

Lanthanum functionalized highly ordered mesoporous media: implications of arsenate removal

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Introduction

Human activities and natural processes release arsenic into ground and surface waters creating potentially serious environmental problems for humans and other living organisms [1]. In recognition of this threat, a new arsenic limit of 10lg/l, lowered from the current 50g/l, will become effective in 2006 for drinking water systems in the United States. Consequently, there is an urgent demand for an economical, highly effective, and reliable technique that is capable of meeting this new maximum contaminant level for arsenic. Many adsorbents have been developed for arsenic removal since adsorption is considered a promising technology, due in part to its ease of set up [2–5]. Activated alumina has been one of the best available adsorbents for point-of-entry/point-of-use (POE/POU) adsorption systems, and has been extensively studied due to its selective characteristics and effectiveness for arsenic adsorption [6]. However, the pH of the influent, which controls the presence of arsenic species, needs to be controlled to achieve maximum arsenic adsorption capacity. When activated alumina is regenerated, its adsorption capacity is reduced by 30–40%. Furthermore, due to a slower adsorption reaction, activated alumina requires relatively longer empty-bed contact times (3–5 min) than ion exchange resins. Therefore, a highly effective adsorbent for arsenic removal is needed.

M41S mesoporous silicate molecular sieves have a self-assembled molecular array of surfactant molecules

as a structure-directing template, which results in very sharp and ordered pore distributions of inorganic materials, as well as a high surface area and pore volume [7]. Using these advanced properties, Fryxell et al. [8] synthesized copper-chelated, ethylenediamine immobilized mesoporous silicate as an anion adsorbent. Their media have had positively charged hosts with 3-fold symmetry that matched the geometry of tetrahedral anions, resulting in a high selectivity for arsenate, as well as a high sorption capacity of about 140mg (arsenate)/g. Yoshitake et al. [9,10] tried to synthesize aminosilane-functionalized MCM-41, SBA-1, and MCM-48, which were coordinated with each cation (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , or H^+), and evaluated the arsenate adsorption properties. Fe-coordinated diamino-functionalized MCM-41 was found to have the largest arsenate adsorption capacity (2.5mmolAs/g) and a distribution coefficient of more than $2.0 \cdot 10^5$, even at an arsenate concentration below 100mg/l. Both cases, however, tried to utilize complicated synthesis procedures in which expensive and toxic chemicals were used, resulting in a significant limitation for large-scale application.

Thus, in this study, we have attempted to develop a simplified, economical, nontoxic synthesis route for mesoporous materials immobilized with lanthanum oxide, which has been known to have a high IEP and selectivity for arsenic species. As a medium having a higher sorption capacity than activated alumina, lanthanum oxide has a higher isoelectric point (IEP) of 11.1 than activated alumina of 9.2 [11]. Lanthanum is extracted from bastnaesite and monazite [12] and is one of the cheapest rare-earth elements. It is also known to be nontoxic and environmentally friendly [13]. Aduwum [14] investigated the adsorption process of lanthanum oxide and binary lanthanum–aluminum oxide for the removal of selenium, which has a behavior very similar to arsenic. Lanthanum oxide has adsorption capacities of 30–40

mg (Se)/g of media. Wasay et al. [15,16] studied the adsorption process of a lanthanum-impregnated silica gel and lanthanum-impregnated alumina in removing fluoride, phosphate, selenite, and arsenate ions. Their adsorption isotherm results showed that there was no interference from other anions such as Cl⁻, Br⁻, I⁻, NO₃⁻, and SO₄²⁻. Meanwhile, as a supporting silicate of highly-dispersed lanthanum oxide, the mesoporous silica molecular sieve SBA-15 was synthesized and used in this study. The uniform, two-dimensional, hexagonal (space group p6mm) mesopore channels of SBA-15 can be tailored by changing synthesis conditions. The mesoporous silica SBA-15 molecular sieves usually have a surface area of 600–1000m²/g, pore volume of 0.6–1.3cm³/g, and pore size of 50–100Å without poreexpanding chemicals.

The objectives of this study were as follows: (1) to develop novel adsorbents by synthesizing highly ordered mesoporous silica SBA-15 and incorporating lanthanum oxide using an incipient-wetness impregnation technique; (2) to characterize the physicochemical properties of these media using several fine characterization techniques such as XRD, N₂ gas isotherm analysis, and FTIR, (3) to evaluate the adsorption capacities by examining the adsorption kinetics and isotherms of arsenate, and (4) to understand the adsorption behavior of the media in connection with the physicochemical characterizations discovered using the above fine tools.

Materials and methods

Synthesis of lanthanum-impregnated SBA-15 and conductivity tests

SBA-15 was synthesized using triblock copolymer (Pluronic P123, EO₂₀PO₇₀EO₂₀, Aldrich) as a structure-directing reagent and tetraethyl orthosilicate (Aldrich) as a silica precursor. A 4-g triblock copolymer

was dissolved in 60ml of deionized water for 30min and 120ml of 2M hydrochloric acid solution was added. The mixed solution was stirred for 30min. Tetraethyl orthosilicate (TEOS) was then added to the mixture and heated at 35_C for 20h. The mixture was transferred into a Teflon bottle and heated at 90 _C for 24h without stirring. The solid product was then filtered using 0.45- μ m filter paper and dried at room temperature under a vacuum before calcination. The mole fraction of each component for as-synthesized SBA-15 was 1mol TEOS:5.854mol HCl:162.681mol H₂O:0.0168mol triblock copolymer. Calcination was performed in an oven at 550_C for 6h with air to remove the triblock copolymer organic component. The calcined SBA-15 was preserved at room temperature under a vacuum. La(NO₃)₃ · xH₂O (x = 3–5, Aldrich_) was selected as the lanthanum precursor and incorporated into SBA-15 using an incipient-wetness impregnation technique [17]. The mixture was dried in a hood at room temperature for one day.

