



## Mesoporous aluminosilica monoliths for the adsorptive removal of small organic pollutants

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### ARTICLE INFO

#### Article history:

Received 7 February 2011

Received in revised form 19 October 2011

Accepted 31 October 2011

Available online 7 November 2011

#### Keywords:

Mesoporous aluminosilica

Monoliths

Cubic structures, Organic pollutants

Nano-adsorbent

Anilines

Adsorption

Removal

### ABSTRACT

Water treatment for the removal of organic or inorganic pollutants has become a serious global issue because of the increasing demand for public health awareness and environmental quality. The current paper, reports the applicability of mesoporous aluminosilica monoliths with three-dimensional structures and aluminum contents with  $19 \leq \text{Si}/\text{Al} \leq 1$  as effective adsorbents of organic molecules from an aqueous solution. Mesoporous cubic  $Pm\bar{3}n$  aluminosilica monoliths were successfully fabricated using a simple, reproducible, and direct synthesis. The acidity of the monoliths significantly increased with increasing amounts of aluminum species in the silica pore framework walls. The batch adsorption of the organic pollutants onto (10 g/L) aluminosilica monoliths was performed in an aqueous solution at various temperatures. These adsorbents exhibit efficient removal of organic pollutants (e.g., aniline, p-chloroaniline, o-aminophenol, and p-nitroaniline) of up to 90% within a short period (in the order of minutes). In terms of proximity adsorption, the functional acid sites and the condensed and rigid monoliths with tunable periodic scaffolds of the cubic mesopores are useful in providing easy-to-use removal assays for organic compounds and reusable adsorbents without any mesostructural damage, even under chemical treatment for a number of repeated cycles.

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### 1. Introduction

Water pollution results in serious health problems, particularly in third world countries. The considerable contamination of the aqueous environment by organic pollutants still requires the development of quick and simple methods for the removal, separation, and determination of these compounds [1,2]. A common problem in many industries is the disposal of large volumes of wastewater containing major classes of these organic compounds, which are carcinogenic and mutagenic, with high toxicological potentials. Among these discharged pollutants, aniline compounds are one of the most important organic intermediates that are widely used in the manufacture of conducting polymers, rubbers, drugs, dyes, and pesticides [2]. The potential use of aniline compounds resulted in their large-scale disposal into wastewater. For example, nitroaniline is a highly toxic agent to humans that is absorbed through the skin or through inhalation [3]. Exposure to this organic sub-

stance can result in a condition called methemoglobinemia, which is characterized by changes in the blood. Hemoglobin is specifically converted into methemoglobin. Such a conversion results in the impairment of blood cells, consequently reducing their capacity to transport oxygen [4].

Efficient techniques for the removal of these highly toxic compounds from water have drawn significant interest [5]. Among the possible techniques for water treatments, the adsorption process by solid adsorbents shows potential as one of the most attractive and efficient methods for the purification and separation of trace organic contaminants in wastewater treatment [5]. Various adsorbents, such as organic clay [6], silica gel [7], zeolites [8], montmorillonite [9], resins [10], polymers [11], activated carbons [12a],  $\alpha\text{-Al}_2\text{O}_3$  [12b], and iron powders [13], have been used for the removal of aniline compounds from wastewater. Although these solid materials are commonly used as efficient adsorbents for the removal of organic pollutants from contaminated water, particularly activated carbons, the development of new adsorbent materials that can enhance the adsorption capacity and affinity and of reproducible and reversible assays is still necessary [3,14,15].

