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Insight into the adsorption of tetracycline onto amino and amino–Fe^{3+} functionalized mesoporous silica: Effect of functionalized groups

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ABSTRACT

In order to study the influences of functionalized groups onto the adsorption of tetracycline (TC), we prepared a series of amino and amino–Fe^{3+} complex mesoporous silica adsorbents with diverse content of amino and Fe^{3+} groups (named N,N-SBA15 and Fe-N,N-SBA15). The resulting mesoporous silica adsorbents were fully characterized by X-ray powder diffraction, Fourier transform infrared spectrometer and N_2 adsorption/desorption isotherms. Furthermore, the effects of functionalized groups on the removal of TC were investigated. The results showed that the periodic ordered structure of SBA-15 was maintained after modification of amino/Fe^{3+} groups. The functionalized amino groups decreased the adsorption capacity while the coordinated Fe^{3+} increased the adsorption capacity. The adsorption kinetics of TC fitted pseudo-second-order model well and the equilibrium was achieved quickly. The adsorption isotherms fitted the Langmuir model well and with the Fe^{3+} content increased from 3.93% to 8.26%, the Q_{max} of the adsorbents increased from 102 to 188 mmol/kg. The solution pH affected the adsorption of TC onto amino complex adsorbents slightly while influenced the adsorption onto Fe-amine complex adsorbents greatly. The adsorption of TC on SBA15 and N,N-SBA15 may be related to the formation of outer-sphere surface complexes, while the adsorption of TC onto Fe-N,N-SBA15 was mainly attributed to the inner-sphere surface complexes. This study could offer potential materials that have excellent adsorption behavior for environmental remediation and suggested useful information for the preparing other adsorbents in environmental applications.

Introduction

Tetracycline-antibiotics, one of the most antibiotics, are used worldwide in controlling the infection from both humans and animals. Furthermore, tetracycline-antibiotics are also used for agricultural purpose and animal growth promoter (Ötker and Akmehmet-Balcıoğlu, 2005; Kim et al., 2010). However, most of tetracycline-antibiotics are poorly absorbed by human and animals after intake, about 25%–75% of added compounds are excreted or released as metabolite forms into environment *via* feces or urine (Chee-Sanford et al., 2001). Tetracycline (TC), the second most widely used antibiotics in the world (Yu et al.,

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2009; Luo et al., 2011), like other tetracycline-antibiotics, is difficult to be degraded because of the main structure-naphthol ring. The mass used tetracycline-antibiotics make the large amount TC residue into environment. As serious environmental pollution, TC residue in the environment induces resistant microorganisms and brings a threat to the human health (Xu and Li, 2010; Gu et al., 2007). Recently, residues of TC are frequently detected in sewage, agricultural wastewater, surface water, groundwater and even drinking water (Chen et al., 2014; Chen and Zhou, 2014; Tong et al., 2014; Tang et al., 2015). However, natural biodegradation and conventional water treatment are not effectual for the removal of TC from aqueous solution (Ji et al., 2009; Lv et al., 2015). Therefore, great attentions have been focused on the developing efficient technologies for TC removal.

Recently, many methods have been used for removing TC from aqueous solution, such as oxidation, photo-catalysis, membrane separation, biodegradation and adsorption (Zazouli et al., 2009; Zhao et al., 2010; Wang et al., 2015; Chang and Ren, 2015; Alvarez-Torrellas et al., 2016). Compared with other methods, adsorption has received increasing attention due to the lower total cost, higher efficiency and friendliness (Dai et al., 2014). Many adsorbents such as soils, clays, activated carbon, graphite and mesoporous silica are used to remove TC from aqueous solution (Ji et al., 2009; Sassman and Lee, 2005; Figueroa et al., 2004; Ahmed et al., 2015). Among these adsorbents, ordered mesoporous silica has got great interest because of its high surface area, large pore volume, controllable pore size and stable aqueous dispersion (Puanngam and Unob, 2008). However, due to the abundant silanol groups present on the channel walls, the mesoporous silicates have lower adsorption capacities for antibiotics. Therefore, introduction of the functional groups on the mesoporous silica surface and framework was created to enhance the adsorption property (Bui and Choi, 2009; Rivera-Jimenez et al., 2010; Vu et al., 2010a, 2010b). Accordingly, amino and Fe groups were successfully functionalized to control the antibiotics delivery and increase the adsorption capacity, separately (Rivera-Jimenez et al., 2010; Wu et al., 2013). In recent years, some researchers have prepared amino/Fe functionalized mesoporous silica by first grafting amino groups and then coordinating Fe, and investigated the adsorption behavior for removal of pollutants from aqueous solutions (Zuo et al., 2012). Our previous study confirmed that amino–Fe functionalized SBA15 has high adsorption efficiency for TC due to the complexation between Fe and TC (Zhang et al., 2015a, 2015b). To the best of our knowledge, the interaction between functionalized groups (amino and Fe) and TC was not clear, especially the coexisting of them on the surface of mesoporous silica.

In this article, diverse content of functionalized groups was introduced on mesoporous silica SBA15 and the influences of groups on the removal of TC were investigated. The characteristics of prepared materials have been thoroughly evaluated by X-ray powder diffraction (XRD), Fourier transform infrared spectrometer and N_2 adsorption/desorption isotherms. The influence of amino and Fe^{3+} groups on the adsorption properties was also investigated by kinetic and isotherm measurements. Furthermore, batch experiments were carried out to study the fundamental adsorption behavior at different pH and ionic strength/species.

1. Methods and materials

1.1. Reagents

Tetraethyl orthosilicate (TEOS, 98%) and Pluronic P123 (PEO20PPO70PEO20, Mav = 5800) were obtained from Alfa Aesar Corp. The hydrochloride salt of TC was obtained from Sigma Co. and used without further purification. Toluene, acetonitrile, methanol, isopropanol (HPLC grade) and 3-(2-aminoethylamino)-propyltrimethoxysilane were purchased from Alfa Aesar Corp, all other chemicals were analytical grade. Water with a resistivity greater than 18.2 MΩ/cm (Milli-Q) was used for all experiments.

1.2. Synthesis of amino/Fe^{3+} incorporated mesoporous silica

SBA15 was prepared by using TEOS as the silica source and pluronic P123 as the templating reagent (Wu et al., 2013). Amino-incorporation SBA15 was synthesized by a step-wise fashion using grafting techniques. First, 1.5 g SBA-15 was prepared at 120°C, *in vacuo* for 2 hr, then the prepared materials were suspended in 150 mL of anhydrous toluene and stirred for approximately 1 hr under a dry N_2 flow. Next, diverse amount of 3-(2-aminoethylamino)-propyltrimethoxysilane was added and the mixture was stirred under reflux at 100°C for 24 hr under a dry N_2 flow. The products were filtered, washed with dry toluene and isopropanol consecutively. Finally, the samples were dried overnight named as N,N-SBA15 (N1, N2, N3). Fe^{3+}-amine complex SBA15 was prepared by immobilized Fe^{3+} onto N,N-SBA15. One gram (1.0 g) samples were mixed with a 0.1 mol/L isopropanol solution of ferric trichloride for 24 hr. The mixture was filtered, washed with isopropanol and dried overnight named Fe-N,N-SBA15 (FeN1, FeN2, FeN3). To investigate the influence of dosage of 3-(2-aminoethylamino)-propyltrimethoxysilane and ferric trichloride onto the adsorption process, different contents of amino/Fe^{3+} adsorbents were prepared by changing the proportion of 3-(2-aminoethylamino)-propyltrimethoxysilane and ferric trichloride.

1.3. Characterization of adsorbents

The synthesized samples were characterized by XRD patterns using a X' pert PRO-MPD diffractometer (Pannlutical, Holland). All XRD patterns were collected in the 2θ range between 0.5 and 3° with a scanning rate of 0.01°/min. The textural properties of the samples were measured *via* nitrogen adsorption–desorption isotherms at −196°C(77 K) using a Micromeritics ASAP2020HD88 (Mike, USA). Fourier transform infrared spectrometer was obtained in a Tenson 27 FTIR Spectrometer (Bruker, Germany) *via* KBr pellet method. Powder samples were analyzed at 4/cm resolution an averaged over 400 scans in the absorption band range of 4000–400/cm. The CHN elemental analysis was conducted on a Vario ELIII (Elementar, Germany). The sorbent was digested with acid mixture of hydrogen nitrate–perchloric acid–hydrofluoric acid compound (5:4:5, V/V/V) by the constant temperature electric heating plate, and Fe^{3+} content was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Elan 5000, Perkin Elmer, USA). The zeta potential

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