In order to determine the optimum temperature for completing the oxidation of lanthanum precursors, calcinations were conducted under different temperatures, followed by conductivity tests. The SBA-15 impregnated with the highest percentage (80%) of lanthanum (designated to La₈₀SBA-15) was calcined in an oven with the programmed temperature ranging from room temperature to a planned temperature with a temperature increase of 0.5 _C/min. The percentages of lanthanum impregnation onto SBA-15 in this study can be explained by the following equation:

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The solids were then calcined at a predetermined terminal temperature for 4h. After calcination, solids were kept in a vacuum chamber until conductivity tests were performed. The conductivity tests followed the procedure

described by Jang et al. [17]. Experimental results of conductivity showed that the conductivities decreased with an increase in final temperature because lanthanum ions incorporated into SBA-15 were oxidized more as a result of the higher temperature. The conductivity of material treated with 550_C was the same as that of deionized water, implying the complete oxidation of the lanthanum precursor. Therefore, all lanthanum-impregnated SBA-15 media used in all subsequent experiments were synthesized using the final temperature of 550_C.

Characterization of media

Using a Stoe high-resolution X-ray diffractometer (Microphotonics, Allentown, PA) equipped with Cu K α radiation (40kV, 25mA), X-ray diffraction patterns in a short range (0.8–2.1 θ) were obtained for a series of lanthanum-impregnated SBA-15 and calcined SBA-15. A wide range (10–70 θ) of X-ray diffraction patterns was obtained for media impregnated with 80% of lanthanum by weight (designated as La₈₀SBA-15), which has the largest percentage of lanthanum (44.4%) based on the mass of the media. N₂ gas adsorption–desorption isotherms were performed at 77K using a Micromeritics ASAP 2400 analyzer (Norcross, GA). Media were dehydrated at 393K for one day before performing the isotherm tests. The BET specific surface area (A_{BET}) was calculated using the linear portion of the BET equation with a relative pressure in the range of 0.05–0.2. The primary mesopore size distributions (PSD) of the media were obtained using the recently developed Kruk, Jaroniec and Sayari (KJS) approach, which is the Barrett, Joyner and Halenda (BJH) method with the corrected Kelvin equation [18]. The pore diameter corresponding to the maximum PSD was denoted as $W_{\text{KJS}} (A^\circ)$. Using the adsorption branch of the hysteresis loop in the nitrogen adsorption isotherm, this method can accurately calculate

pore size distribution under the assumption of a cylindrical pore shape [18,19]. As an alternative to the a_s plot method [$a_s = V_{ads}(P/P_0)/V_{ads}(0.4)$], the b_s plot method was used to estimate the primary mesopore volume (V_p) for simplicity reasons. Based on the Frenkel, Halsey and Hill (FHH) theory, the V_{ads} of the a_s equation is replaced by the statistical thickness of the adsorbed gas layer, yielding the following equation: $b_s = [\ln(0.4)/\ln(P/P_0)]^{(1/2.7)}$ [20]. The micropore volume (V_{micro}) and the area (A_{micro}) were obtained by t-plot method. The total pore volume (V_t) was determined at a relative pressure of 0.99. Infrared spectra were obtained by a Mattson Galaxy 5020 FTIR spectrometer (Mattson Instruments, Madison, WI) in order to obtain information on both the change of functional groups on the oxide surface and the structural stability after lanthanum impregnation at room temperature. Potassium bromide was mixed with the sample as a pretreatment.

Arsenate adsorption kinetics

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, Sigma) was used without any modification as the arsenate source for a stock solution. A stock solution of arsenate (133mmol/l) was prepared with 0.01M $NaNO_3$ solution based on deionized water. A Photronix reagent-grade water system was used to prepare all of the deionized water. The adsorption isotherm and kinetic data with various amounts of lanthanum-impregnated SBA-15 were compared with activated alumina (AA-400G, ALCAN), which is a widely used commercialized product for arsenic removal and has a specific surface area (BET) of 350–380m²/g [21].

Arsenate kinetic studies were conducted with mesoporous adsorbents (SBA-15 impregnated with various amounts of lanthanum) and activated alumina. An aliquot

of 1000ml of deionized water prepared with 0.01M NaNO₃ was poured into a reaction bottle for each kinetic study. After injecting arsenate stock solution to make the initial arsenate concentration of 0.267mmol/l, the solution was stirred with a magnetic stirrer at a velocity of 500 rpm. The pH of the solution was adjusted to 7.2 ± 0.02 with an automatic pH titrator, and the temperature was maintained at 20 ± 0.5 °C for one hour before 0.15g of media was injected. In order to maintain a constant pH during kinetic studies, the automatic titrator was installed in the reactor and connected to a pH electrode and small tubes that ran from two pumps, titrating with small volumes of acid (HNO₃, 0.01M) and base (NaOH, 0.01M) stock solutions. One of the two pumps, connected to either the acid or base stock solution, was operated when the pH drifted ± 0.02 pH units from the initial pH. An aliquot of 5ml of suspension was withdrawn at 2–60min intervals and filtered through a 0.45-µm Uniflo filter for arsenate analysis. The pseudo second-order kinetic equation was found to fit well for many of the chemisorption processes using heterogeneous materials [22,23]. Therefore, all of the kinetic data from our experiments were fitted with a pseudo second-order kinetic model in estimating the rate constants, initial sorption rates, and adsorption capacities of arsenate. The pseudo second-order kinetic rate equation is expressed as [22]:

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