



Mesoporous hybrid Zn-silicate derived from red palygorskite clay as a high-efficient adsorbent for antibiotics



Wenbo Wang^{a, c}, Guangyan Tian^{a, b}, Li Zong^{a, c}, Qin Wang^{a, c}, Yanmin Zhou^d,
AiQin Wang^{a, c, *}

^a Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

^b University of the Chinese Academy of Sciences, Beijing 100049, PR China

^c Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou 730000, PR China

^d College of Animal Science and Technology, Nanjing Agricultural University, Nanjing 210095, PR China

ARTICLE INFO

Article history:

Received 1 May 2016

Received in revised form

6 July 2016

Accepted 23 July 2016

Available online 26 July 2016

Keywords:

Palygorskite
Zinc silicate
Hydrothermal
Aureomycin
Tetracycline
Adsorption

ABSTRACT

A hierarchical mesoporous hybrid Zn-silicate adsorbent with superior adsorption performance for aureomycin (AMC) and tetracycline (TC) has been successfully synthesized by employing an “all-into-one” strategy and one-pot hydrothermal reaction, using naturally abundant, low-cost red palygorskite clay (RPAL), sodium silicate and zinc salts as raw materials. The morphologies and crystal forms of the Zn-silicates can be tuned by altering the dosage of Zn^{2+} ions. Low-crystalline sheet-like Zn-silicates were formed at the Si/Zn ratio of 3:1 and 2:1, and zinc orthosilicates were obtained at the Si/Zn ratio of 1:1 and 1:2. A systematic study on their adsorption abilities for the antibiotics AMC and TC indicates that the sheet-like Zn-silicate has higher adsorption capacity for AMC and TC than zinc orthosilicate, and the Zn-silicate with Si/Zn ratio of 3:1 has the best adsorption capacity of 384 mg/g for AMC and 337 mg/g for TC, which is obviously higher than that of RPAL (154 mg/g for AMC and 140 mg/g for TC). The adsorption properties are dependent on the pore size and surface charges, instead of specific surface area. The average pore sizes of 10.62–11.50 nm and the negative surface charge (−42.54 mV) resulting from the $-Si(M)O^-$ groups are beneficial to the adsorption for both AMC and TC. The adsorption process mainly involves with monolayer coverage, and chemo-adsorption plays a key role for the enhanced adsorption capacity. The results suggest that the Zn-silicates derived from natural abundant clay mineral have superior performance, and could be candidates to remove AMC and TC from the wastewater with high amounts of AMC and TC.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Over the past decades, low-cost, stable, safe and high-efficient adsorbents have received considerable attention in both academia and industry. Silicates, as the materials of “greening 21st century materials world” [1], have been especially considered because they are recognized as potential adsorption materials suitable for large-scale applications due to their excellent stability and safety [2–5]. For a long time, synthetic silicates played important roles in industry, and many mesoporous silicates have

been produced by a synthetic route using pure chemicals as raw materials [6,7]. However, synthesis of silicates is usually subject to long time, low efficiency, and high cost. So, natural silicate clay minerals have been especially considered as adsorbents because they are inexpensive and eco-friendly, and can be easily available in nature.

Palygorskite (PAL) is a special natural silicate clay mineral with one-dimensional nanorod-like crystal morphology and theoretical formula of $Si_8Mg_5O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$ [8]. It is composed of two continuous tetrahedral sheets and one discontinuous octahedral sheet [9], in which each ribbon is connected to the next by the inversion of SiO_4 tetrahedron along a set of Si–O–Si bonds to form nano-channels with the size of 0.37 nm × 0.64 nm along the *c*-axis of the rod [10,11]. The octahedral cations in the crystalline framework of PAL can be partially replaced by di- or tri-valent cations. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral

* Corresponding author. Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China.

E-mail address: aqwang@licp.cas.cn (A. Wang).

sheet and the substitution of Al^{3+} (or Fe^{3+}) for Mg^{2+} in the octahedral sheet may generate negative charges and form structural defects [12], and so a considerable number of exchangeable cations exists in the interlayer to compensate the structural negative charges. The unique rod-like morphology, affluent surface groups, high specific surface area and ion-exchange capability of PAL make it easy to hold heavy metal ions [13], tetracycline [14], dyes [15,16], color matter [17] or herbicide [18], so PAL is commonly recognized as potential adsorbent and received wide attention in industrial and environmental fields.

