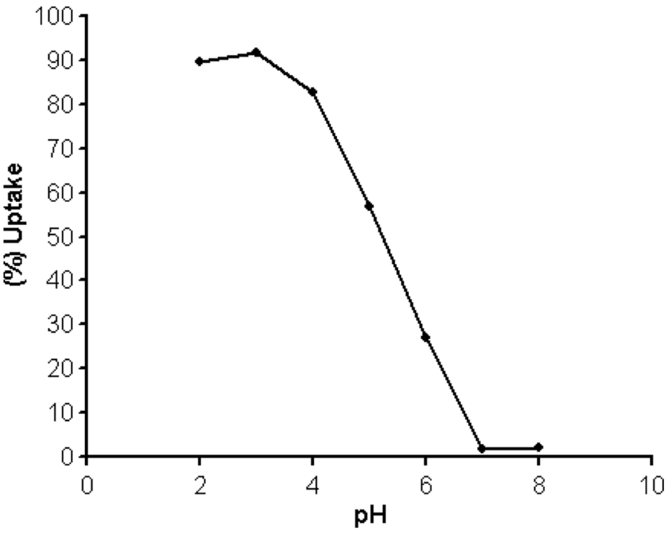


FIG. 3. Effect of pH on adsorption of Mo onto the Zr10MCM-41 adsorbent.

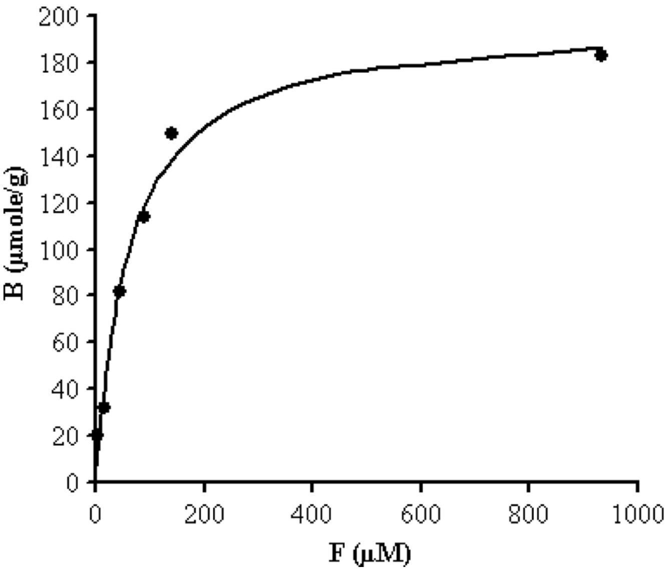


FIG. 5. Experimental adsorption data (points) and Langmuir isotherm fit (line).

TABLE 3
Fitting parameters of adsorption model isotherms

	Fitting parameters		
Langmuir	R^2	K_l (L μmol^{-1})	q_{max} (μmol g^{-1})
	0.99	0.01	238.1
Freundlich	R^2	K_f (μmol g^{-1} nM^{-1})	m
	0.91	198.52	0.30

and K_l is the 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. The 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 3). For comparative purposes the experimental data have been fitted to the well-known Freundlich equation:

$$B = K_f F^m \tag{2b}$$

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 3 it may be calculated that both equations fit reasonably well the experimental data, although the Langmuir equation provides a better fitting than the Freundlich one.

CONCLUSIONS

Mesoporous zirconium silicate (Zr10MCM-41) with Si/Zr mole ratio 10 has been successfully synthesized by a nonthermal route and is a promising adsorbnent for Mo removal from aqueous solutions. The modification of MCM-41 by zirconium ion is a rapid, simple, and inexpensive method compared with the modification by organic modifiers. The high content of silanol groups and the excellent properties of mesoporous zirconium silicate endow the adsorbent with an improved adsorption ability of 238.1 μmol g^{-1} and fast kinetics of less than 30 min for Mo.

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