Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3862-3868

Mesoporous Lanthanum Tungstate as a Novel Sorbent for Removal of Heavy Metal Ions from Aqueous Media

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A supramolecular templating approach to the preparation of mesoporous lanthanum tungstate using lanthanum nitrate and dodecyl sulfate following digestion in sodium tungstate solution is presented. N_2 adsorption-desorption measurements have been made to determine the surface area and pore size. Calcined and uncalcined materials have been used to study the sorption behaviour of Cr(III), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Tl(I) and Pb(II) ions and methyl mercury from aqueous solution.

Key Words: Mesoporous, Lanthanum tungstate, Metal ions, Surfactant, Methyl mercury sorption.

INTRODUCTION

A wide variety of toxic inorganic and organic chemicals are discharged to the environment as industrial wastes, causing serious water, air and soil pollution. Heavy metals are found in wastewaters originating from chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries[1,2]. Such metals exert a serious effect on the fauna and flora of lakes and streams. One of the potential remedies to this problem is the use of adsorption technologies. Activated carbons[3] and a number of low-cost adsorbents such as agricultural residues and peat[4-7] have been used for the removal of heavy metal cations. Several porous materials are also suggested[8,9].

In the past few years, there has been increasing interest in developing inorganic adsorbents, particularly for the efficient removal of organic pollutants from aqueous solutions. Modified clays[10-14] and layered double hydroxides (LDHs)[15] have drawn attention as promising adsorbents. Mesoporous silica were also used for the adsorption of organic substrates[16,17].

In this paper the sorption potential of mesoporous lanthanum tungstate materials in removal of toxic and heavy metals from aqueous media have been reported.

EXPERIMENTAL

All the chemicals used were of analytical grade from E. Merk (Germany).

Synthesis: In a typical synthesis, 9.52 g of lanthanum nitrate (2.2×10^{-2} mol) was dissolved in 50.0 mL of distilled water and ethanol (50 mL, 0.87 mol) and aqueous ammonia (12 mL, 32 wt %, 0.20 mol) was added to it. The mixture was stirred for 10 min (450 rpm) and to this mixture, 1.09 g (6.6 mmol) of surfactant (dodecylsulfate-sodium salt) was added at once. A white precipitate formed instantaneously and the mixture was left under stirring for 2 h at room temperature. The resulting solid was recovered by filtration (whatman filter paper, No. 541) washed with distilled water and dried in air at ambient temperature. The solid collected was then digested in an aqueous solution (70 mL) of sodium tungstate (0.1M) for 48 h with intermitted slow shaking at room temperature. The resultant product was filtered, washed with distilled water and dried in air at ambient temperature (I_{s2-} uncalcined). A small portion of this solid was calcined in air furnance at 550°C for 6 h (I_{s2-} calcined).

N_2-Sorption isotherms: N_2 adsorption-desorption isotherms of the samples were measured at 77K on Micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method[18] while surface area of the adsorbent was measured by Brunauer-Emmet-Teller (BET) method[19].

Adsorption of metallic cations: The sorption of heavy metals on lanthanum tungstate was studied using the batch method. The experiments were conducted using 0.1 g of adsorbent with 10 mL of solutions containing heavy metal ions with concentration of 0.05 M in all experiments at 26.6 ± 1°C in 50 mL glass flask. The flasks were shaken in a shaking water-bath together for 3 h and solutions containing heavy metals were filtered through whatman filter paper (No.541). The metal ion concentrations were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The per cent adsorption (%) and distribution ratio (K_d) were calculated using the equations.

$$\text{adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, respectively and

$$K_d = \frac{\text{Amount of metal in absorbent}}{\text{Amount of metal in solution}} \times \frac{V}{m} \quad \text{mL/g}$$

where V is the volume of the solution (mL) and m is the weight of the adsorbent (g).

The per cent adsorption and K_d (mL/g) can be correlated by the following equation[20]:

$$\text{Adsorption (\%)} = \frac{100\ K_d}{K_d + \frac{V}{m}}$$

The amount of metal ions adsorbed, q (mg/g adsorbent) was obtained as follows:

$$q = [(C_i - C_f)\cdot V]/m$$

where C_i and C_f are the initial and equilibrium concentrations (mg/L), respectively; V is the volume of the aqueous solution (L) and m is the mass of the adsorbent (g)[21].

Adsorption of organic pollutant: One typical organic pollutant, namely methyl mercury was studied. I_{s2-} calcined (0.1 g) were contacted with 10 mL of solution. After stirring for a period of 3 h, the solutions were filtered through whatman filter paper (No. 541). The exact concentrations of methylmercuric chloride were determined by using inductively coupled plasma-atomic emission spectrometer (ICP-AES).

RESULTS AND DISCUSSION

The physical characteristics of the calcined mesoporous lanthanum tungstate are given in Table-1.

TABLE-1
PHYSICAL CHARACTERISTICS OF THE LANTHANUM TUNGSTATE

Sample	BET Surface area	Mean Surface area	BJH ads. Average. Pore diameter	BJH des. Average. Pore diameter	Total Pore vol.	BJH ads. Pore vol.	BJH des. Pore vol.
	$m^{2\cdot} g^{-1}$	$m^{2\cdot} g^{-1}$	Å	Å	$cm^3.g^{-1}$	$cm^3.g^{-1}$	$cm^3.g^{-1}$
Is_2-calcined	29.02	203.20	367.33	297.94	0.15	0.28	0.28

The N_2 adsorption isotherm for calcined sample (I_{s2-} calcined) is given in Fig. 1.

The isotherm was a typical form similar to mesoporous silica, having a hysteresis curve near the relative pressure of 1.0 (Fig.1). Taner and pinnavaia[22] have defined and differentiated the terms framework-confined porosity and textural porosity. The framework-confined porosity represents the porosity contained within the uniform channels of the templated framework. The presence of framework-confined pores is indicated by the adsorption step, which is centered in the relative pressure (p/po) region from 0.1 to 0.8 in the N_2-adsorption-desorption isotherm. Textural porosity represents the porosity which arises from non-crystalline intraaggregate voids and spaces formed by interparticle contacts. The presence of textural porosity can be verified by appearance of a well-defined hysteresis loop in the N_2-adsorption-desorption isotherms in the p/po region from 0.8-1.0. I_{s2-} calcined had a framework-confined porosity and a textural porosity (Fig. 1), also exhibited a wide open pore structure, particularly suitable for fast adsorption of hydrophobic molecules. I_{s2-} calcined seems to have low pore volume (0.15 cm^3/g), low surface area (29 m^2/g). The pore size distribution (PSD) of calcined sample is given in Fig. 2.

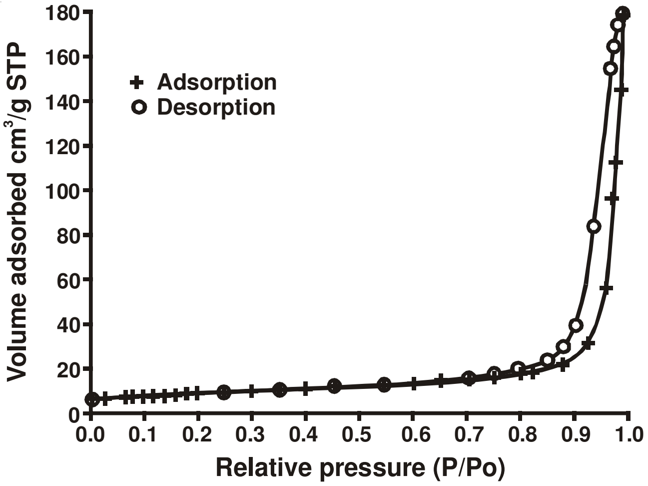

Fig. 1. N_2 sorption isotherm of lanthanum tungstate

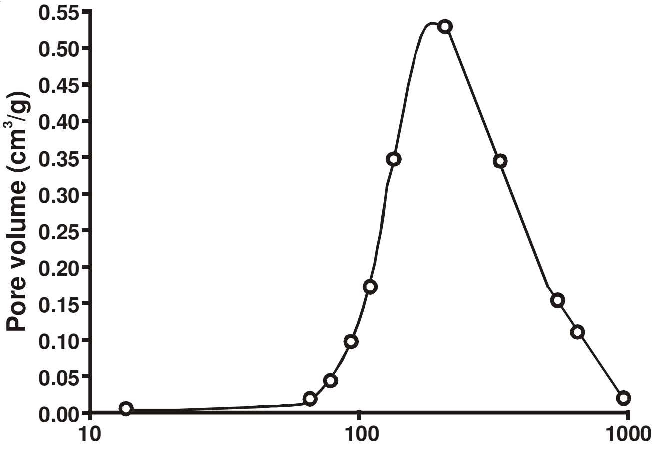

Fig. 2. Pore size distribution curve of the lanthanum tungstate (Is_2-uncalcined) obtained by BJH method

As shown in Fig. 2, the uncalcined material exhibited highly enlarged pores with relatively narrow pore size distribution (PSD) with an average diameter of 297.94 Å. I_{s2-} calcined exhibited wide hydrophilic channels which allow the transport of water-soluble species such as mercury with little resistance.

Adsorption of metallic cations: The adsorption of Cr(III), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Tl(I) and Pb(II) onto lanthanum tungstate was studied at 27°C by the metal concentration of 0.05 M while keeping all other parameters constant. The results are shown in Tables 2 and 3.

TABLE-2
ADSORPTION PARAMETERS OF HEAVY METAL IONS ON I_{s2}- UNCALCINED

Metal ions	Uptake (%)	K_d (mL/g)	Sorbed (mg/g)
Cr(III)	14.14	16.47	36.40
Cr(VI)	34.37	52.37	86.31
Mn(II)	7.35	7.93	20.88
Fe(III)	14.92	17.54	41.33
Co(II)	12.99	14.92	37.13
Ni(II)	8.20	8.93	24.06
Cu(II)	22.09	28.35	69.90
Zn(II)	NA	NA	NA
Ag(I)	6.08	6.47	32.36
Cd(II)	NA	NA	NA
Hg(II)	32.88	48.99	343.00
Tl(I)	1.28	1.29	12.26
Pb(II)	22.76	29.47	227.92

NA: negligible adsorption

As shown the adsorption capacity was relatively high, depending on the nature of the metal ion. Though no kinetic measurements were made yet, the adsorption of all cations was very fast. For comparison, we used results obtained by Dai *et al.*[23]. The extent of metal adsorption capacity can be represented by distribution coefficient, K_d, which is defined as the ratio of the amount of metal ions in solid matrix to those in liquid matrix as listed in Tables 2 and 3. The results showed that I_{s2-} uncalcined itself had a little binding affinity for most of cations except mercury.

Adsorption of organic pollutant: Using I_{s2-} calcined and I_{s2-} uncalcined and solution with initial concentration of 100 ppm of methylmercuric chloride, the adsorption data shown in Table-4 was obtained. The capacity was relatively high for both adsorbents, reaching 72.84 and 62.24 % uptake, respectively. As shown in Table-4, owing to the open pore structure of mesoporous lanthanum tungstate, the adsorption is particularly fast.

TABLE-3
ADSORPTION PARAMETERS OF HEAVY METAL IONS ON I_{s2}- CALCINED

Metal ions	Uptake (%)	K_d (mL/g)	Sorbed (mg/g)
Cr(III)	27.04	37.12	69.67
Cr(VI)	34.16	51.89	85.80
Mn(II)	5.42	5.73	15.38
Fe(III)	24.60	32.62	68.13
Co(II)	NA	NA	NA
Ni(II)	5.20	5.49	15.26
Cu(II)	40.16	69.39	127.09
Zn(II)	3.93	3.82	12.42
Ag(I)	4.86	5.11	25.89
Cd(II)	2.20	2.25	12.37
Hg(II)	82.69	477.78	826.54
Tl(I)	NA	NA	NA
Pb(II)	26.22	35.54	267.29

NA: negligible adsorption

TABLE-4
METHYLMERCURIC CHLORIDE ADSORPTION ONTO MESOPOROUS LANTHANUM TUNGSTATE

Sample	Uptake (%)	Sorbed (mg/g)	K_d (mL/g)
Is_2-uncalcined	72.84	268.19	7.28
Is_2-calcined	62.24	164.83	6.22

Conclusion

This work describes novel and structurally related nanoporous adsorbent for the removal of metallic cations and organic pollutant, respectively. The material is thermally stable up to 550°C. Heavy metal ions and organic pollutants are known to be toxic and especially cadmium, arsenic, mercury, chromium, copper, lead, nickel, selinum, silver, zinc, magnesium, iron, cobalt and thallium and methyl mercury are released into the environment in quantities that pose a risk to living systems. I_{s2-} uncalcined and I_{s2-} calcined materials have relatively high capacity for mercury ion and methyl mercury. These results suggest that the mesoporous lanthanum tungstate can be used as a good mercury and methyl mercury adsorbents and have great potential applications in removal of mercury and methyl mercury from aqueous systems.

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(*Received*: 19 July 2006; *Accepted*: 9 March 2007) AJC-5492