Nano-modeling Adsorption of Aniline Compounds onto Mesoporous Structures

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Abstract: The considerable contamination of the aqueous environment by organic pollutants still requires the development of effective adsorbents these compounds. The current work reports the applicability of mesoporous aluminosilica monoliths with three-dimensional structures and aluminum contents with 19 ≤ Si/Al ≥ 1 as effective adsorbents of aniline molecules from an aqueous solution. To better understanding the role of microscopic geometry and the nanoscale pore orientation of mesostructures, theoretical models have been developed. In addition, the atomic charge distribution in the interior structures was investigated to give insight about the effect of active site surfaces in the enhancement of the adsorption process. Our experimental results suggest that the acidity of the adsorbents significantly increased with increasing amounts of aluminum species in the pore framework walls. The natural surfaces of active acid sites of monoliths strongly induced the removal and adsorption of environmentally toxic aromatic amines from wastewater. The relative adsorption affinity of the mesocage adsorbent for organic pollutants was decreased in the order of p-nitroaniline < o-aminophenol < p-chloroaniline < aniline. Generally, this adsorption model enables the development of simple and effective technique for the removal wastewater treatment.

Key-Words: Nanomodel adsorbent, aniline compounds, theoretical studies, 3D microscopic geometry.

1 Introduction

Water pollution results in serious health problems, particularly in the developing countries. The considerable contamination of the aqueous environment by organic pollutants still requires the development of simple and fast methods for the removal, separation, and determination of these compounds [1, 2]. In addition, a common problem in many industries is the disposal of large volumes of wastewater containing major classes of these organic compounds, which are mutagenic and carcinogenic, 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. p-Chloroaniline is a highly toxic agent to humans that is absorbed through the skin or through inhalation [3]. Efficient techniques for the removal of these highly toxic compounds from water have drawn significant interest [4].

Pollutants adsorption by solids is considered as a promising and efficient technique for water treatment, [5]. Recently, ordered mesoporous silica materials incorporating functional active sites, such as metals and molecules, have been found to have potential uses as intelligent materials [6]. The hybrid materials based on mesoporous silicas are presently regarded as flexible and versatile construction units for targeting applications. However, the functional sites of such materials are expected to possess unique properties caused by the small confined space.

Recently, we fabricated 3D cubic aluminosilica mesostructures with uniform and large pores ≤ 10 nm through direct preparation using copolymer P123 (EO20PO70EO20) or F108 (EO141PO44EO141) templates [7]; they are thermally and hydrothermally stable. These aluminosilica mesostructures are highly promising candidates for the adsorption of nanoscale molecules (biomolecules) or colorant dyes.

In the current study, hexagonal p6mm and cubic pm3n aluminosilica mesocage with mesoporous cavities have been fabricated based. The prepared mesocage enable us to study the removal and adsorption of aniline molecules from aqueous solution. Moreover the micro/meso-structural properties were calculated using theoretical modelling (Fig. 1), in particular the effect of molecular orientation in the functional acid sites. Generally this
adsorption model enables the development of simple and effective technique for the removal wastewater treatment.

Fig. 1 3D cubic Pm3n geometrical modeling of meso and micro scale structures of the aluminosilica (A, B) and the model of charged cluster aluminosilica monoliths with p-Cl-Ar-NH₂ adsorption (C).

2 Experimental

2.1 Chemicals

All materials were used as produced without further purification. Tetramethylorthosilicate (TMOS), and aluminum nitrate enneahydrate (Al(NO₃)₃·9H₂O), p-nitroaniline (p-NO₂-Ar-NH₂), o-aminophenol (o-NH₂-Ar-OH), p-chloroaniline (p-Cl-Ar-NH₂), and aniline (Ar-NH₂), and the n-alkyl-oligo(ethylene oxide) surfactant, C₁₈H₃₅(OCH₂CH₂)₁₀OH, polyoxyethylene(20) oleyl ether (Brij 98) were obtained from Sigma-Aldrich Company Ltd. USA. The solubilizing alkane agent such as dodecane (C₁₂H₂₆) was obtained from Wako Company Ltd. Osaka, Japan.

