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Chemical modification of silica-gel with diethylenetriamine via an end-group protection approach for adsorption to Hg(II)

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Four kinds of silica-gel supported diethylenetriamine adsorbents with different structures, were prepared by so-called "heterogeneous-direct-amination" (hetero-DA), "homogeneous-direct-amination" (homo-DA), "heterogeneous end-group protection" (hetero-EGP), and "homogeneous end-group protection" (homo-EGP) methods, respectively. The obtained products were named SG-HE-dD, SG-HO-dD, SG-HE-pD and SG-HO-pD, respectively (where SG means silica-gel; HE means heterogeneous, HO means homogeneous, d means direct, p means protected and D means diethylenetriamine). Their structures were characterized by FT-IR, elemental analysis, porous structure analysis and thermogravimetric analysis. The adsorption capabilities of such adsorbents towards Hg(II) were studied and evaluated by static method. SG-HE-pD and SG-HO-pD showed higher performance towards Hg(II) adsorption than corresponding counterparts SG-HE-dD and SG-HO-dD, even though the former two possessed lower contents of diethylenetriamine (DETA). The kinetics data indicated that the adsorption process was governed by the film diffusion and followed pseudo-first-order rate model for SG-HE-dD, SG-HO-dD and SG-HE-pD and pseudo-second-order model for SG-HO-pD. The Langmuir model was applied to fit the experimental equilibrium data for all adsorbents. The end-group protection method exhibited its advantage in preparation of effective adsorbent for metal ions uptake compared to the direct-amination method.

1. Introduction

As a result of heavy metal ion release from industrial wastewater, water pollution has become a serious problem. Waste streams contain solutions of metal ions, such as mercury, nickel, copper, lead, and so on. In particular, mercury compounds which are harmful to human health and aquatic life must be removed from sewage down to extremely low concentrations. Many literatures have discussed the removal of metal ions from aqueous solutions using approaches based upon adsorption, solvent extraction and polymeric membranes [1–4]. Recently, researches have reported the application of organic molecule-functionalized mesoporous silica-gel for the removal of metal ions from aqueous solution [5–7]. In this method, the organic molecule anchored on the surface of silica-gel relied on coordination bonding to the metals. Thus the approach featured advantages over those used in other methods because of its good selectivity for metal ions and free operation. Moreover, silica-gel was used as an matrix, not only due to the facility of immobilization process, but also to be relatively simple in comparison to organic polymers, with faster metal ion-exchange kinetics, good swelling resistance in different solvents, and chemical stability [8]. It followed that a similar polyamine approach could be applied to metal ion-containing aqueous solutions via chelation on amine groups using silica-gel modified with polyamines [9–10].

Anchoring an organic polyamine on the silica-gel surface via covalent bond is the most reliable method for preparing silica-gel-based adsorbents [11,12]. The direct heterogeneous synthesis and homogeneous synthesis have often been used for these purposes [13–15]. However, it is difficult to avoid the bridging reaction for the polyamine completely owing to N-alkylation at different amine groups. These bridging structures can greatly affect the adsorption properties of adsorbents [16]. Adsorption capacity was considered as the most important parameter for evaluating an adsorbent. Higher adsorption capacity always means better adsorption property. So, researchers always consider the increase of adsorption capacity as the major goal to design and prepare novel adsorbents. Generally, two routes which are increasing the functional group content or enhancing the utilization of functional groups were used to increase the adsorption capacity of adsorbent. Thus, as N-containing adsorbents, increasing the amount of amine group or enhancing the utilization ratio of N is the principal aims to

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prepare new adsorbents. However, our previous investigations showed that introduction of excessive groups into adsorbents could induce the decrease of adsorption capacity and utilization of functional groups due to the intra- or inter-functional groups of cross-linking reactions [17,18].

In order to avoid the cross-linking side-effect, Suzuki and Yokoyama have reported a simple method, end-group protection method, to introduce diethylenetriamine into chloromethylated polystyrene beads [19]. Our research group has attempted to adopt the similar method to load diethylenetriamine on the surface of silica-gel using 3-chloropropyltrimethoxysilane (CPTS) as coupling agent and compared the differences between direct-amination and end-group protection methods [20]. The results showed that although the utilization ratio of N was remarkably improved, the amount of amine group anchored on the silica-gel surface was not desirable, which caused a low adsorption capacity. The reason may be that the active chloropropyl group in CPTS can further react with the tertiary amine formed between the CPTS and end-protected diethylenetriamine to form quaternary ammonium structure, which affected the availability of organoalkoxysilanes for functionalization.

Different from CPTS, the coupling agent 3-glycidoxypropyltrimethoxysilane (GPTS), whose epoxy group cannot react with the tertiary amine, may overcome the disadvantage of CPTS. For comparative purposes, in the present study we prepared the silica-gel supported diethylenetriamine via the methods so-called “heterogeneous-direct-amination” (hetero-DA), “homogeneous-direct-amination” (homo-DA), “heterogeneous end-group protection” (hetero-EGP), and “homogeneous end-group protection” (homo-EGP), respectively, using GPTS as coupling agent. FT-IR analysis, elemental analysis, porous structure analysis and thermogravimetry analysis were used to characterize the prepared adsorbents. The feasibility of these adsorbents for application to removal Hg(II) from aqueous solutions will be assessed. Just as we expected, the adsorbent with high adsorption capacity for Hg(II) was obtained by the homo-EGP method. Now, the preparation, characterization and comparison in adsorption property of this adsorbent are reported.

