Applied Catalysis B: Environmental 142–143 (2013) 817–827

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

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

Synthesis and characterization of large pore cubic mesoporous silicas functionalized with high contents of carboxylic acid groups and their use as adsorbents

Wei-Chieh Chang[a], Juti Rani Deka[a], Hao-Yiang Wu[b], Fa-Kuen Shieh[a,*], Shu-Ying Huang[a], Hsien-Ming Kao[a,**]

[a] *Department of Chemistry, National Central University, Chung-Li 32054, Taiwan, ROC*
[b] *Department of Neurological Surgery, Tri-Service General Hospital National Defense Medical Center, 325, Sec. 2, Cheng-Kung Rd, Nei-Hu Dist, Taipei 11490, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 11 March 2013
Received in revised form 3 June 2013
Accepted 18 June 2013
Available online 27 June 2013

Keywords:
Carboxylic acid functionalization
Cubic mesoporous silica
Methylene blue
Paraquat

ABSTRACT

Well-ordered cubic FDU-12 type mesoporous silicas functionalized with various contents of carboxylic acid group (—COOH), up to 40 mol% based on silica, were synthesized via co-condensation of tetraethyl orthosilicate (TEOS) and carboxyethylsilanetriol sodium salt (CES) under acidic conditions using Pluronic F127 triblock copolymer as template. The materials thus obtained were characterized by a variety of techniques including powder X-ray diffraction (XRD), nitrogen adsorption–desorption, transmission electron microscopy (TEM), ^{13}C and ^{29}Si solid-state nuclear magnetic resonance (NMR) measurements. The materials were used as adsorbents for removal of methylene blue (MB) in aqueous solutions and as an antidote for intoxication of herbicide paraquat (PQ). Due to the —COOH functionalization, three-dimensional pores, high surface areas, and electrostatic interactions between the adsorbent and the adsorbates, the prepared adsorbents possessed very high adsorption capacities and extremely rapid rates for MB and PQ adsorption. The kinetic regression results revealed that the overall adsorption process was controlled by external mass transfer and intra-particle diffusion jointly. The Langmuir isotherm model showed better fit with the experimental adsorption data than the Freundlich isotherm model, implying a monolayer adsorption mechanism. The present results show that the prepared —COOH functionalized cubic mesoporous silicas have great potentials for removing pollutants and herbicides from aqueous solutions in environmental and clinical applications.

1. Introduction

The recent discovery of ordered mesoporous silica materials has opened prospects for the development of new technologies in catalysis, separation, drug delivery, and nanoscience, owing to their tunable size mesopores, high surface areas, versatile possibilities of surface functionalization, and diversity in composition, structure, and morphology [1–4]. Of particular current interest are mesoporous silicas consisting of three-dimensional (3D) interconnected cage-type large pores (e.g., pore diameter > 5 nm). Such types of cubic mesoporous silica materials are expected to be superior to two-dimensional (2D) hexagonal counterparts, especially for applications involving selectively tuned diffusion, immobilization of large molecules, or host–guest interactions within nanostructured materials as the 3D interconnected pores offer better pore accessibility than the cylindrical pores [5–9]. Several researchers have successfully synthesized ordered mesoporous materials with large pores, which possessed cubic structures with three-dimensional connectivity [10–13]. However, the applications of pure silica materials are limited due to their inherent catalytically inactive nature of mesopore surface. The surface properties of pure mesoporous silica materials are therefore needed to be modified by incorporating species with desired functionalities. It has been recognized that the content of functional organic groups plays a key role in governing many important properties of the hybrid materials [14], and therefore have wider applications including adsorption [15–17], catalysis [18–20], gas separation [21,22], drug delivery [23] and sensing [24]. Removal of organic pollutants from industrial and municipal wastewater is a great challenge to water suppliers worldwide [25–27]. The dying industry discharges organic pollutants and causes the increasing concern in environmental issues [28–30]. Dyes are generally non-degradable and constitute a problematic group of pollutants.

---

* Corresponding author.
** Corresponding author. Tel.: +886 3 4275054; fax: +886 3 4227664.
E-mail address: hmkao@cc.ncu.edu.tw (H.-M. Kao).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.06.018

Methylene blue (MB), a heterocyclic aromatic chemical compound having IUPAC name 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride with the molecular formula $C_{16}H_{18}N_3SCl$ [31] is the most commonly used substance for dying cotton, wood, and silk. However, it can cause eye burns and short period of rapid or difficult breathing on inhalation. In addition to those pollutants produced by textile industrial factories, overuse of herbicides is another constant source of worry to the environment, since herbicides give rise to toxicity and normally be persisted in soil due to less available for biological breakdown in the soil solution [32]. Besides that, herbicides are relatively cheaper, easily obtained and with acutely toxic so as to be used as “suicide agents” in some areas [33]. One particular herbicide, 1,1′-dimethyl-4,4′-bipyridinium dichloride, popularly known as paraquat (PQ), is a cationic non-systemic contact herbicide that has been worldwide used [34]. However, PQ is known to be extremely toxic and can result in a considerably higher fatality rate than other suicide chemicals, if accidentally ingested or purposely administered [35]. As an effective therapy for acute PQ poisoning has not yet been established, it is of great interest in the development of an effective adsorbent as antidote or filter for the removal of herbicides from poisoned circulation system or contaminated environment.

