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Adsorption of aromatic compounds on porous covalent triazine-based framework

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ABSTRACT

Covalent triazine-based frameworks (CTFs) are an emerging class of polymers whose adsorption properties of organic chemicals are not well understood. The main objective of this work was to evaluate combined effects of the functional groups of aromatic solutes and the triazine structure of a synthesized CTF on adsorption in aqueous solutions. Adsorption of the hydroxyl-, amino-, nitro-, and sulfonate-substituted monocyclic and bicyclic aromatic compounds was generally stronger than their non-substituted, nonpolar counterparts (benzene and naphthalene). When compared with Amberlite XAD-4 resin, one of the most common and widely used polymeric adsorbents, the CTF showed much stronger adsorption toward the polar and/or ionic compounds. To explain the adsorption enhancement of CTF, several specific, non-hydrophobic mechanisms were proposed, including hydrogen bonding (hydroxyl- and amino-substituted compounds), electrostatic attraction (anionized compounds), and π–π electron-donor–acceptor (EDA) interaction (nitroaromatic compounds) with the triazine structure of CTF. The hypothesized mechanisms were further supported by the observed pH dependence of adsorption. Resulting from size exclusion, adsorption of large-size dissolved humic acids on the homogeneous, nanopored (1.2 nm in size) CTF was negligible and did not affect adsorption of aromatic solutes. Additional advantages of fast adsorption/desorption kinetics and complete adsorption reversibility made CTF a superior adsorbent for aromatic compounds.

1. Introduction

Covalent triazine-based frameworks (CTFs, Fig. 1) are an emerging class of polymers first synthesized in 2008 by ionothermal trimerization of aromatic nitriles [1]. Because of the very large specific surface area, homogeneous pore structure, diverse functionality, and high chemical and thermal stability [1–5], CTFs are considered a promising candidate for energy gas storage and catalytic support materials [1,6,7]. Recently, it was reported that CTFs are effective adsorbents for the removal of ionic dyes from aqueous solutions [8,9].

Some of the conventional synthetic porous organic materials such as polymeric resins have been already widely used as adsorbents for organic contaminants in water and wastewater treatments in recent years [10]. Adsorption of organic compounds on polymeric resins may be affected by several mechanisms including hydrophobic effect, hydrogen bonding, and π–π interaction – their relative importance depends on the physicochemical properties of adsorbates and surface chemistry of adsorbents [11–13]. Azanova and Hradil [11] studied adsorption of benzene, phenol, and aniline on typical resin adsorbents (macroporous and hypercrosslinked styrene-divinylbenzene copolymers) and concluded that the adsorption was mainly driven by hydrophobic effect. Streat and Sweetland [12] reported that adsorption of polar pesticides such as simazine, chlorotoluron, and isoproturon to hypercrosslinked polymeric resins was controlled by both hydrophobic effect and hydrogen bonding. Investigation on the adsorption of aromatic compounds over hypercrosslinked polystyrene resins as high-performance liquid chromatography stationary phase further revealed that the retention mechanism included not only hydrophobic effect but also significant π–π interaction [13].

Despite the current wide application of polymeric resins as adsorbents for many purposes, there are several critical factors that restrict the dissemination of the technology. One of the main disadvantages is insufficient mechanical rigidity and solvent-sensitivity of the polymer matrix, which would result in swelling of the polymer matrix [13]. Furthermore, polymeric resins in general consist of irregular-shaped pores with a wide pore size distribution, from the microporous region (<2 nm), through the mesoporous region (2–50 nm), and into the macroporous region (>50 nm) [14]. Pore swelling [15] and heterogeneous pore structure [16] could possibly lead to multiphasic and/or slow adsorption/desorption kinetics and impaired size-selective adsorption. It was found in our previous study that the combination of very large specific

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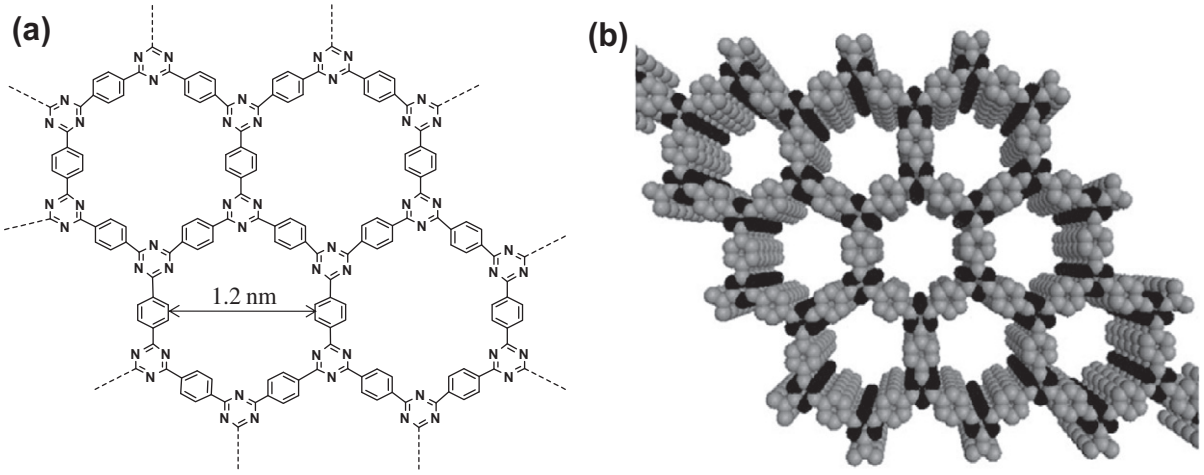

