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Efficient removal of Cd^{2+} by the mesoporous silica functionalized by APTES

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Abstract. Amino-functionalized mesoporous silica (AFMS) with high amino loading, high surface area, and large pore size was synthesized using the anionic surfactant N-lauroylsarcosine sodium (Sar-Na) as template and 3-aminopropyltriethoxysilane (APTES) as co-structure directing agent (CSDA). The synthesized AFMS was characterized by N_2 adsorption-desorption, TEM and elemental analyzer. The results of the removal of Cd^{2+} from aqueous solution showed that the pH value of aqueous solution affected the removal efficiency of Cd^{2+} greatly, and that unary adsorption isotherm of Cd^{2+} on the AFMS was well described by the Sips isotherm model, in which the adsorption capacity was 2.43 mmol/g for Cd^{2+}, much higher than the literature data.

Introduction

Industrial activity generates large quantities of aqueous effluents that contain high levels of toxic heavy metals, resulting in the discharge of industrial wastewater. Treatment of contaminated water is a critical environmental issue due to the heavy metals, apart from being hazardous for living organisms when exceed the specific limits, have accumulating characteristics in nature as they cannot be biodegraded. Recently, cadmium is used in a wide variety of industrial processes such as alloy preparation, metal plating, mining, ceramics and other industrial activities, resulting in a variety of syndromes such as renal function hypertension, hepatic injury, lung damage and teratogenic effects [1, 2]. Many techniques, such as ion exchange, precipitation, adsorption, membrane processes, reverse osmosis, sedimentation, electro-dialysis, etc., have been employed for separation of heavy metals from wastewater [3, 4]. Among these methods, adsorption is efficient and simple. At present, many kinds of adsorbents such as chitosan [5], Peganum harmala seeds [6], and activated carbon [7] have been employed for cadmium ion removal. However, these adsorbents suffer from low adsorption capacities and/or low removal efficiencies.

As adsorbents for capturing heavy metal ions, amino-functionalize mesoporous silica (AFMS) materials might be ideal candidates because of their unique large surface area, high adsorption affinity due to an easy formation of coordination bonds between metal ions and amino groups, and high regeneration characteristics [8, 9]. In this study, the AFMS with high amino loading, high surface area, and large pore size was synthesized through an anion surfactant route and the removal of Cd^{2+} on the AFMS was investigated.

Experimental

The AFMS was prepared by followed our previous work [10]. Typically, 1.7604 g N-lauroylsarcosine sodium (Sar-Na, from Merck) was completely dissolved in 70 ml deionized water under stirring at room temperature. Afterwards, 10 ml of 0.1 mol/l HCl solution was added to the Sar-Na solution under vigorous stirring for 1 h, and then a mixture of 3.0 ml tetraethyl orthosilicate (TEOS) and 1.0 ml APTES was added to the above prepared solution under vigorous stirring for 10 min. The resulting mixture was aged at room temperature for 2 h and the synthesis was then carried out hydrothermally without agitation in a closed 100 ml reaction kettle placed in an oven at

80 °C for 20-48 h. The product was filtered and the solid was washed with deionized water and then dried for 10 h at 80 °C prior to a further analysis or use. The surfactant in the dried sample was removed by an extraction method. Typically, 1.0 g of the dried solid was dispersed in a mixture solution of 100 ml of ethanol and 25.2 g of 3.3 mol/l ethanol amine at room temperature by agitation and then the mixture was refluxed at 90 °C for 12 h. The solid was recovered by filtration, washed with ethanol, and dried. The above extraction procedure was repeated twice. Various techniques such as N_2 adsorption-desorption, TEM, and elemental analyzer were used to characterize the synthesized materials.

Batch experiments were performed to measure metal adsorption capacities of AFMS. Cadmium (II) nitrate [$Cd(NO_3)_2$] was added into deionized water to prepare 10 mmol•l^{-1} Cd^{2+} solution, which was diluted to the desired one when used. In order to prevent the precipitation of cadmium ion during the adsorption experiment, different pH values of reactant system were obtained using 0.05 mmol/l hydrochloric acid. After 0.06 g sample was added into 100 ml metal solution, the solution was stirred for different time at room temperature and the sample was filtered. The residual metal concentration in the solutions was measured using an atomic absorption spectrometer (A Analyst 800, PerkinElmer, America).

The regeneration of the used adsorbent was carried out using 5 ml of 0.1 mol/l EDTA solution to treat 0.05 g of the Cd^{2+} adsorbed AFMS under vigorous stirring at 50 ℃for 1 h, followed by washing with deionized water for several times and drying at 80 ℃. The regenerated AFMS adsorbent was then used for the next adsorption.

