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Removal of Cd(II) from Aqueous by Adsorption onto Mesoporous Ti-MCM-48

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Abstract. The cubic Ti-containing MCM-48 (Ti-MCM-48) with the mesoporous structure was synthesized. The equilibrium and kinetic were chiefly studied. It was found that the maximum of Cd(II) on this adsorbent occurred in the pH 8 with an adsorption maximum of 83.57 mg g⁻¹. The Langmuir equation has a good correlation with the experimental data. Kinetic data of adsorption reactions and the adsorption equilibrium parameters were described by pseudo-second order equation which indicated well linear correlation. We also deep investigated adsorption mechanism of cadmium on Ti-MCM-48, which provide a theoretical basis for silicon mesoporous materials. It was concluded that Ti-MCM-48 had large surface area, thermal stability and high porosity showing application potentials in pre-treatment and environmental cleaning.

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1. Introduction

Heavy metal pollution has become a serious worldwide environmental problem. The most harmful metals found in the aquatic system are Cd, Ni, Zn, Cr, Pb and Cu. Cadmium like the other heavy metals can contaminate surface waters in significant amount via the miss-management of industrial effluents. Cadmium which is highly toxic can cause serious damages to the kidney and bone. Itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy are all the harmful effects cause by cadmium [1]. Many separation techniques, such as ion-exchange [2,3], precipitation [4-6], adsorption [7,8], membrane processes [9], have been employed for separation of heavy metals from wastewater. Adsorption is one of the few promising alternatives for this purpose, especially using efficient adsorbent.

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With the increase in environmental water pollution, there is a growing demand to develop novel adsorbents of higher efficiency for heavy metal ions removal from aqueous media than those commercially available. Mesoporous materials as novel adsorbents have been paid more attention in adsorption field [10,11], because of their homogeneous pore size, thin pore walls and large surface area. A review of the literature shows that a majority of studies have been based on hexagonal-phase mesoporous silica (MCM-41) with a uniform two-dimensional pore network [12,13]. However, to our knowledge, the studies concerning the heavy metal adsorption like Cd(II) on the functionalized MCM-48 with three-dimensional and cubic pore system are comparatively scarce at present.

In order to evaluate the water-treat capacity of the functionalized MCM-48, this work describes adsorption of trace amounts of Cd(II) from samples using the surface-modified MCM-48 mesoporous silica. The effects of various adsorption conditions on the extraction efficiency of Cd(II) such as pH, adsorption capacity, thermodynamic parameters and time were investigated.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) and hexadecyltrimethyl ammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd. TiF_4 was purchased from Sigma chemical reagent company. NaOH and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were purchased from Shanghai Chemical Reagent. All the analytical grade chemicals were used without further purification. Deionized water was used for solution preparation and washing.

2.2. Synthesis.

Ti-MCM-48 was synthesized as described in Shuai Yuan et al. [14] and characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR) and nitrogen adsorption-desorption isotherm

2.3. The adsorption process of Cd(II).

Heavy metal ion adsorption tests of the Ti-MCM-48 were performed in batch mode. 50 mg of the adsorbents were added into 20 ml solution containing different concentrations to adjust pH from 4 to 10. The mixture was stirring for a certain time, followed by centrifugation at 4000 rpm for 10 min. The residual metal concentration in the solution was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). For all adsorption tests, deviations between initial and final pH were less than 0.1 pH units. Adsorption experiments were repeated three times. In all experiments, standard and blank solutions were prepared.

3. Results and discussions

3.1. The effect of solution Ph

Adsorption of Cd^{2+} was performed in different pH solutions. Approximately 50 mg mesoporous Ti-MCM-48 was put into a stoppered vial, and then 20 mL of analyte containing 50 mg L⁻¹ Cd^{2+} was added. The pH value of suspension was adjusted from 4 to 10.