Many techniques have been developed to remove organic pollutants from aqueous solutions, including adsorption [17], ion-exchange [36], membrane filtration [37], and chemical oxidation [38]. Among the possible techniques, adsorption is one of the most promising and efficient techniques for removal of trace amount of contaminants in wastewater due to low cost, high efficiency and simplicity of the technique. Activated carbon has been widely used for this purpose because of its high adsorption capacity. However, the high cost of production and regeneration make it uneconomical. Therefore, inorganic adsorbents with high surface areas have been used as alternatives to carbon-based adsorbents [39–41]. For example, mesoporous materials MCM-41 [42] and SBA-15 [43] have been investigated for the removal of dyes from aqueous solutions and they showed effective adsorption performance because of large pore size, high surface area, and the interaction between the basic dye and surface hydroxyl groups.

The surface modification of mesoporous silica is an essential requirement in order to generate sufficient binding affinity for the material to be used for adsorption. A selective surface functionalization can introduce positive/negative charges on the silica surface, which in turn permits electrostatic interactions between the adsorbent and the adsorbates. Carboxylic acid group (—COOH) is an important functional group in organic chemistry, and can be easily deprotonated in neutral and basic environments to form negatively charged moieties. The formed negative moieties in the prepared silicas can be used as synthetic ion channels, acidic catalysts and for removing the cationic species from aqueous solutions as well [44–46]. The —COOH functionalized mesoporous silicas were used for dye removal, and the removal efficiencies were determined to be much higher than the non-functionalized mesoporous silicas [47–49]. Recently, we have reported the application of —COOH functionalized benzene-bridged periodic mesoporous organosilicas (PMOs) for efficient removal of MB [50]. The exceptionally high loadings of —COOH, up to 80Ymol% based on silica, have increased the adsorption capacity and adsorption rate tremendously. Cage-like cubic porous structure is reported to be superior to the hexagonal structures such as MCM-41 and SBA-15, in terms of mass transfer and pore blocking [51]. Considering the advantages associated with the cubic mesostructure, in this study the effort was devoted to the synthesis of well ordered —COOH functionalized cage-like mesoporous silicas with large pores via co-condensation tetraethoxysilane (TEOS) and carboxyethylsilanetriol sodium salt (CES) under acidic conditions using Pluronic F127 triblock copolymer as template. The synthesized materials were then used as adsorbents for adsorption of MB, a cationic dye, and herbicide PQ from aqueous solutions. The —COOH group is believed to provide the silica surface with a sufficient quantity of negative charges to achieve relatively strong interactions with MB and PQ. To the best of our knowledge, there is no detailed study on the synthesis of large pore cage-like mesoporous silicas functionalized with high contents of —COOH moieties and their applications for adsorption of MB and PQ. The present work demonstrates that large pore cubic mesoporous silicas functionalized with —COOH groups are promising candidates for removing pollutants and herbicides from aqueous solutions in environmental and clinical applications.

2. Experimental

2.1. Materials

TEOS, F127 and MB were received from Sigma–Aldrich. CES (25 wt.% in water) was purchased from Gelest. PQ was obtained from ACROS organic. All chemicals were used as received without any further purification.

2.2. Sample preparation

The synthesis procedures of FDU-12 type cubic mesoporous silica materials were modified slightly according to the previously reported literature [10]. In a typical synthesis of —COOH functionalized large pore mesoporous silicas, non-ionic copolymer surfactant F127 (1.0 g) and the pore expander 1,3,5-trimethylbenzene (TMB) (1.0 g) were dissolved in HCl (60.0 mL, 2 M) mixed with KCl (2.5 g). The solution was stirred at room temperature for 24 h. A premixed solution of TEOS and CES was then added dropwise to the above mixture under vigorous stirring and the solution was stirred continuously for another 24 h at 40 °C. The reaction mixture was treated hydrothermally at 100 °C for 72 h. The resultant white precipitate was filtered, washed with water and dried at 70 °C. The molar composition of the reaction mixture was $(1 - x)/100$ TEOS: $x/100$ CES: 0.004 F127: 6 HCl: 139 H_2O: 0.42 TMB: 1.7 KCl, where x is the molar percentage ratio of CES/(TEOS + CES). The template was removed from the as-synthesized materials (0.5 g) by adding H_2SO_4 (100.0 g, 48 wt.%) and heating the mixture at 90 °C for 24 h. The product was then filtered and washed with acetone. To completely remove any ester groups that might have formed during the treatment with H_2SO_4, the material (0.3 g) was re-treated with 2 M HCl (30.0 mL). Subsequently, the sample was recovered by washing with water and dried at ambient temperature. The final products were denoted as FTC-*x*, where *x* represents the molar percentage ratio of CES/(TEOS + CES).

2.3. Adsorption equilibrium experiments

2.3.1. MB adsorption

The FTC-*x* adsorbents were tested for adsorption of MB and PQ. To perform the MB adsorption experiments, FTC-*x* (4.0 g) was first dispersed in the MB solution (5 mL) and shaken at 25 °C in 300 rpm using a rotating oscillator incubator. The solution was then centrifuged to separate the adsorbed dye and the residual amount of dye in the solution was measured at 292 and 664 nm for MB using a UV-Vis spectrometer (SP-722). The amount of dye adsorbed (Q_e) was calculated using the equation,

$$Q_e = \left[\frac{(C_0 - C_e) \times V}{m} \right] \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of the dye solution (mg/L), V is the volume (L), and m is the adsorbent