Results and Discussion

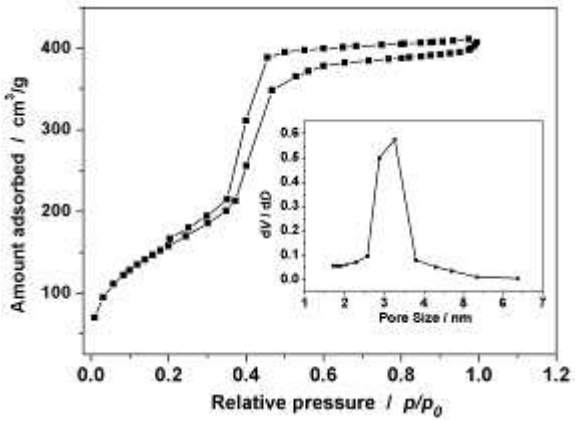

Fig. 1 Adsorption-desorption isotherms of N_2 and the BJH pore size distribution plots (inset) of the sample

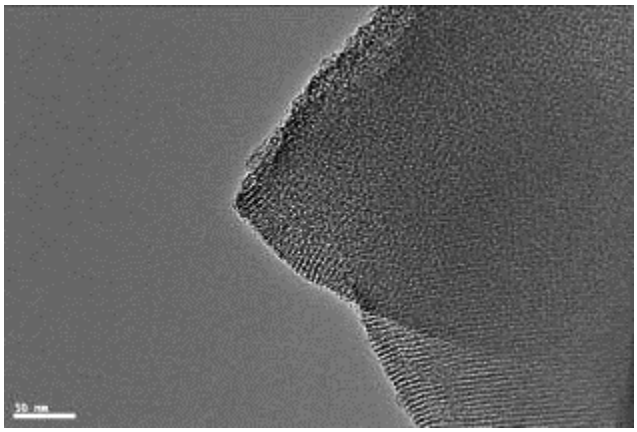

Fig. 2 TEM image of the resultant sample

Fig. 1 depicts the adsorption-desorption isotherms of N_2 on the extracted sample at -196 ℃ and its corresponding BJH pore size distribution plot from the adsorption branch. From Fig. 1, the adsorption isotherms of N_2 display a type IV isotherm, implying that the synthesized sample should be of mesoporous materials. For the extracted sample, the estimated BET surface area is 590 m^2/g and the pore size distribution plot (shown in the inset part of Fig.1) calculated by the BJH method is centered at about 3.5 nm. The TEM image of the extracted sample is presented in Fig. 2. From fig. 2, it can be seen that a well ordered meso-structure was obtained after extraction, in agreement with the result of N_2 adsorption-desorption.

The effect of the solution pH on the adsorption of Cd^{2+} by the extracted sample is shown in Fig. 3, in which the removal efficiency of Cd^{2+} is represented by R, calculated by the equation (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the Cd^{2+} in mmol/l, and C_t is the concentration of Cd^{2+} at any time in mmol/l. It was found that the adsorption efficiency increased quickly with increased in the solution pH from 3.5 to 5.o, then decreased slowly after the pH value of 5.0, indicating that the

adsorption of Cd^{2+} depends on the solution pH greatly. This phenomenon can be explained as follows: on the one hand, the concentration of protonated amine groups is increased with decreasing pH values, resulting in the number of binding sites available for Cd^{2+} uptake is decreased and consequently the adsorbed amount of Cd^{2+} is relatively lower; on the other hand, amino-groups are deprotonated and the adsorption sites for Cd^{2+} are increased with increasing pH. However, at pH values higher than 5.0, Cd^{2+} precipitated out because of the high concentrations of -OH ions in the aqueous solution [11].

