Organic Functionalized Porous Silica Nanoparticles for Adsorption of Cd (II) Ions from Aqueous Solutions

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Abstract. In this study, several different kinds of organic functionalized porous silica nanomaterials were firstly synthesized via soft template method, separately. And then, the adsorption for Cd (II) ions of organic functionalized porous silica nanomaterials has been studied. Besides, the effect of the adsorption time and Cd (II) ions concentration on the absorption efficiency has also been investigated. The results showed that the adsorption had already been completed within 30 min. In addition, the equilibrium adsorption concentration of vinyl functionalized porous silica sorbents, or ureido functionalized porous silica sorbents for Cd (II) was about 150 mg/L.

1. Introduction
Organic-functionalized porous silica materials with different functional groups have attracted a great amount of attention because of their potential applications in separation, adsorption, catalysis, drug delivery [1-4]. Besides, the combination of the properties of organic and inorganic building blocks within a single material is particularly attractive because of the possibility to combine the enormous functional variation of organic chemistry with the advantages of a thermally stable and robust inorganic substrate [5], this is particularly applicable to adsorption and heterogeneous catalysis.

At present, to obtain diversified functional porous silica materials, three general methods (post-grafting, co-condensation, and PMOs (periodic mesoporous organosilicas)) were developed [6-11]. The post-grafting refers to the subsequent modification of the inner surfaces of mesostructured silica phases with organic groups, nevertheless, this may lead to pore blocking. On the contrast, pore blocking is not a problem in the co-condensation method and PMOs. However, the surface of PMOs prepared by hydrolysis and condensation reactions of bridged organosilica precursors of the type (R'O)3Si-R-Si(OR')3 was still need to be modified[12].

Herein, a facile preparation method for obtaining organic-functionalized porous silica materials with different functional groups has been adopted. At the same time, the adsorption for Cd (II) ions of organic functionalized porous silica nanomaterials has been studied.

2. Experiments
2.1. Materials
Tetraethyl orthosilicate (TEOS, 98%), vinyltriethoxysilane (VTES, 99%), [3-[Tri (ethoxy) silyl] propyl] urea (UPTES, 99.9%) and 3-Aminopropyltriethoxysilane (APTES) were obtained from
Sinopharm Chemical Reagent Co. Ammonia solution (\(\text{NH}_3\cdot\text{H}_2\text{O},\ 25\%-28\%\)), sodium dodecyl sulfonate (SDS), cetyl trimethyl ammonium bromide (CTAB), \(\text{CdCl}_2\) and ethanol were purchased from Damao Chemical Reagent Company in Tanjing.

2.2. Preparation of organic functionalized porous silica nanomaterials

The typical synthetic procedure of organic functionalized porous silica is as follows: CTAB and SDS with different mass ratios \((R_{m\text{SDS}:m\text{CTAB}})\) as dual surfactants template were dissolved into aqueous solution (or adding ethanol) at room temperature. After stirring for 30 min, a certain amount of TEOS and VTES (or UPTES, or APTES) and 0.5 ml of \(\text{NH}_3\cdot\text{H}_2\text{O}\) was dropwise added in sequence into the above mixture under stirring, and then the resultant mixture was stirred for 7 h. White products were collected by centrifugation and washed with water and ethanol and dried under 50 °C for future use.

The as-synthesized products were collected and then extracted by refluxing in certain amount of ethanol containing concentrated aqueous HCl solution for 20 h to completely remove the surfactant. The final surfactant-free products were collected after filtration, water washed and air dried at 50 °C. The final solid product was identified as vinyl functionalized porous silica, ureido functionalized porous silica and amino functionalized porous silica.

2.3. The study of adsorption for \(\text{Cd(II)}\) ions

Adsorption of \(\text{Cd(II)}\) ions from aqueous solutions was investigated in batch experiments. To measure the maximum adsorption capacity, vinyl functionalized porous silica prepared with \(R_{m\text{SDS}:m\text{CTAB}}=0.4:0.06\), and ureido functionalized porous silica prepared with \(R_{m\text{CTAB}:m\text{SDS}}=0.016:0.01\) as sorbents, respectively. Various concentrations of \(\text{Cd(II)}\) solutions (10, 50, 100, 150, 250 mg/L) at pH 7, this pH were applied for all experiments. And the equilibrium adsorption time (10, 30, 50, 70, 90 min) were studied, keeping the concentration of sorbents constant at 15 mg/100 mL. The concentrations of the metal ions in the aqueous phases were measured by using a FAAS. Adsorption capacity (mg/g) was calculated as the difference in \(\text{Cd(II)}\) ions concentration of the pre- and post-adsorption solutions divided by the weight of dry sorbents. The adsorption capacity of \(\text{Cd(II)}\) ions can be obtained from equilibrium binding data according to Eq. As follow [13-14].

\[
Q = \frac{(c_i - c_f)V}{1000W}
\]

where \(Q\) represents the adsorption capacity (mg/g); \(C_i\) and \(C_f\) are the initial and final concentrations of \(\text{Cd(II)}\) (mg/L), respectively. \(V\) is the volume of the solution (mL); \(W\) is the mass used of vinyl functionalized porous silica, or ureido functionalized porous silica sorbents (mg).

3. Results and discussion

3.1. The morphologies of organic functionalized porous silica

The amino functionalized porous silica had not been obtained in this study, in contrast, vinyl functionalized porous silica and ureido functionalized porous silica had been prepared in different mass ratio of CTAB to SDS. Fig.1 showed the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of vinyl functionalized porous silica prepared with different mass ratio of CTAB to SDS, \(R_{m\text{CTAB}:m\text{SDS}}=(a,a1)\ 0.4:0.03, \ (b,b1)\ 0.4:0.06\) and \((c,c1)\ 0.4:0.09\), respectively.
3.2. Adsorption of organic functionalized porous silica for Cd(II) ions

To determine the rate of loading Cd (II) ions on the organic functionalized porous silica, batch experiments were carried out. The Cd (II) ions concentration in suspensions was analyzed in 20 min interval. Figure 3 shows the time strong dependence of the adsorption capacities of Cd(II) ions on vinyl functionalized porous silica prepared with R_{nCTAB:nSDS}=0.4:0.06, or ureido functionalized porous silica prepared with R_{mCTAB:mSDS}=0.016:0.01 sorbents. As seen from Figure 3, Cd (II) adsorption of vinyl functionalized porous silica sorbents increased with the time during the first 20 min and then the curve levels off as equilibrium was reached, while Cd(II) adsorption of ureido functionalized porous silica sorbents increased with the time during the first 30 min and the curve levels off as equilibrium was reached.
Figure 3. Adsorption rates of Cd(II) ions on the sorbents at room temperature: concentration of Cd(II) = 100 mg/L, pH = 6.8.

Figure 4 shows the Cd(II) ions concentration strong dependence of the adsorption capacities of Cd(II) ions on vinyl functionalized porous silica prepared with R_{nCTAB:nSDS}=0.4:0.06, or ureido functionalized porous silica prepared with R_{nCTAB:nSDS}=0.016:0.01 sorbents.

Figure 4. Adsorption capacity of organic porous silica sorbents for Cd (II) at room temperature: pH = 6.8, time = 30 min.

As seen from Figure 4, the adsorption capacity was increased gradually with increasing the concentration of Cd (II) ions. However, the equilibrium adsorption concentration of vinyl functionalized porous silica sorbents, or ureido functionalized porous silica sorbents for Cd (II) was about 150 mg/L.

This fast adsorption equilibrium of these two organic porous silica sorbents were most probably not only due to geometric shape of porous sorbents structure, but also owing to chemical reaction between Cd(II) ions and vinyl and ureido groups on the surface of organic porous silica sorbents.
4. Summary
In conclusion, the two kinds of organic functionalized porous silica with different morphologies had been obtained by changing the mass ratio of CTAB to SDS. Besides, the adsorption of these two porous silica for Cd (II) ions had also been researched. The results showed that the max adsorption capacity was about 46 mg/g within 30 min. And the equilibrium adsorption concentration of vinyl functionalized porous silica sorbents, or ureido functionalized porous silica sorbents for Cd (II) was about 150 mg/L. It was expected that this facile preparation method of organic porous silica can be useful for other porous materials, and used adsorbing other metal ions.

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6. References
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