Fig. 1. (a) The chemical structure and pore size of covalent triazine-based framework (CTF). (b) Schematic representation of CTF adopted from Ref. [1], C: gray balls; N: black balls; H atoms are omitted for clarity.

surface area and open, uniform pore structure of zeolite-templated microporous carbon makes it a superior adsorbent for aromatic compounds [17]. Similarly, as the next-generation framework polymers CTFs possess rigid, permanent, and homogeneous porosity, and therefore may open up new opportunities for efficient and selective adsorption of organic contaminants from water in many environmentally relevant applications.

The main objective of this study was to systematically investigate the properties and controlling factors of aromatic compound adsorption on a porous CTF prepared by ionothermal trimerization of 1,4-dicyanobenzene. The synthesized adsorbent was characterized by a variety of experimental and spectroscopic techniques with respect to structural, porosity, and surface characteristics. Aqueous-phase batch experiments were performed to examine adsorption of eight monocyclic aromatic compounds (benzene, phenol, aniline, benzenesulfonate, nitrobenzene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, and 4-methyl-2,6-dinitrophenol) and four bicyclic aromatic compounds (naphthalene, 2-naphthol, 1-naphthylamine, and 2-naphthalenesulfonate). The adsorbate compounds are of great environmental concern and vary pronouncedly in terms of hydrophobicity, hydrogen-bonding ability, and π-electron-donor/acceptor ability. Adsorption of CTF was further compared with that of a commercial Amberlite XAD-4 resin, one of the most efficient polymeric adsorbents that are extensively used in water and wastewater treatment [18–20], environmental analysis [21–23], biotechnology [24], and food processing [25,26]. The effect of pH on adsorption of selected compounds was also evaluated to further understand the mechanisms controlling adsorptive interactions. Changing pH might significantly affect speciation reaction of the polar adsorbate molecules, as well as surface chemistry properties of CTF. Impact of presence of model dissolved humic acids on adsorption, adsorption/desorption kinetics, and adsorption reversibility of selected compounds was also assessed.

2. Materials and methods

2.1. Adsorbates

The tested adsorbates are as follows: benzene (Alfa Aesar), phenol (Sigma–Aldrich), aniline (Guoyao. Co., Ltd.), nitrobenzene (Fluka), 1,3-dinitrobenzene (Aldrich), 1,3,5-trinitrobenzene (Supelco), 4-methyl-2,6-dinitrophenol (Fluka), benzenesulfonate (sodium salt, Fluka), naphthalene (Sigma–Aldrich), 2-naphthol (Aldrich), 1-naphthalenamine (Sigma), 2-naphthalenesulfonate (sodium salt, Sigma), and pyrene (Aldrich). NaCl, HCl, NaOH, and $ZnCl_2$ were purchased from Nanjing Chemical Reagents Co. Ltd. All adsorbates and other reagents were of chemical grade or higher and were used without further purification. Water solubility (S_W), *n*-octanol–water partition coefficient (K_{OW}), *n*-hexadecane–water partition coefficient (K_{HW}), and/or acid dissociation constant (pK_a) of the adsorbates are summarized in Supporting Information (SI) Table S1. Chemical structures and molecular sizes of the adsorbates are given in SI Fig. S1.

2.2. Adsorbents

The covalent triazine-based framework (CTF) adsorbent was prepared by ionothermal trimerization of 1,4-dicyanobenzene according to literature method [1]. Briefly, 1.06 g of anhydrous $ZnCl_2$ stored in an anaerobic glove box (M. Braun, Germany) was mixed with 1 g of 1,4-dicyanobenzene (Aldrich) in an anaerobic glove box and the mixture was then transferred into a quartz tube. The tube was evacuated using a mechanical pump to a pressure below 10^{-2} Pa and was then sealed and heated at 400 °C for 40 h. After cooling to room temperature, the obtained material was repeatedly washed with distilled water and 1.0 M HCl to remove residual $ZnCl_2$. The resulting black powder was filtered, followed by washing with distilled water and tetrahydrofuran and drying in vacuum at 150 °C overnight.

The commercial polymeric adsorbent Amberlite XAD-4 was purchased from Rohm & Haas (USA). Prior to use, the XAD-4 resin was extracted with anhydrous ethanol in a Soxhlet apparatus for 8 h, followed by washing with water and drying at 50 °C overnight.

2.3. Characterization of adsorbents

Elemental analysis of CTF was performed using an elemental analyzer of Vario MICRO (Elementar, Germany) to determine the C, H, and N contents. X-ray diffraction (XRD) pattern of CTF was collected from a Rigaku D/max-RA powder diffraction-meter (Rigaku, Japan) using Cu Kα radiation. Transmission Fourier transform infrared (FTIR) spectrum of CTF was measured using a Nexus 870 spectrometer (Nicolet, USA). Nitrogen adsorption/desorption isotherms of CTF and XAD-4 were obtained on a Micrometrics ASAP 2020 (Micromeritics Instrument Co., USA) apparatus at −196 °C (77 K).