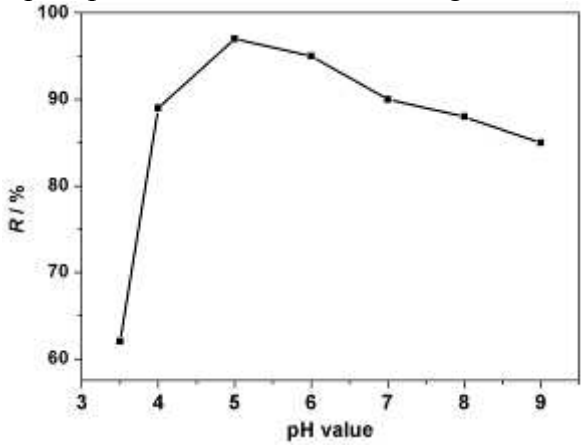

Fig. 3 Effect of pH on Cd^{2+} removal

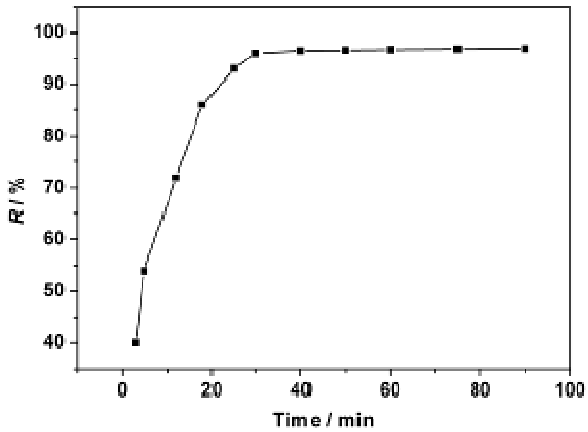

Fig. 4 Kinetic study of Cd^{2+} on AFMS at pH value of 5.0

The uptake of Cd^{2+} in AFMS is shown in Fig. 4, from which it can be seen that the adsorptive rate is highly fast because the adsorption equilibrium can be reached within 30 minutes. This is due to the fact that AFMS synthesized by the anionic surfactant-templated method possesses a large and uniform pore size distribution because of the introduction of CSDA [12], resulting in a less diffusion resistance to Cd^{2+}.

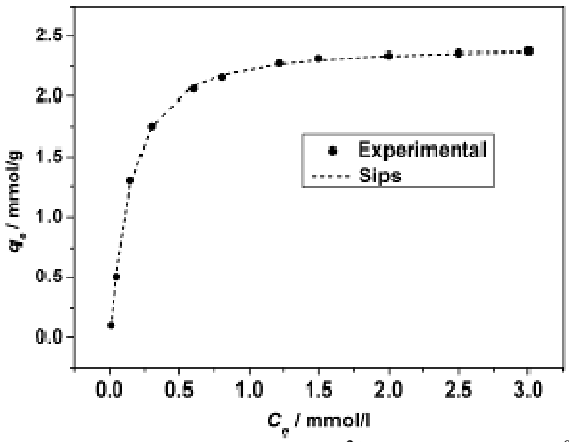

Fig. 5 Adsorption isotherms of Cd^{2+} on AFMS at 25 ^{0}C and an pH value of 5.0. Symbol is the experimental data and point line is the Sips model correlation

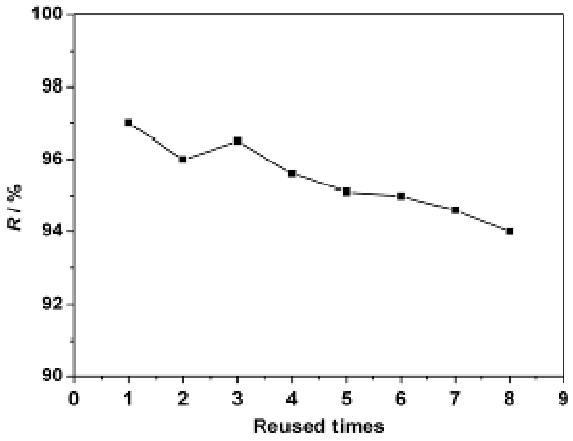

Fig. 6 Reused property of the extracted sample

The adsorption isotherm of Cd^{2+} on AFMS at 25 ℃ is shown in Fig. 5. The isotherm has a sharp increase in the adsorbed amount at low metal-ion concentrations, indicating that the removal efficiency is greatly high due to the high adsorption potential of the AFMS adsorbent to Cd^{2+}. The isotherm data can be appropriately described by the Sips isotherm model (equation (2)) [13], as shown in Fig. 5 by the point line.

$$q_e = \frac{q_m k_s c_e^{1/n}}{1 + k_s c_e^{1/n}} \tag{2}$$

where q_m is the saturation adsorption capacity, C_e is the equilibrium concentration of the metal ions, K_S is the equilibrium adsorption constant, and n is the parameter characterizing the system heterogeneity, the larger is the parameter the more heterogeneous is the system [13]. From the fitted results of Sips model, n and K_S are 0.80 and 11.61 $(mmol/l)^{1/n}$ respectively. The extracted saturation

adsorption capacities for Cd^{2+} on AFMS from Sips model is 2.43 mmol/g, much higher than 0.25 mmol/g on the mono amino groups modified silica [7]. This reason may be that the N content in the extracted is high (6.14 mmol/g), resulting in more binding sites for capturing Cd^{2+}.

The reusability of an adsorbent is crucial in practical applications. Fig. 6 shows the results on 8 adsorption-regeneration cycles of Cd^{2+} on the extracted sample. It is clearly seen that the removal efficiency is still above 94% after 8 adsorption-regeneration cycles, indicating that EDTA is an effective desorption effluent and the synthesized AFMS adsorbent is rather reusable.

Conclusions

AFMS adsorbent with high amino loading, high surface area, and large pore size was synthesized by the anionic surfactant-templated method. The synthesized adsorbent was used for the removal of Cd^{2+} from aqueous solutions. The measured isotherm data is well described by the Sips model. The synthesized adsorbent shows much higher adsorption capacities than the literature data for Cd^{2+} removal.

Acknowledgements

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