2.2 Preparation of aluminosilica monolith mesocages

The simple preparation for monolithic aluminosilica adsorbents was based on the direct templating of the microemulsion liquid crystalline phase of the Brij 98 surfactant. In this direct preparation of cubic Pm3n aluminosilica monoliths, for example, at the Si/Al ratio of 9 (w/w) and at a Brij 98/tetramethyloctohsilicate (TMOS) ratio of 0.5 (w/w), the precursor solution [1 g of Brij 98, 0.5 g dodecane, 2 g TMOS, 0.569 g Al(NO₃)₃, 2.5 g H₂O-HCl (at pH= 1.3), and 10 g of ethanol] was stirred for 30 min to form a homogenous 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 d to complete the drying process. To obtain membrane samples with aluminum contents at Si/Al ratio of 19, 10, 4, 2.3, 1.5, and 1, the composition of Al(NO₃)₃ was varied from 0.7 × 10⁻³ to 13.6 × 10⁻³ mole ratio (Table 1). The mass ratio of surfactant to alkane was kept at 2:1 for all syntheses of the mesoporous aluminosilica membranes. The organic moieties were removed by calcination at 550 °C in air for 5 h. The calcined aluminosilica membranes clearly had stable and tough discs with 1.2 mm thickness and ~12 mm in length. The transparency of the membrane was lost during calcination, as previously reported for silica HOM-type monoliths [8].

2.3. Batch adsorption of aniline compounds

The batch adsorption of the anilines p-nitroaniline (p-NO₂-Ar-NH₂), o-aminophenol (o-NH₂-Ar-OH), p-chloroaniline (p-Cl-Ar-NH₂), and aniline (Ar-NH₂) onto (0.2 g) aluminosilica monoliths was performed in an aqueous solution at different temperatures (30 °C to 45 °C, ±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 × 10⁻³ mol/L to 8 × 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 p-NO₂-Ar-NH₂, o-NH₂-Ar-OH, p-Cl-Ar-NH₂, and Ar-NH₂ molecules, respectively. The adsorption amount (qₑ, mmol. g⁻¹) of the molecules at the equilibrium step was determined according to the following equation.

3 Results and discussion

3.1 Formation of hexagonal and cubic adsorbents

In the microemulsion mesophase systems, addition of an alkane with long alkyl chain lengths (C₁₂-alkane) to the lyotropic hexagonal (surfactant/TMOS/aluminum salt) composition substantially affected the formation of the 3D mesophase and the enlargement of pore sizes of the aluminosilica mesostructures. Our findings show (Fig. 2 and Table 1) that the increase in the Al contents increased the unit-cell constants (apm3n= d₃₁₀√5) of the cubic Pm3n structures, as evidenced from the shift of all reflection peaks to a low 2θ angle. This is mainly
due to the effect of the aluminum salt, which changed the micellar aggregate sizes and volume fractions of the sphere core and the corona of the surfactant at specific synthesis compositions [9]. Figure 3 shows evidence of the formation of the 3D aluminosilica monoliths based on the phase transformation mechanism of hexagonal P6mm-cubic Pm3n structures. The N$_2$ adsorption isotherms (Fig. 3B) of aluminosilica monoliths showed an H2-type hysteresis loop and well-defined steepness of isotherms, indicating that uniform cage-like pore structures were characteristic of the cubic aluminosilica monoliths [Reference, our and others]. Generally, the adsorption branches significantly shifted toward a lower relative pressure (P/P$_0$) with increasing aluminum contents. With both hexagonal and cubic Pm3n, the decrease in these textural parameters was observed because of the structural ordering degradation with high aluminum contents of monoliths (see Table 1).

Table 1: Synthesis conditions, structural and textural parameters of cubic Pm3n aluminosilica membrane adsorbents fabricated using microemulsion phases of Brij 98 as soft templates with a wide range of Si/Al mole ratios. Unit lattice constant (a$_{Pm3n}$ = d$_{210}$/$\sqrt{5}$), BET surface area (SBET), and NLDFT pore size distribution (PSD), and pore volume (Vp) are indicated.

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>Synthesis conditions</th>
<th>Structure parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>$10^2$T/mole, $10^3$Al (NO$_3$)$_3$/mole, Brij 98/TMOS w/w</td>
<td>a nm, S$_{BET}$ m$^2$/g, R nm, Vp cm$^3$/g</td>
</tr>
<tr>
<td>4</td>
<td>1.31 0.7 0.5 14.1 703 4.3 0.73</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>1.31 5.8 0.5 14.9 445 4.0 0.68</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.31 13.6 0.5 15.2 390 3.9 0.43</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 Representative HRTEM and FTD (inserts) patterns of hexagonal P6mm (A) and cubic Pm3n (B) aluminosilica monoliths with Si/Al mole ratios of 19.

The transmission electron microscopy (TEM) images (Fig. 2) show that the 2D hexagonal and 3D mesoscopic qualities of aluminosilica monoliths still retained their long-range structural ordering over a large area even for samples with Si/Al ratios as high as 4. The overall TEM lattice images and the corresponding Fourier transform diffractogram (FTD) patterns (inserts) indicate the formation of hexagonal P6mm and cubic Pm3n structures. With low silica contents (1.5 ≤ Si/Al ≤ 1), representative TEM images (data not shown) reveal a short-range ordering or even wormlike mesopore channels that are interconnected in large size domains. These hexagonal and cubic monoliths with pore cavities show promise for the removal and decontamination of aniline compounds from aqueous water (see below).

The coordination state of the aluminum species was investigated using $^{27}$Al NMR (data not shown). In all the aluminosilica samples (19 ≤ Si/Al ≤ 1), two $^{27}$Al peaks centered at the chemical shift of -1 and 58 ppm, indicating the existence of octahedral (Al$^{VI}$, AlO$_6$, extra framework) and tetrahedral (Al$^{IV}$, AlO$_4$, framework) aluminum sites, respectively. Tetrahedrally coordinated aluminum sites were significantly increased with increasing aluminum contents in the mesoporous monoliths. The coordination and location of aluminum sites in the frameworks play a key role in the generation of the surface acidity of aluminosilica monoliths, which enhanced the adsorption capacity of the aniline pollutants.

3.2. Theoretical modelling of 3D geometrical orientation of mesocage adsorbents

The theoretical modelling of aluminosilicate structure was carried out to investigate the effect of atom arrangement in the lattice symmetry on the pore orientation and the 3D geometry. Furthermore, the charge distribution and orbital shape were also calculated to give insight about the effect of Al sites on the adsorbent acidity. Modelling Calculations were carried out using semiempirical MP3 methods implemented on Gaussian03 program package. This software is developed by Gaussian Inc. [11]. The crystal structure was defined on the bases of the
cluster model of spherical aluminosilicates (AlSi4O12) which consists of two types of oxygen linkage (i.e., oxygen-bonded to Si or Al and siloxane species, respectively). The first group is mainly responsible for the creation of Brönsted acid sites. The siloxane orientation may contribute to the crystal shape formation. This spherical aluminosilicates (AlSi4O12) cluster unit was used for construction of nano-scale alumiosilicate model (Fig. 1). Furthermore, Fig. 1B shows the electron density distribution on the structural model of aluminosilicate. It can be observed that the atoms oriented at the edges of cubic Pm3n symmetry can form micropore cavity with 0.7 nm diameter toward the inner side of the mesopore surfaces (~4.2 nm), as evidenced from N2 isotherms (Fig. 3 & Table 1).