2. Experimental

2.1. Materials and methods

Silica-gel obtained from Tenghai Chemical Institute, Qingdao, Shandong, China, with particle size in the range 60–100 mesh was treated and activated as before [17]. The silylant agent 3-glycidoxypropyltrimethoxysilane (GPTS, Qufu Wanda Chemicals Factory, China) and salicylaldehyde (Sal, Shanghai Chemical Factory, China) were used without further purification; diethylenetriamine (DETA) and toluene were distilled under reduced pressure just before use. Solvents used were of analytical reagent grade. Stock solutions of Hg(II) (0.1 mol dm^{-3}) were prepared as follows: analytical reagent grade $Hg(NO_3)_2 \cdot H_2O$ was dissolving in 20 cm^3 (0.5 mol dm^{-3}) of HNO_3 to avoid hydrolysis, then diluted to 1000 cm^3. The buffer solution of pH 1.0–2.0 was adjusted to a desired value with HNO_3/H_2O and pH 3.0–6.0 was adjusted with sodium acetate/acetic acid solutions.

N analysis of all products was subject to elemental analysis by the Elementar VarioEL III instrument, Elementar Co., Germany. Infrared spectra of the silica-gel were reported in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 32 scans using a Nicolet MAGNA-IR 550 (series II) spectrophotometer. KBr pellets were used for solid samples and NaCl windows for liquid samples. The nitrogen adsorption–desorption measurements were recorded by an ASAP Micromeritics 2020, American. The mass loss determinations were performed on a Germany Netzsch sta409pc luxx, using 20–30 mg of the sample under nitrogen at a heating rate of 10 K min^{-1}. The concentration of Hg(II) was determined using a 932B-model atomic adsorption spectrometer (AAS, GBC, Australia), equipped with air–acetylene flame.

2.2. Preparation of SG-HE-dD, SG-HO-dD, SG-HE-pD and SG-HO-pD

The preparation of SG-HE-dD, SG-HO-dD, SG-HE-pD and SG-HO-pD (where SG means silica-gel; HE means heterogeneous, HO means homogeneous, d means direct, p means protected and D means diethylenetriamine) was according to the approach described in Ref. [21]. The typical procedures as follows.

Hetero-DA method: 20.0 g of silica-gel reactivated with 20 cm^3 (92.0 mmol) of GPTS in toluene, under reflux of the solvent in dry nitrogen. After filtering and washing, the solid (SG-G) was dried. Then SG-G (10.0 g) was reacted with DETA (26.1 cm^3, 240.1 mmol) and the solid was filtered, washed and dried, to obtain the product, SG-HE-dD.

Homo-DA method: GPTS (10 cm^3, 46.0 mmol) reacted with DETA (10 cm^3, 92.0 mmol) in methanol (100 cm^3). The mixture was refluxed under a nitrogen atmosphere for 12 h and the solution was concentrated to approximately 60 cm^3. The resulting compound GD reacted with 10.0 g of silica-gel suspended in 100 cm^3 of dry toluene. The final solid was filtered, extracted and dried, to obtain the product, SG-HO-dD.

Hetero-EGP method: The Schiff base, diethylenetriamine bis-salicylaldehyde (DETA-bS), was first produced by the method described in the literature [22]. DETA-bS (30.0 g) reacted with 10.0 g of SG in methanol. After refluxing, the solid was filtered, extracted and dried, to obtain the compound, SG-HE-DS. The salicylaldehyde was liberated during hydrolysis and the product SG-HE-pD was obtained as reported [19]. The product SG-HE-DS (6.3 g) was stirred with 100 cm^3 of HCl (6 mol dm^{-3}) at 333 K for 24 h and salicylaldehyde was liberated as yellow oil during the hydrolysis. Yellow product SG-HE-pD in the hydrochloride form was filtered off, washed with ethanol and dried under vacuum. The resulting product in the free amine form was obtained by stirring with distilled water by adding sodium hydroxide (pH 8.0–9.0) till pH of solution remained at 8.0–9.0 for 2 h. Then it was washed by distilled water until the washings were neutral.

Homo-EGP method: 24.0 g of DETA-bS reacted with 8 cm^3 (37.5 mmol) of GPTS in 100 cm^3 of methanol. The mixture was refluxed under dry nitrogen atmosphere and the solvent was evaporated subsequently. This condensed solution reacted with silica-gel of 8.0 g in dry toluene. After refluxing, the solid was filtered, washed and dried to give the product named SG-HO-DS. The resulting product SG-HO-pD was obtained during hydrolysis as previously described [19].

2.3. Effect of pH on adsorption

The effect of pH on the adsorption of Hg(II) was studied by adding 50.0 mg of silica-gel adsorbents to 1 cm^3 of 0.1 mol dm^{-3} Hg(II) and 19 cm^3 of buffer solution at different pH values in 100 cm^3 Erlenmeyer flask. This mixture was mechanically shaken for 24 h at 303 K to attain equilibrium. Then a certain volume of the solutions was separated from the adsorbents and the residual concentration of Hg(II) was detected by means of AAS. The adsorption amount was calculated according to the equation.

$$q = \frac{(C_0 - C)V}{W} \tag{1}$$

q, the adsorption amount (mmol g^{-1}), C_0 and C, the initial and the final concentrations of metal ions in solution, respectively