Journal of Hazardous Materials 305 (2016) 8–14

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Adsorption of quinolone antibiotics in spherical mesoporous silica: Effects of the retained template and its alkyl chain length

Zhijie Liang[a], Zhiwei Zhaob[b,*], Tianyi Sun[a], Wenxin Shi[a,*], Fuyi Cui[a]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[b] Department of National Defense Architecture Planning and Environmental Engineering, Logistical Engineering University, Chongqing 401311, China

HIGHLIGHTS

- The retained template enhanced the adsorption of the hydrophobic PPCPs in MCM-41.
- The enhanced effect depended on the alky chain length of the templates.
- Organic partition phase formed by the alkyl chains induced the enhanced effect.

ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 31 October 2015
Accepted 18 November 2015
Available online 21 November 2015

Keywords:
Meso-silica materials
PPCPs
Adsorption
Template effect
Octanol/water partition coefficient

ABSTRACT

In this study, mesoporous silica (meso-silica) MCM-41 and those with the templates retained were synthesized and characterized. Adsorption capacities of the synthesized materials towards typical quinolone antibiotic pollutants, enrofloxacin and norfloxacin as representative, were investigated, and effects of the alkyl chain length of the templates on the adsorption capacity were evaluated. The results of this study indicated that the retained templates enhanced the adsorption capacities (Q_{max}) of the meso-silica MCM-41 toward hydrophobic enrofloxacin, but had an inhibitory effect on that towards hydrophilic norfloxacin, which were attributed to the hydrophobic inter-environment created by the long alkyl chains of the retained templates. Importantly, the adsorption capacity increased with the increase of the alkyl chain length of the retained templates.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are extensively used and most of the PPCPs tend to be discharged into waters after used via hospitals, sewage treatment plants, and medical manufactures [1,2]. PPCPs are regarded as emerging contaminants in the aquatic environment and have attracted increasing concerns due to their potential toxicity to eco-system [3,4]. Hence, various techniques have been developed to reduce the level of PPCPs in water [5–7]. Among of these techniques, adsorption is regarded as one of the most promising and environmentally friendly techniques [8], and numerous kinds of absorbents have been developed, such as activated carbon [9], meso-silica materials [10], metal-organic framework [11], and clay [12] etc.

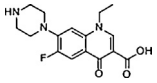
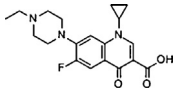
In the past two decades, the meso-silica materials have attracted great research interest in the area of the pollutants adsorption for water treatment, due to the excellent pore accessibility and the possibility of functionalization [13]. Bui and Choi [12] firstly reported that the meso-silica SBA-15 showed high ability in the removal of carbamazepine and diclofenac. Recently, great efforts have been given to surface modification of the meso-silica materials to enhance the adsorptive ability towards PPCPs [14]. Hongsawat et al. [15] pointed out that the meso-silica grafted with phenyltrimethoxy groups had an enhanced adsorption capacity towards ciprofloxacin. However, some drawbacks still exist in the surface modification of the meso-silica materials, such as complicated modification routes and consumption of chemicals.

Typically, the meso-silica materials are synthesized with sol-gel method under acidic or alkali condition, and molecular surfactant aggregates are commonly used as templates with etramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) as silica precursor. Finally, the meso-silica materials are gained after the templates are removed by calcination or extraction. However, some previous reports demonstrated that adsorption capacities of the

* Corresponding author.
E-mail addresses: zhjliang@outlook.com (Z. Liang), hit_zzw@163.com (Z. Zhaob), tianyi0328@163.com (T. Sun), SWX@hit.edu.cn (W. Shi), cuifuyi@hit.edu.cn (F. Cui).

http://dx.doi.org/10.1016/j.jhazmat.2015.11.033
0304-3894/

Table 1
Chemical formulas, molecular weight (MW), ACS NO., octanol/water partition coefficients (log K_{ow}), and structure of targeted pollutants.

Compound	Formula	MW(g/mol)	ACS no.	Log K_{ow}[a]	Structure
Norfloxacin	$C_{16}H_{18}FN_3O_3$	319.24	70458-96-7	−0.31	
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	359.40	93106-60-6	0.7	

[a] From ChemSpider Database, http://www.chemspider.com.

silica-based mineral materials towards organic pollutants could be enhanced by surfactant modification [16–18]. Hence, our hypothesis is that whether the retained template and its properties can affect the adsorption capacity of the meso-silica materials towards PPCPs.

In this study, meso-silica MCM-41 and those with templates retained were synthesized and characterized, and the adsorption capacities of these meso-silica materials towards typical quinolone antibiotics were compared. More specially, this paper aims to (1) evaluate the effects of the retained template and its alkyl chain length on PPCPs removal, and (2) investigate the mechanism of the effects from the aspect of the properties of the targeted PPCPs.