The calculated atomic charges (Fig. 1C) of Al, Si, O-siloxane cross-linked frameworks, O-bridge Si, and O-bridge Al are 1.48, 1.35, -0.6, -0.57, -0.99, respectively. It is clear that the oxygen atoms in the Si–O–Al linkages are more negative than other oxygen in the linkage species, indicating to the high acid sites in this linkages compared with other sites in the frameworks.

3.3 Batch adsorption method of aniline molecules

The adsorption amount (qe, mmol. g⁻¹) of the molecules at the equilibrium step was determined according to the following equation:

\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]

where V is the solution volume (L); m is the mass of monolithic adsorbents (g); and C₀ and Cₑ are the initial and equilibrium adsorbate concentrations, respectively. Figure 4A shows the time-rate dependence of the adsorption amount of molecule solutes using mesocage cubic Pm3n monolithic adsorbents at specific conditions (i.e., 40 °C, adsorbent dose of 10 g/L, adsorbate concentration of 1.6 × 10⁻³ M, and constant shaking rate). Figure 4B shows the temperature-dependent kinetic response of the p-Cl-Ar-NH₂ adsorption. Results indicated that the increase in the temperature resulted in the increased activation energy of the adsorbates in the aqueous phase and consequently enhanced the adsorption amounts.

The percentage uptake (% U) of the adsorbate solutes at the adsorption equilibrium was calculated using the following equation:

\[ % \text{U} = \frac{(C_0 - C_e)}{C_0} \times 100 \]

Results show (Fig. 5) that percentage uptake (% U) of organic pollutants onto both hexagonal and cubic adsorbents was increased in the order of p-NO₂-Ar-NH₂ < o-NH₂-Ar-ONH < p-Cl-Ar-NH₂ < Ar-NH₂. Based on this adsorption behavior, the lower adsorption effectiveness of these organic pollutants was clearly consistent with the higher basicity (i.e., higher pKₐ) of these adsorbates, except with o-NH₂-Ar-ONH. However, the pKₐ values are 4.6, 3.97, 9.7, and 1.01 for Ar-NH₂, p-Cl-Ar-NH₂, o-NH₂-Ar-ONH, p-NO₂-Ar-NH₂ molecules, respectively.
acid sites because of the adsorption of organic molecules onto the aluminosilica monoliths in aqueous solutions [10]. The tendency of organic molecules to coordinate with Lewis acid sites is minimal. The number of Bronsted acid sites for aluminosilica monolith adsorbents is the key factors for the enhanced adsorption uptake with high Al contents. The thermodynamic equilibrium constant, $K_c$ of the adsorbed molecules deduced from the following equation: 

$$K_c = q_i / (1-q_i)$$

where $q_i$ is the ratio of the amount of molecule adsorbed at a time ($q_i$) to that adsorbed at infinity ($q_{\infty}$), (i.e. $q_i = q_i / q_{\infty}$).

From the value of $K_c$, the Gibbs free energy change, $\Delta G$, can be derived. The plot of $\ln K_c$ vs. $1/T$ (Fig. 5) gives the numerical values of $\Delta H$ of the adsorption of organic pollutants, $\Delta G$ and $\Delta S$, using the following relations (Table 1):

