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Adsorption characteristics of phenolic and amino organic compounds on nano-structured silicas functionalized with phenyl groups

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ABSTRACT

Phenyl-functionalized mesoporous silicas (Ph-MSs) were synthesized as adsorbents of bisphenol A (BPA) from aqueous solutions via co-condensation method. Ph-MSs with different compositions, which were prepared using 10%, 15%, 20%, and 30% of phenyltriethoxysilane (PhTES) in silica precursors, were used in the adsorption of BPA in order to investigate the effect of surface hydrophobicities on the uptake of hydrophobic organic compounds. Material characterizations were carried out including X-ray diffraction, N_2 adsorption/desorption measurement, elemental analysis, Fourier transform infrared spectroscopy, and measurement of point of zero charge. The higher composition of PhTES offered higher hydrophobicity to the prepared Ph-MSs, whereas decreasing their structural order and surface area. Adsorption capacity of Ph-MSs for BPA depended on the surface area rather than the surface hydrophobicity. However, the adsorption data at low concentrations showed that the adsorption affinities for BPA were in the order of Ph-MS30 > Ph-MS20 > Ph-MS15 > Ph-MS10, which were fully consistent with the order of their surface hydrophobicities. Among the prepared materials, Ph-MS20 was selected as a representative adsorbent, and used to investigate further adsorption characteristics. Several aromatic compounds including *p-t*-butylaniline, *p-t*-butylphenol, aniline, and phenol, which had the similar molecular structures with BPA, were also adopted as adsorbates for the adsorption onto Ph-MS20. The selective adsorption behavior of Ph-MS was discussed using the equilibrium isotherms of the adsorbates on Ph-MS20.

1. Introduction

There have been growing concerns over the potential health threats by endocrine disrupting chemicals (EDCs) which may interfere with human hormones. The exposure to EDCs, which can occur through the contact with soil, water, or air contaminated with chemicals, is one of the most important topics in recent environmental studies [1–3]. Bisphenol A (BPA), one of EDCs, is an organic compound used to produce polycarbonate plastics and epoxy resins. These chemical products containing BPA are widely used as containers of food and drink, dental sealants, and baby bottles [4–9]. Low concentrations of BPA have been identified in wastewater, river water, effluents after treatment of landfill leachate, and even in finished-water samples because BPA is not completely removed during the conventional water and wastewater treatment processes [10–13]. This can lead to the presence of BPA in aquatic environment and drinking water.

It is necessary to reduce the amount of BPA in water, wastewater, and drinking water treatment plants to the levels less than the concentrations required to prevent adverse health effects. Among the several alternatives for the removal of EDCs, adsorption technology has been recognized as an effective and economic method [2,14,15]. Many researches on the BPA removal from aqueous solutions have been carried out using adsorbents such as mineral, carbon materials, and zeolites [16–19]. However, most of adsorption processes does not seem to remove BPA selectively, and thus high concentrations of another organic pollutant can be primarily captured, saturating adsorption sites.

In recent years, mesoporous silicas, which have the possibility of modifying surface functional groups and the unique structural and surface chemistry, have been intensively studied for the adsorption of pollutants in water [20–26]. In particular, high adsorption selectivity for some EDCs was obtained via simple grafting hydrophobic functional groups onto the surface of mesoporous silica. The molecular form of organic pollutants as well as the functional groups on the surface of the mesoporous silicas was the key factor in the selective adsorption of EDCs on the mesoporous adsorbents [27–30]. In the previous work [31], we reported that organic–inorganic hybrid mesoporous silicas incorporated with phenyl groups showed large adsorption capacity and higher adsorption selectivity for BPA against phenol than

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activated carbon (AC) from aqueous solutions. The high adsorption selectivity may be ascribed to the hydrophobic and hydrophilic surface groups of the hybrid adsorbents interacting with two benzene rings and two hydroxyl groups of BPA, respectively [31].

In this work, we prepared phenyl-functionalized mesoporous silicas (Ph-MSs) with different compositions and thus different surface hydrophobicities via co-condensation method. Adsorption characteristics of BPA from aqueous solutions were investigated using the prepared materials. In addition, the selective adsorption behavior of Ph-MS was discussed using the equilibrium adsorption isotherms of the organic compounds including phenol, aniline, *p*-*t*-butylphenol, and *p*-*t*-butylaniline, which had the similar molecular structures with BPA.

2. Experimental

2.1. Reagents

Silica sources, tetraethoxysilane (TEOS, 99%) and phenyltriethoxysilane (PhTES, 99%), were obtained from Aldrich. Hexadecyltrimethylammonium bromide (CTAB, 99%, Sigma), sodium hydroxide (NaOH, 98%, Junsei), and ethanol (99.8%, Ducksan) were used to synthesize adsorbents. Bisphenol A (BPA, 99%, Aldrich), phenol (99%, Aldrich), *p*-*t*-butylphenol (99%, Aldrich), *p*-*t*-butylaniline (99%, Aldrich) and aniline (99.5%, Aldrich) were used as adsorbates. All reagents were used as received without further purification.