Mesoporous molecular sieves have received increasing interest from the scientific community because of their unique properties [16–20]. Mesoporous materials have been identified as promising adsorbents for biochemical molecules, such as amino acids,

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peptides, and proteins [16]. For instance, mesoporous silica can also be used to remove some organic and inorganic pollutants from water [15,17,18]. Bibby and Mercier used cyclodextrin-functionalized mesoporous silicas as adsorbents for different water-soluble aromatic molecules, including p-nitrophenol and p-nitroaniline [19]. The open-framework nature and large pore size (2–50 nm) of mesoporous adsorbents are the key components for the fast adsorptivity and accessibility of the molecules to the binding sites [18,19]. Arumugam and Perumal reported that neutral alumina adsorbents could be used for developing a new purification process for pharmaceutical and chemical wastes, such as benzophenone, aniline, p-nitroaniline, and resorcinol [20]. Zeolites with different pore orientations and organizations have been used to remove p-nitroaniline molecules from an aqueous medium [21].

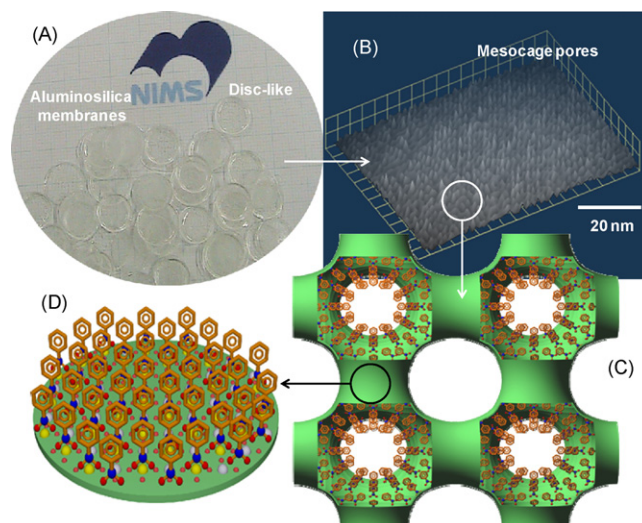
Recently, the increasingly stringent device requirements based on mesoporous materials for advanced applications, such as catalysis [22], sensing [23], molecular transport and separation [24], and multifunctional designs [25], have demanded modulated pore structures, functional surface chemistry, and the incorporation of heteroatoms, such as aluminum [22,26–32]. In this regard, the synthesis of aluminosilica monoliths with high acidity and structural integrity may result in the expansion of widespread applications [33–35]. The current research efforts focus on two critical issues: (1) the fabrication of three-dimensional (3D) cubic  $Pm\bar{3}n$  nanoscale monolithic discs as membrane platforms and (2) the design of easy-to-use, portable, and reusable chemical adsorbents for the removal of up to 90% of organic pollutants within a short period (in the order of minutes) from an aqueous solution.

## 2. Experiments

### 2.1. Synthesis of cubic $Pm\bar{3}n$ aluminosilica monolithic adsorbents

The simple synthesis process for monolithic aluminosilica adsorbents was based on the direct templating of the microemulsion liquid crystalline phase of the Brij 56 surfactant. In this direct synthesis of cubic  $Pm\bar{3}n$  aluminosilica monoliths, for example, at the Si/Al ratio of 9 (w/w) and at a Brij 56/tetramethylorthosilicate (TMOS) ratio of 0.5 (w/w), the precursor solution [1 g of Brij 56, 0.5 g dodecane, 2 g TMOS, 0.569 g  $\text{Al}(\text{NO}_3)_3$ , 2.5 g  $\text{H}_2\text{O}-\text{HCl}$  (at pH 1.3), and 10 g of ethanol] was stirred for 30 min to form a homogeneous sol–gel solution. The resulting optical gel-like mixture was placed in a graduate ingot. The mixture subsequently acquired the shape and size of the cylindrical casting vessel. The monoliths were gently dried at room temperature for 2 h and then allowed to stand in a tightly closed ingot for 1 day to complete the drying process (Scheme 1).

To obtain monolithic samples with various aluminum contents at the Si/Al ratio of 19, 10, 4, 2.3, 1.5, and 1, the molar composition of  $\text{Al}(\text{NO}_3)_3$  was varied from  $0.7 \times 10^{-3}$  mol to  $13.6 \times 10^{-3}$  mol (see Table S1, Supporting information). The organic moieties were removed by calcination at 550 °C under air for 5 h. The calcined cage cubic  $Pm\bar{3}n$  monoliths clearly had stable and tough discs with 1.2 mm thickness and ~12 mm length. In turn, the transparency of the monoliths was lost by calcination [18,36]. In addition, Al/SBA-15 aluminosilica powder was synthesized using the conventional hydrothermal method (see Supplementary materials). Advanced characterization techniques, such as  $\text{N}_2$  adsorption isotherms, X-ray diffraction (XRD), transmission electron microscopy (TEM) and three-dimensional TEM surfaces (3D TEM), energy dispersive X-ray microanalyzers (EDX),  $^{27}\text{Al}$  magic-angle spinning nuclear magnetic spectroscopy ( $^{27}\text{Al}$  MAS NMR), and  $\text{NH}_3$  temperature-programmed desorption ( $\text{NH}_3$ -TPD), were used for the determination of the structural, textural, and physicochemical properties of aluminosilica adsorbents (see Supplementary materials).



**Scheme 1.** Aluminosilica monoliths with a disc-like shape (A) and mesocage pores (B) as adsorbents (C) of organic compounds (I–IV) inside the mesocage cavity and onto pore surfaces of 3D cubic  $Pm\bar{3}n$  structures (D). Note that 3D TEM image (B) was recorded with aluminosilica monoliths with a Si/Al ratio of 4.

### 2.2. Batch adsorption method of organic pollutants

The batch adsorption of the organic pollutants (I, II, III, and IV) onto (0.2 g) aluminosilica monoliths was performed in an aqueous solution at different temperatures (30–45 °C,  $\pm 0.1$  °C range). The adsorption process was performed using a shaker thermostat, where the shaking rate was kept constant for all experiments. The initial concentration of adsorbates in the range of  $5 \times 10^{-3}$  mol/L to  $8 \times 10^{-4}$  mol/L was measured using a Shimadzu 3700 model solid-state ultraviolet–visible spectrophotometer at specific wavelengths of 287, 289, 289, and 262 nm for I, II, III, and IV molecules, respectively. The adsorption amount ( $q_e$ ,  $\text{mmol g}^{-1}$ ) of the molecules at the equilibrium step was determined according to the following equation:

$$q_e = \frac{C_0 - C_e}{V} m \quad (1)$$

where  $V$  is the solution volume (L);  $m$  is the mass of monolithic adsorbents (g); and  $C_0$  and  $C_e$  are the initial and equilibrium adsorbate concentrations, respectively. The percentage uptake (%U) of the adsorbate solutes at the adsorption equilibrium was calculated using the following equation:

$$\% U = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

The fraction of the coverage mesocage adsorbent surfaces ( $f_c$ ,  $\text{g/m}^2$ ) occupied by the pollutant molecules was calculated according to the following equation:

$$f_c = \frac{M\beta}{S} \quad (3)$$

where  $M$  is the molecular area of pollutant molecules in the range of 63–70  $\text{\AA}^2$  [17],  $S$  ( $\text{m}^2/\text{g}$ ) is the surface area of the monolithic adsorbents, and  $\beta$  is the number of molecules adsorbed per unit area of mesocage adsorbents. However,  $\beta$  can be calculated as follows:  $\beta = (q_e/S) \times N_A$ , where  $N_A$  is Avogadro's number ( $6.02 \times 10^{23}$   $\text{mol}^{-1}$ ).

The intraparticle diffusion of pollutants into mesocage adsorbents can be determined by plotting the fractional attainment of equilibrium  $F_e = q_t/q_f$  against  $t^{1/2}$  according to Fick's second law relationship [37]:

$$F_e \left( \frac{q_t}{q_f} \right) = \frac{6}{r\sqrt{Dt/\pi}} \quad (4)$$

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