$$\Delta G = -RT \ln K_c$$

$$\ln K_c = (-\Delta H/RT) + \Delta S/R$$

where $\Delta H$, $\Delta S$, $\Delta G$, and $T$ are the changes in enthalpy, entropy, and in Gibbs free energy, and the temperature in Kelvin, respectively. $R$ is the gas constant. The plot of $\ln K_c$ vs. $1/T$ (Fig. 6) gives the numerical values of $\Delta H$ of the adsorption of organic pollutants, $\Delta G$ and $\Delta S$ are calculated and presented in Table 2. The thermodynamic equilibrium constant, $K_c$, increased with temperature for all adsorption assays, whereas the absolute value of $\Delta G$ increases with decreasing temperature. This result indicates that adsorption is spontaneous and more favorable at high temperature, which confirmed an endothermic adsorption process. In addition, the $\Delta S$ value decreases in this sequence: Ar-NH$_2$ > p-Cl-Ar-NH$_2$ > o-NH$_2$-Ar-OH > p-NO$_2$-Ar-NH$_2$, contributing to a greater value of $K_c$ and greater stability of thermodynamic adsorption. The reusability of the hexagonal and cubic adsorbent monoliths is of particular interest in developing recyclable adsorption systems (Fig. 7). After a complete adsorption process, the solid monoliths were collected and repeatedly washed with an acidic aqueous solution [HCl=1x10$^{-3}$ M] and then dried at 200°C for 12 h under air to remove the remaining molecular adsorbates. Reused hexagonal and cubic adsorbents are still effective for the adsorption of organic adsorbates after six recycles (Fig. 7). However, no significant changes in the adsorbent affinity toward the removal of organic pollutants, for example with p-Cl-Ar-NH$_2$ from the aqueous solution were observed after several cycles.

### Table 2 Illustration of the kinetic and thermodynamic parameters of the adsorption of [1.6 × 10$^{-3}$ M] organic pollutants into hexagonal aluminosilica monolith adsorbents [10 g/L] with a Si/Al ratio of 1.0

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$T$ °C</th>
<th>$K_c$</th>
<th>$\Delta G$</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
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<tr>
<td>Ar-NH$_2$</td>
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<td>3.7</td>
<td>-3.30</td>
<td>1.10</td>
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<td>1.13</td>
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<td>-3.98</td>
<td>1.15</td>
<td>80.0</td>
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<tr>
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<td>45</td>
<td>4.9</td>
<td>-4.25</td>
<td>1.16</td>
<td>80.0</td>
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<tr>
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<td>-3.02</td>
<td>0.59</td>
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Fig. 6 Illustration of the relationship plot between $\ln K_c$ against $1/T$ of the adsorption of the organic pollutants [1.6 × 10$^{-3}$ M] onto [10 g/L] hexagonal aluminosilica monoliths with Si/Al ratio of 1.

### 4. Conclusion

In conclusion, ordered hexagonal and cubic aluminosilica adsorbents were fabricated using a simple, reproducible and direct synthesis. The aluminosilica adsorbents attained the ordering and uniform hexagonal and cubic pores even with relatively high aluminum contents. Adsorption theoretical models were developed to explain the adsorbed molecules into the microscopic geometry and the pore orientation of aluminosilica monoliths. In addition, the electronic structures were also
calculated to give insight about the surface properties during the adsorption process. Results indicated that the adsorption uptake of organic pollutants onto both hexagonal and cubic the adsorbents was increased in the order of $p$-NO$_2$-Ar-NH$_2$ < o-NH$_2$-Ar-OH < $p$-Cl-Ar-NH$_2$ < Ar-NH$_2$. The adsorption uptake also depends on the amount of surface functional groups. Results also revealed that the hexagonal and cubic adsorbents are still effective for the adsorption of organic adsorbates after six recycles. Such integration of nano-adsorbents is the key to the further development of the environmental cleanup of toxic organic molecules.

Fig. 7 Reusability study of up to six times for the removal assay of $[1.6 \times 10^{-3}\text{ M}]$ p-Cl-Ar-NH$_2$ onto [10 g/L] hexagonal and cubic Pm3n aluminosilica adsorbents fabricated with a Si/Al ratio of 1 at 40 °C. Note that the efficiency (E) was calculated from the % ratio of the uptake (%U) per reuse cycle (No.) and the initial uptake obtained from the initial use of the adsorbents.

Acknowledgement

M. Ismael thanks Chemistry Department, Sohag University, for granting leave of absence.

References


