



Synthesis and characterization of bifunctional mesoporous silica adsorbent for simultaneous removal of lead and nitrate ions



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ABSTRACT

A novel acid-base bifunctional adsorbent was synthesized using a three-stage process involving (i) synthesis of MCM-41 mesoporous silica (MS) carrier, (ii) acidic modification of the carrier by aluminum isopropoxide dosing (Al-MS), and (iii) basic modification by amino groups post-grafting (Al-MS2). Large spatial hindrance amino groups were selected for the basic modification step to avoid spontaneous recombination and neutralization reactions between the two antagonist functional groups. X-ray diffraction, transmission electron microscopy, NH_3 -based temperature-programmed desorption, Fourier transform infrared spectroscopy, and N_2 adsorption–desorption techniques were used to characterize the samples obtained at each step. Then, the simultaneous adsorption capacities of lead (Pb(II)) and nitrate (NO_3^-) ions were investigated and compared. The results revealed that Al-MS2 had good adsorption efficiency for Pb(II) and NO_3^- , achieving maximum adsorption capacities of $712 \mu\text{mol/g}$ for Pb(II) and $1120 \mu\text{mol/g}$ for NO_3^- at pH 5.0. The proposed mechanism for the simultaneous removal of Pb(II) and NO_3^- by the adsorbents were also discussed. The results showed that Al-MS2 was successfully modified with two antagonist adsorption groups, thus providing a new strategy for designing multifunctional adsorbents for the simultaneous removal of toxic metal cations and anions from wastewater.

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1. Introduction

Contamination from heavy metal cations and toxic anions, such as copper, lead, sulfate, chromate, arsenate, and nitrate, is a major environmental concern because such ions can accumulate in animals, plants, and humans, subsequently causing fatal diseases because of their toxicity and carcinogenicity [1]. Advanced treatment processes must be used to decrease the concentrations of toxic ions in effluents from industrial or domestic sources such as ion exchange, reverse osmosis and nanofiltration, coagulation, precipitation, and adsorption [2,3]. Among these techniques, adsorption is very popular owing to its simplicity and low cost [4,5]. Considering that most adsorbents only adsorb either a type of cationic or anionic ion, it is necessary to develop bifunctional adsorbents that can remove both cations and anions simultaneously, thereby simplifying the treatment of toxic ions-containing wastewater. Porous materials have been selected as the most potential bifunctional adsorbents because of their intrinsic high specific surface area and stable interconnected frameworks with an active pore surface for easy modification [6].

The preparation of mesostructured silicas since 1992 [7] and to this date has diversified the field of applications in adsorption [8,9], catalysis [10], energy storage [11], electrochemistry [12], and biomedical engineering [13]. The most well-known representative of this class of material is MCM-41 (constituting an hexagonal arrangement) [14]. However, pure MCM-41 has an electronically neutral framework and lacks Brønsted acid sites, it only exhibits weak hydrogen-bonded types of sites [15–17]. Through introduction of additional functional groups, the physical and chemical properties of MCM-41 can be conveniently modified [18–26]. Some researchers have reported the introduction of tetrahedral aluminum into silica frameworks that results in the creation of higher Brønsted acid containing, thus enabling the capture of cations [27,28]. Other researchers have proved that amino-functionalized mesoporous silica is very effective for the removal of anions; additionally, the used adsorbent can be regenerated through a simple acid washing process [18,29]. However, we are unaware of any prior investigations in the preparation of acid- and amino-functionalized mesostructured silicas for the simultaneous removal of toxic metal cations and anions because the antagonist functions co-existing in a single matrix would typically instigate spontaneous recombination and neutralization reactions.

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In this study, we aimed to design a bifunctional adsorbent that can simultaneously uptake toxic metal cations and anions using a three-step process. First, the MCM-41 mesoporous silica (MS) was synthesized. Second, the material (Al-MS) that contains higher Brønsted acid prepared by isomorphous substitution of Al for Si. Third, the surface of Al-MS was modified with 3-aminopropyltriethoxysilane to obtain Al-MS1 using a grafting technique to afford high exposure of amino group loading. Then Al-MS1 was modified with cyanuric chloride before the immobilization of diethylenetriamine to obtain Al-MS2, which could remove anions from aqueous solution after protonation. Owing to the introduction of the large spatial hindrance amino groups, the challenge of the incompatible nature of the two antagonist functions in one matrix was successfully resolved. Thus, a bifunctional adsorbent containing acidic sites and basic sites isolated from each other was prepared. The adsorbent was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), NH_3 -based temperature-programmed desorption (NH_3 -TPD), Fourier transform infrared (FTIR) spectroscopy, and N_2 adsorption–desorption. The simultaneous adsorption properties of Pb(II) and NO_3^- ions from $\text{Pb}(\text{NO}_3)_2$ aqueous solution were then investigated. The results present a gateway to designing multifunctional adsorbents for the simultaneous removal of cations and anions from wastewater.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), ethanol (99.8%), ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 29%), tetrahydrofuran (THF), *n*-hexane, toluene, lead nitrate dihydrate ($\text{Pb}(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$, analytical grade), and hydrochloric acid (HCl, 37%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Aluminum isopropoxide, 3-aminopropyltriethoxysilane (APTES, 97%), cyanuric chloride (CC), and diethylenetriamine (DETA) were purchased from Sigma–Aldrich (China). Deionized water was used in all experiments and was obtained from a Milli-Q water purification system (Millipore SAS-67120 Molsheim, France).