2.2. Syntheses and characterizations

Phenyl-functionalized mesoporous silicas (Ph-MSs) were synthesized via co-condensation of TEOS and PhTES [31,32]. In a typical synthesis of an 20% PhTES-substituted MCM-41 derivative (Ph-MS20), 3.98 g of 1.0 M NaOH and 14.10 g of deionized water were mixed together, and 0.33 g of CTAB was dissolved in the aqueous NaOH solution at 50–60 °C. TEOS of 1.27 g and 0.37 g of PhTES were added to the solution to obtain a homogeneous mixture under vigorous stirring. The mixture was stirred for 48 h at room temperature. The resultant white precipitates were filtered, washed with water and ethanol, and then dried at 100 °C overnight *in vacuo*. The molar composition of the mixture was 1.0 total siloxane (0.80 TEOS and 0.20 PhTES):0.12 CTAB:0.5 NaOH:130 H_2O. Template was removed by stirring a suspension of the solid product (3.3 g/L) in acidic ethanol of 0.15 M HCl at 78 °C for 20 h. The extracted material was filtered, washed with ethanol three times, and dried at 100 °C for 20 h *in vacuo*. The 10%, 15%, and 30% PhTES-substituted MCM-41 type materials were prepared by similar procedures with Ph-MS20, and denoted as Ph-MS10, Ph-MS15, and Ph-MS30, respectively. MCM-41 was synthesized by such the way as the preparation of Ph-MSs, using TEOS only as a silica precursor.

X-ray diffraction (XRD) patterns were obtained using Cu Kα radiation (λ = 1.5418 Å) on a powder X-ray diffractometer (X'pert-PRO MRD/X'pert PRO MPD, PANalytical, Netherlands). Data were measured in the range from 1.5° to 10° of 2θ values with a step size of 0.010° and a step time of 4 s. Unit cell parameter, a_{hex} ($=2d_{100}/\sqrt{3}$, was determined from d_{100} reflections for MCM-41 type materials. N_2 adsorption/desorption measurements (ASAP 2010, Micromeritics, USA) were performed at 77 K. Prior to the measurements, samples were outgassed at 373 K overnight. Surface areas of MCM-41 and Ph-MSs were determined by BET method. Total pore volume was obtained from adsorption data, and micropore volume was obtained using *t*-plot method. Pore sizes of MCM-41 and Ph-MSs were obtained by BJH method and Horvath–Kawazoe (HK) method. Hydrophobicity of sample was obtained by water vapor adsorption measurement [33]. After drying samples at 80 °C for 3 h, they were allowed to adsorb water vapor in a closed container containing liquid water at 25 °C for 6 h. During experiments, it was ensured that samples were not in direct contact with the liquid water. The amount of water vapor adsorbed was estimated by weighing the samples before and after water vapor adsorption, and expressed in the percentage of weight increase of samples. Elemental analysis was performed using elemental analyzer (EA 1108, Fison, Italy) to estimate the number of organic groups incorporated into the prepared samples. Fourier transform infrared (FTIR) spectra were obtained using a spectrophotometer (Spectrum GX & AutoImage, Perkin-Elmer, USA) at a spectral resolution of 4 cm^{-1} after drying samples at 105 °C for 4 h. Point of zero charge (PZC) of Ph-MSs was determined through the method described by Mustafa et al. [34] using a pH meter (720A plus, Orion Research, USA). In order to measure PZC of the prepared samples, 40 mL of 0.1 M $NaNO_3$ solutions were taken in different flasks. The pHs of the solutions were adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 using HNO_3 and NaOH solutions, respectively. Approximately 0.2 g of sample was, then, added to each flask, and was shaken at 298 K for 24 h. The difference between initial and final pH (ΔpH) was plotted against initial pH values, and PZC value was determined as the pH value at which the value of ΔpH was zero in the plot.

2.3. Adsorption

The effect of pH on the adsorption of BPA onto Ph-MS20 was investigated in the pH range from 4 to 11. A series of 250 mL-stoppered amber vials were filled with BPA solutions of 20 mg/L. Ph-MS20 of 0.05 g was then added to the solutions, and the vials were shaken at 200 rpm for 6 h. Then, concentrations of BPA were measured using an UV–Vis spectrophotometer (8453 UV–Vis Spectrophotometer, Agilent, USA).

In order to estimate the equilibrium adsorption time for the uptake of BPA by Ph-MSs, time-dependent adsorption studies were performed using separate vials for each time interval. Concentrations of the vials were measured at different time intervals from 10 to 360 min to ensure the adsorption equilibrium. Initial BPA concentrations were fixed at 20 mg/L.

Equilibrium isotherms were obtained by a batch equilibrium technique. Typically, 50 mg of adsorbent was mixed with 250 mL of aqueous solutions containing desired concentrations of organic compounds ranging from 10 to 260 mg/L. The mixtures were shaken with a shaking speed of 200 rpm at 25 °C for 6 h using shaking water bath. Initial pHs of the solutions were in the range of 6.2–7.5 for different concentrations of organic compounds. After finishing adsorption experiments, adsorbents were filtered using 0.45 μm membrane. Concentrations of BPA, phenol, *p*-*t*-butylphenol, aniline, and *p*-*t*-butylaniline were obtained by measuring the absorbance of the solutions using UV–Vis spectrophotometer at wavelengths of 278, 276, 275, 278 and 274 nm, respectively. Calibration plots of absorbances versus concentrations for BPA, phenol, *p*-*t*-butylphenol, aniline, and *p*-*t*-butylaniline showed linear variations up to 40, 20, 40, 30 and 40 mg/L, respectively. Samples with higher concentrations of the aromatic compounds over the linear ranges were diluted with distilled water for the accurate determination of the concentrations. The amount of organic compound adsorbed onto the adsorbent, q_e (mg/g), was calculated by a mass balance relationship:

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

where C_0 is the initial concentration of aqueous solution (mg/L), C_e the equilibrium concentration (mg/L), V the volume of solution (L), and m the mass of adsorbent (g). Langmuir adsorption isotherm was used to model the adsorption behaviors: