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Adsorptive removal of pharmaceutical antibiotics from aqueous solution by porous covalent triazine frameworks☆

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ABSTRACT

The exposures of pharmaceutical antibiotics in water solution caused potential risks for ecological environment and human health. In the present study, porous covalent triazine frameworks (CTFs) were synthesized and the adsorption behavior of sulfamethoxazole (SMX) and tylosin (TL) was investigated. The CTFs were characterized by X-ray diffraction, transform infrared and N_2 adsorption/desorption. Sulfamethoxazole displayed much stronger adsorption than tylosin on microporous CTF-1 adsorbent due to the pore-filling effect. While the adsorption of bulky tylosin on microporous CTF-1 was suppressed because of the size exclusion effect. Additionally, the porous CTF_{DCBP} showed stronger adsorption affinity and faster adsorption kinetics than other porous adsorbents, which was attributed to wide pore size distribution and open pore structure. Findings in this study highlight the potential of using porous CTFs as a potential adsorbent to eliminate antibiotics from water, especially for selective adsorption of bulky molecular pollutant.

1. Introduction

In the present, pharmaceutical antibiotics are widely used in human therapy, animal husbandry and fishery. These antibiotics can't be completely used by organs and tissues, and large proportion of antibiotics in form of original drug or metabolite are discharged into the soil and water environment (Sarmah et al., 2006; Kolpin et al., 2002; Ingerslev and Halling-Sorensen, 2001). A series of adverse effects, including variety of toxic effects, bacteria antibiotic, and serious threat to the ecological safety and human health, will be generated by the antibiotics residues and their transformed products (Schmitt et al., 2006; Boxall et al., 2003). Therefore, it is very important for developing advanced technical methods to eliminate pharmaceutical antibiotics from aqueous solution.

Adsorption treatment has been recognized as an effective approach to remove organic pollutants from the water. Activated carbon as the high adsorption capacity and relatively low price has been widely used for eliminating small sized and hydrophobic organic contaminant substances. However, adsorption of bulky compounds such as bulky pharmaceutical antibiotics and natural organic polyelectrolytes on activated carbon might be dramatically suppressed due to the existence of size exclusion effect (Kilduff et al., 1996; Liu et al., 2006). Notably, many antibiotics are large-size molecules and are expected to produce dramatic size exclusion effect when they were adsorbed on microporous activated carbon. Moreover, it has been validated (Ji et al., 2009a, 2010; Nakagawa et al., 2004) that activated carbon after expanding pore size has strong adsorption amount for giant molecules organic chemicals in previous studies.

Since covalent triazine frameworks (CTFs) first synthesized in 2008, it has attracted widespread interesting because of its large surface area, high thermal and chemical stability, and ordered pore structure (Kuhn et al., 2008a, 2008b, 2009a, 2009b; Bojdys et al., 2010;). Additionally, CTFs displayed high adsorption affinity for polycyclic aromatic hydrocarbon compounds in our previous study (Liu et al., 2012, 2013, 2015). The enlarged pores of CTFs are easily to avoid molecular sieve effect when adsorption of bulky molecules.

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Therefore, CTFs is a potential candidate for adsorption giant pharmaceutical antibiotics. However, thus far similar study has not been reported for adsorptive removal of pharmaceutical antibiotics on CTFs.

The main objective of this study was to examine the adsorption mechanisms between the antibiotic and CTFs, and explore the importance of unique adsorbent pore structure, and illustrate the selective adsorption of porous CTF_{DCBP} for bulky molecular compounds. Sulfamethoxazole and tylosin were selected as adsorbate, due to the difference in molecular size, which are facilitate to explain the adsorption affinity and influence of adsorbent porosity.

2. Experimental section

2.1. Materials

1,4-Dicyanobenzene and 4.4'-biphyldicarbonitrile were purchased from Aldrich. Zinc chloride (anhydrous) was stored in an anaerobic glove box. Sulfamethoxazole (SMX) and tylosin (TL) were purchased from Sigma and DebioChem respectively. The properties and chemical structures of SMX and TL were displayed in Supporting Information (SI) Table S1 and Fig. S1 respectively.

2.2. Adsorbents preparation

The covalent triazine frameworks (CTFs) were prepared by ionothermal trimerization according to literature method (Kuhn et al., 2008a). Two kinds of CTFs adsorbents were synthesized respectively by the monomer 1,4-dicyanobenzene (named CTF-1) and 4.4'-biphenyldicarbonitrile (named CTF_{DCBP}). The detail about the synthesis is present in Supporting Information.

2.3. Characterization of adsorbents

Elemental analyses on CTFs were collected in a Germany elemental analyzer of Vario MICRO. X-ray diffraction (XRD) pattern of CTFs were analyzed from a RigakuD/max-RA powder diffractionmeter using Cu Kα radiation. The transform infrared spectra of the samples were measured using a USA Nexus 870 spectrometer. BET and pore size distribution were obtained on a Micrometrics ASAP 2020 apparatus at −196 °C (77 K).

2.4. Adsorption

Adsorption isotherms were performed by batch adsorption experiment. Briefly, 20 mg of CTF-1 and 10 mg of CTF_{DCBP} were introduced into 40 ml glass vials (0.02 M NaCl as the background solution.) receiving with varied initial antibiotics concentrations. The samples were mixed using an orbital shaker protected from light at room temperature for 48 h. After filtration, the solute was analyzed using high-performance liquid chromatography (analysis condition see detail in Supporting Information). All sorption experiments were conducted in duplicate except for the pH effect experiments.

2.5. Pore size distribution of CTFs

N_2 adsorption/desorption isotherms were collected for the pore size distributions of the adsorbents before and after antibiotic adsorption. Two antibiotics adsorption on CTF-1 and CTF_{DCBP} using the above method (see section 2.4). The adsorbents after antibiotic adsorption filtered with 0.45 μm fiber filter and dried at 40 °C using vacuum drying oven. Prior to determine pore size distribution, the CTF-1 and CTF_{DCBP} adsorbents were activated at 200 °C, and the adsorbents after loading the antibiotics were activated at 80 °C.

3. Results and discussion

3.1. Characterization of adsorbents

The results of elemental composition, BET, and pore volume of adsorbents are displayed in Supporting Information (SI) Table S2. Clearly, the CTF-1 is predominated by micropores. While in contrast, CTF_{DCBP} is consist of both micropores and mesopores according to results in Table S2. Obvious vibrations of the triazine structure is listed in SI Fig. S2 according the strong peaks around 1352 and 1507 cm^{-1} (Bojdys et al., 2010), XRD patterns of the two absorbents are compared in SI Fig. S3. Both the absorbents have hexagonal pores as the peaks at 7.2° and 15.1° (Kuhn et al., 2008a). Additionally, CTF_{DCBP} displayed high disordered crystal according to XRD pattern results due to the salt templating effect (Kuhn et al., 2009a).

3.2. Adsorption isotherms

Adsorption isotherms for sulfamethoxazole and tylosin on CTF-1 and CTF_{DCBP} are compared in Fig. 1. The fitting parameters of Freundlich adsorption are listed in SI Table S3. Clearly, adsorption of sulfamethoxazole and tylosin to the CTFs can be well described by Freundlich model. Additionally, the linearity indexs (n) are smaller than 1, revealing the adsorption heterogeneity.

Different trends of the adsorption curves between sulfamethoxazole and tylosin are observed in Fig. 1. Adsorption of antibiotics

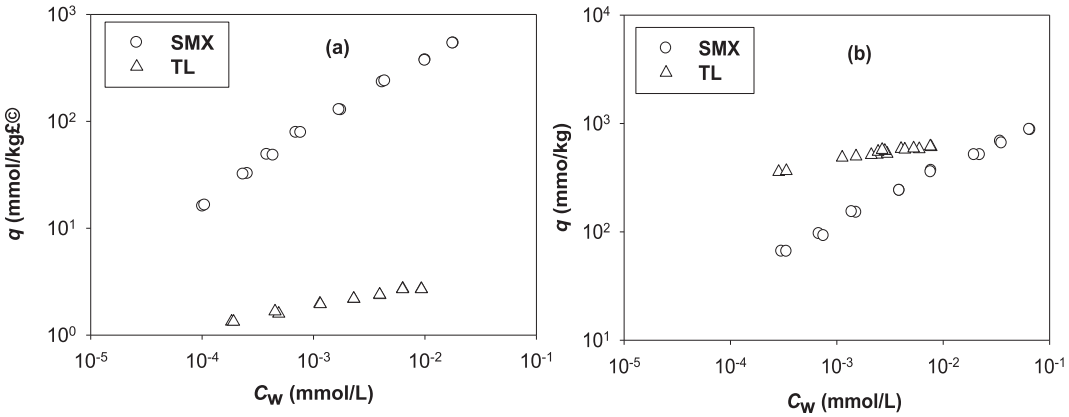

Fig. 1. Adsorption isotherms plotted as solid-phase concentration (q) vs aqueous-phase concentration (C_W) at equilibrium for different antibiotics on CTF-1 (a) and CTF_{DCBP} (b).

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