2.2. Synthesis of MS and Al-MS

Al-MS (Si:Al = 10) was prepared as follows: First, 0.42 g aluminum isopropoxide ($\text{Al}(i\text{-C}_3\text{H}_7\text{O})_3$ dissolved in 50 mL *n*-hexane) was mixed with 4 mL TEOS in 68 mL ethanol under stirring. Then, 20 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ solution was added to the reaction system that was stirred for 30 min. A template solution was separately prepared by dissolving 1 g CTAB in a mixture of 100 mL deionized water and 60 mL ethanol. The TEOS/ $\text{Al}(i\text{-C}_3\text{H}_7\text{O})_3$ mixture was added to the template solution under vigorous stirring at room temperature resulting in a gel. The gel was transferred to a Teflon-lined autoclave and heated at 393 K for 24 h. After reaction, the autoclave was allowed to cool to room temperature, resulting in a white precipitate that was filtered and dried at 393 K. The as-synthesized powder (Al-MS) was calcined at 833 K for 6 h. MS was prepared following the same procedure, but without the addition of aluminum isopropoxide.

2.3. Synthesis of acid-base bifunctional adsorbent

2.3.1. Modification of Al-MS with APTES

1.0 g Al-MS was pretreated at 423 K to remove adsorbed water. Then, Al-MS was added to a mixture containing APTES (5 mL) and toluene (60 mL; toluene was dried prior to use). The reaction

mixture was vigorously stirred under reflux for 20 h in an inert atmosphere. The solid (Al-MS1) was separated by filtration, washed twice with toluene followed by ethanol, and then dried at 373 K for 12 h.

2.3.2. Covalent attachment of CC to Al-MS1

1.0 g Al-MS1 was reacted with a saturated solution of CC in THF (100 mL) under vigorous stirring at 273 K for 6 h. Upon reaction completion, the resulting yellow solid (Al-MS-CC) was filtered, washed thoroughly with hot toluene and ethanol to remove unreacted CC. Finally, the material was dried at 373 K overnight.

2.3.3. Immobilization of DETA on Al-MS-CC

1.0 g Al-MS-CC was reacted with 3 g DETA under vigorous stirring at 318 K for 24 h. The new solid (Al-MS2) obtained from this reaction was washed with ethanol, separated by filtration, and dried at 393 K for 12 h. The chemical structures of Al-MS1 and Al-MS2 were given in Fig. 1.

2.4. Adsorption experiments

Prior to conducting the adsorption studies, 0.1 g Al-MS1 or Al-MS2 was stirred in 100 mL 0.1 mol/L HCl for 6 h at room temperature to convert the amino groups into ammonium moieties [30]. The acidified materials were then recovered by filtration, dried at room temperature overnight before used as adsorbents.

The samples (0.1 g; MS, Al-MS, Al-MS1, Al-MS2) were separately mixed with 50 mL $\text{Pb}(\text{NO}_3)_2$ solution in a Teflon centrifuge tube at an initial concentration ranging from 0.5 to 3 mmol/L. To maintain similar conditions for the cationic and anionic ions, the solution initial pH during the adsorption process was controlled at 5.0. The solution-containing centrifuge tubes were equilibrated for 3 h in a reciprocating shaker at 180 rpm at 298 K. After the adsorption process was completed, each solution was centrifuged for 30 min at 5000 rpm and filtered. The adsorption capacity of Pb(II) or NO_3^- ions of each sample was determined using Eq. (1) (according to Anbia and Lashgari [31]):

$$Q = (C_0 - C_e)V/m \quad (1)$$

where Q is the adsorption capacity (mmol/g), C_0 and C_e are the initial and equilibrium concentrations (mmol/L) of the cations or anions, respectively, V is the volume (L) of solution, and m represents the weight (g) of the adsorbent.

To reduce experimental errors, each experiment was duplicated and the data were averaged. To assess the occurrence of any

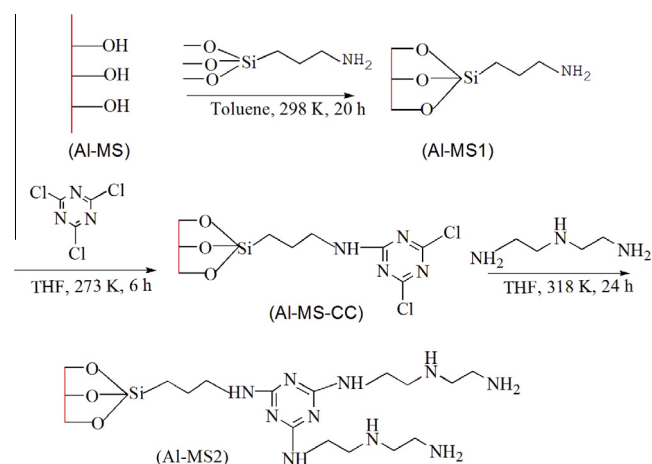


Fig. 1. Reaction schemes for the synthesis of Al-MS1 and Al-MS2.

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