2. Materials and methods

2.1. Synthesis of the meso-silica materials

The meso-silica materials were synthesized with the quaternary ammonium bromide surfactants (TMAB) and tetraethyl orthosilicate (TEOS) as templates and silicon precursor, respectively [19]. Surfactants with the alkyl chain length of 12, 14, and 16 were defined as C_{12}-TMAB, C_{14}-TMAB, and C_{16}-TMAB, respectively. All of the surfactants and TEOS were analytical grade (purity >99%) and purchased from Kelong Chemical Co., Ltd. (Chengdu, China).

The synthesis procedure was similar to that reported by Melendez-Ortiz et al. [19]. 6 g C_{16}-TMAB was dissolved into 800 mL deionized water at room temperature 25 °C, and then 250 mL of ethanol was added followed by 80 mL of aqueous ammonia solution (13 M). After stirred for 5 min, 10 mL of TEOS was poured into the solution immediately, and subsequently stirred for 20 min efficiently. The mixture was aged for 12 h at 25 °C. The solid sample was recovered by filtration and washed with 1000 mL deionized water for three times to remove the free surfactants. After dried at 70 °C, the meso-silica materials with templates retained was achieved, which were defined as C_{16}-MCM-41. Half of the C_{16}-MCM-41 was calcined at 560 °C under air condition to remove the templates, and the achieved material was defined as MCM-41.

According to the same synthesis procedure of C_{16}-MCM-41, C_{12}-MCM-41 and C_{14}-MCM-41 were synthesized with the templates of C_{12}-TMAB and C_{14}-TMAB, respectively.

Finally, all of the synthesized materials were grinded into powder (100 mesh).

2.2. Characterization of the meso-silica materials

The crystal phase of the synthesized materials was detected on an X-ray diffractometer (XRD-6100, Shimadzu, Japan) operated at 40 kV and 30 mA with Cu/Kα radiation, and the diffraction intensity was recorded in the 2θ range of 2–8° at a scanning speed of 2°/min. The Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size were calculated from N_2 adsorption/desorption isotherms determined at −196 °C using an automated nitrogen adsorption analyzer (ASAP 2020, Micromeritics, America). After quantitatively mixed with KBr powder, the mixture was pressed into a tablet and then the Fourier Transform Infrared spectrum (FT-IR) of the synthesized materials was obtained using a FT-IR spectrometer (6700, Nicolet, USA) from 32 scans in the wavenumber range of 400–3200 cm^{-1}. The surface morphology of the synthesized materials was observed under a field-emission scanning-electron microscope (FE-SEM, Quanta™ 250 FEG, FEI, US).

2.3. Adsorption experiment setup and measurements

Enrofloxacin (EF) and norfloxacin (NF) were selected as the representative of PPCPs pollutants, which were both analytical grade (purity >98%) and purchased from Aladdin Industrial Inc. (Shanghai, China). Information about EF and NF is shown in Table 1. Stock solutions of EF and NF (200 mg/L) were prepared with deionized water and stored in the dark at 4 °C.

Adsorption of EF and NF was carried out with batch experiments, separately. 0.02 g absorbent was added into 30 mL deionized water contained in 50 mL brown glass tube with Teflon sealed cap. Certain volume of stock solutions of EF or NF was added to give concentrations (based on the final volume 32 mL) of 0.32–20.00 mg/L for EF or 0.25–12.00 mg/L for NF, and then the pH was adjusted to 7.0 with NaOH (0.01 M) or HCl (0.01 M). Finally, deionized water was added with transferpette (Brand, Germany) to give a final volume of 32 mL according to the added volume of the stock solutions. The tubes were then shaken at 150 r/min and 25 °C in an air bathed shaker (SHZ-82, Jintan, China) for 2 h to reach enough equilibrium (proved by kinetic study shown in Fig. S1 in Supplementary materials). All experiments were performed in triplicates.

Samples were taken and filtrated with 0.45 μm membranes (no targeted pollutant adsorption), then the filtrates were used to detect the concentrations of the residual EF or NF with UV–vis spectrophotometer (Shimadzu UV-2450/2550, Japan) both at 277 nm. Finally, the Langmuir model was applied to the isotherms of EF and NF.

3. Results and discussion

3.1. Characterization of the meso-silica materials

3.1.1. Textural analysis

To investigate the crystallinity of the synthesized materials, the powder were analyzed by X-ray diffraction (XRD) as shown in Fig. 1.

The results show that all of the XRD patterns (2θ) of the crystals exhibit four Bragg peaks, which can be indexed as (1 0 0), (1 1 0), (2 0 0), and (2 1 0) planes of the meso-silica materials, respectively. These patterns confirm the formation of well-ordered MCM-41 or MCM-41-based meso-silica materials (C_{16}-MCM-41, C_{14}-MCM-41, and C_{12}-MCM-41) with hexagonal regularity [20].