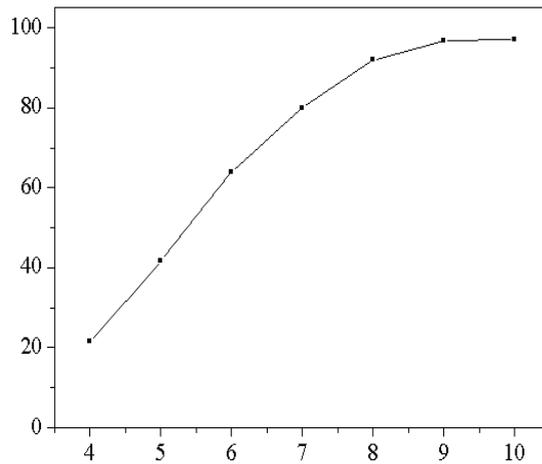


Fig.1 Removal of Cd(II) by Ti-MCM-48 as a function of pH

Fig. 1 shows the effect of pH on adsorption percentage of Cd^{2+} . In acidic condition, parts of metal ions may be adsorbed on the surface of Ti-MCM-48 by ion exchange of Cd^{2+} with H^+ on the Si-OH group. It is a reversible reaction. It indicates that the adsorption percentage of metal ions to Ti-MCM-48 could enhance with the increase of pH, and the reversible reaction would shift to the right with the increase of pH. On the other hand, there is also a concurrent electrostatic adsorption, as Ti-MCM-48 surfaces with negative charge can counteract with H^+ ion under acidic condition. With the OH^- concentration decreasing, OH^- consumes a lot of H^+ , and then Cd^{2+} combines with negative charge to increase the absorption rate [15]. But higher concentration of $[\text{OH}^-]$ would make Cd^{2+} easy to deposit. The optimal pH of 8 enables the absorption efficiency to reach 91.93%.

3.2 The effect of initial concentration.

The effect of the initial cadmium concentration has been examined by changing initial concentration from 50-300 mg L⁻¹. The change in the initial metal ion concentration has a significant effect on breakthrough curve as illustrated in Fig. 2.

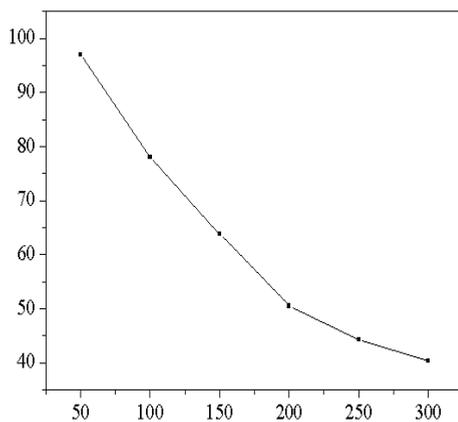


Fig. 2 Removal of Cd(II) by Ti-MCM-48 as a function of initial concentration

The Three Gorges reservoir area has a diversity of wetland resources. Many of the managements When initial concentration is low, i.e., heavy metal ions in solution is small, adsorption is fast. However, when the initial concentration increases, the adsorption rate is reduced. These results indicate that the adsorption of Cd(II) by Ti-MCM-48 was more favorable at lower initial metal ion concentrations than at higher ones.

4. Isothermal models

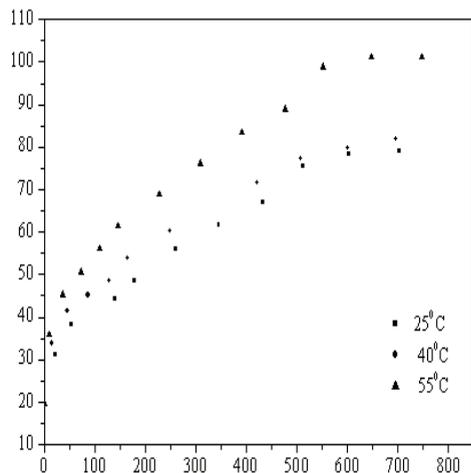


Fig.3 Adsorption isotherm of Cd(II) on Ti-MCM-48

Full adsorption isotherms have been obtained at 25, 40 and 55 °C for the Ti-MCM-48, respectively. The batch adsorption experiments were carried out under the optimal pH of 8 for a 2 h contact time. Fig. 3 displays the isotherms where the amount of cadmium adsorbed is at equilibrium. The Langmuir constant b and maximum adsorption capacity Q0 of adsorbent were also shown in Table 1. The Langmuir monolayer adsorption capacity, Q0, is 83.57 mg g⁻¹

Table 1 Adsorption parameters of the Langmuir isotherms

temperature	Langmuir	q	b	R ²
25°C	$\rho_e q_e = \rho_e / 84.75 + 1.418$	84.75	120.2	0.9938
40°C	$\rho_e q_e = \rho_e / 91.74 + 1.209$	91.74	110.9	0.9920
55°C	$\rho_e q_e = \rho_e / 98.04 + 0.834$	98.04	81.76	0.9919

This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent [16]. Table 2 shows the values of adsorption capacity for the adsorption of Cd(II) on different adsorbents in the literature and in the present study. By comparing the various low-cost adsorbents and some mesoporous materials with our synthesized Ti-MCM-48, it can be stated that Ti-MCM-48 has high adsorption capacity for Cd(II). From

these results, it can be drawn that Ti-MCM-48 is expected to be a good material for removal of Cd(II) in polluted water.

Table 2 Adsorption capacity for cadmium of different common adsorbents

Sorbent	Adsorption capacity (mg g ⁻¹)	Reference
nano-TiO ₂	8.10	17
MCM-41	8.57	18
Quaternary loess	9.37	19
Carbon aerogel	15.53	20
NH ₂ -MCM-41	18.25	21
NH ₂ -SiO ₂	22.48	22
Modified rice husk	31.15	23
Black gram(Cicer arietinum) husk	46.52	24
Oxidized corncob	55.20	25
Ti-MCM-48	83.57	This work

4.1. Thermodynamic parameters.

The thermodynamic parameters included the changes in enthalpy (ΔH^0), entropy (ΔS^0), and Gibbs free energy (ΔG^0). The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plots of $\ln b$ versus $1/T$ (figure not shown) and listed in Table 3.

Table 3 Thermodynamic parameters for the adsorption of Cd(II) on Ti-MCM-48

T (K)	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (J·mol ⁻¹ ·K ⁻¹)
298	-2.270		
313	-3.260	21.77	80.5
328	-4.698		

The negative values of ΔG^0 confirmed the feasibility of the process and the spontaneous nature of adsorption with a high preference of Cd (II) on Ti-MCM-48. The increase of the absolute value of ΔG^0 as temperature rises indicated that the affinity of Cd(II) on Ti-MCM-48 with thermal stability is higher at high temperature. The value of ΔH^0 was positive, indicating that adsorption reaction was endothermic. The positive value of ΔS^0 also showed the increasing randomness at the solid/liquid interface during the adsorption of Cd (II) on Ti-MCM-48.

4.2. Adsorption kinetics.

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. The linear form of *pseudo*-second order kinetics was applied to the experimental results. When the concentration was 100 mg L⁻¹, the linearity was attributed to the *pseudo*-second order model at different temperature. The linearity was attributed to the *pseudo*-second order model at different concentrations at 25 °C. The parameters of *pseudo*-second order sorption kinetics model are listed in Table 4. The correlation coefficients of the *pseudo*-second order model is 0.999 and the calculated sorption capacity values obtained from *pseudo*-second order model are consistent with the experimental values of sorption capacity. Therefore, the sorption kinetics of

Cd(II) ion is better to describe by the *pseudo*-second order model represented [18].

Table 4 Kinetic adsorption parameters obtained using *pseudo*-second order models.

Temperature	K_2	q_e	R^2	Metal concentration (mg L ⁻¹)	K_2	q_e	R^2
25°C	0.02607	32.15	0.9998	50	0.146200	19.49	1.000
40°C	0.03339	34.97	0.9996	100	0.044040	36.77	1.000
55°C	0.05943	38.76	0.9999	150	0.015280	45.87	0.9998
-	-	-	-	200	0.006304	63.29	0.9993

As time increases, adsorption capacity also increased. The applicability of this model implies that the rate-determining step may be chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [26]

4.3. Adsorption mechanisms

Based on the previous kinetic and isothermal studies, it is considered that the ion-exchange and surface complexation occur simultaneously during the adsorption process. We also tested H⁺ concentration diversification of the solution, pH was dropped by 0.4 units. We infer that one titanium atom bonds with two hydroxyl of the MCM-48 surface, and the structure of -Si-O-Ti-O-Si- forms on the surface of Ti-MCM-48. Since the absorption processes in the condition of pH 8, the titanium atom on the surface hydrolyzes easily to form coordination structure of -(O)₂-Ti-(OH)₂. After absorption, the Cd(II) would bond to the hydroxyls of -(O)₂-Ti-(OH)₂.

5. Summary

In this work, the adsorption process is strongly affected by parameters such as pH, time, and temperature. The plot of pH versus percentage adsorption shows significant adsorption at pH 8.0 for the Cd(II) ions with adsorption capacity of 83.57 mg g⁻¹. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The whole adsorption reaction was spontaneous and endothermic. The *pseudo*-second order kinetics demonstrated that adsorption process is correlated with time. The findings discussed in this paper indicate that this procedure is a chemical reaction involving ion-exchange and surface complexation. Ti-MCM-48 which has large surface area and high adsorption capacity compared with other materials is expected to be applied widely in polluted water in future.

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