However, most of the PAL minerals are formed by the deposition mechanism in marine, bay, lagoon, and lake environments, and are mainly found in Tertiary sediments [19]. So, the deposit and formation condition of PAL minerals is complex, and many associated minerals co-exist in the natural PAL minerals, which affected the well growth of the rod crystals of PAL [20]. Red PAL (RPAL) clay mineral is widely distributed on earth with zonal distribution of mineral and huge resource reserves. Compared with high-grade PAL mineral, RPAL is a complex mixture mineral that is mainly composed of PAL, quartz, calcite, chlorite and dolomite [21], and so its colloidal, reinforce and adsorption performance are poor. The complex components and poor properties of RPAL at its pristine state make it difficult to be used as useful material for industrial applications. Although the application of PAL as adsorbent is promising, it is still challenging to develop a high-efficient adsorbent using the low-grade PAL with poor performance as the raw material. Recently, the evolution and restructuring of RPAL crystal via a simple hydrothermal reaction were confirmed to be an effective route to fabricate new hybrid silicate adsorbents, and it is encouraging that the hybrid adsorbent shows adsorption performance superior to raw PAL [22–24]. This means that low-grade PAL with poor performance can be used as the natural silica sources to produce high-performance silicate adsorbent [25].

Metal silicates as high-efficient adsorbents stand out among numerous adsorbents, because not only they have excellent adsorption capacity, but also low cost, and safety and stability advantages [26]. Zinc silicate is a representative metal silicate with different crystalline phases, including zinc orthosilicate (Zn_2SiO_4), hemimorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$], and zinc phyllosilicate [$\text{Zn}_3\text{Si}_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$]. It has been intensively considered as luminescent phosphors [27], lithium-ion batteries (LIBs) [28] and glass ceramics [29]. It was rarely exploited as adsorbent for organic pollutants despite it has been proved to be an excellent adsorbent for toxic metal ions [30]. More importantly, synthesis of the hybrid Zn-silicate from natural clay minerals has not yet been considered, despite its potential as high-performance adsorbent.

Antibiotics (i.e., aureomycin (AMC) and tetracycline (TC)) are emerging fetal pollutants with severe harm to organism, ecosystem and human health because they can kill the microorganism and induce the generation of “super-bacteria” that cannot be killed by conventional drugs [31]. In order to remove antibiotics, various mesoporous materials such as mesoporous silica [32], mesoporous carbons [33], hypercrosslinked resins [34], and metal oxide [35] have been developed. The presence of mesopores and surface charges in these adsorbents make them showing better capability to hold or capture antibiotic molecules. In comparison with other adsorbents, silicates are assuredly more cheap and eco-friendly, so they are recognized as promising adsorbents for antibiotics. Based on this, as inspired by the “from nature, for nature” idea, the Zn-silicate adsorbents were fabricated through a facile one-pot hydrothermal process using RPAL as the main starting material. This process achieved the development of new mesoporous adsorption materials by utilizing low-grade clay resources. The structure of the hybrid adsorbent was characterized, and its adsorption properties for AMC and TC were systematically evaluated.

2. Experimental

2.1. Materials

Red palygorskite clay (RPAL) was taken from Jingyuan Mine located on Jingyuan county of Gansu Province, China (the digital photograph of the RPAL Mine is shown in Fig. S1, see Supplementary Materials). Before use, natural RPAL was rolled for 1 time, ground and passed through a 200-mesh sieve. Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, A.R. grade) and sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, A.R. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Aureomycin (AMC, USP grade) and tetracycline (TC, USP grade) were purchased from Aladdin Reagent Inc. (Shanghai, China). The molecular structures of AMC and TC are shown in Fig. S2 (Supplementary Materials). All other reagents are of analytical grade and all solutions were prepared with deionized water.

2.2. Preparation of the hybrid Zn-silicate adsorbents

Natural RPAL powder (1.2 g) was dispersed in 25 mL of the aqueous solution containing 7.8 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ to form a homogeneous suspension. Then, calculated amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with the Si/Zn molar ratio of 3:1, 2:1, 1:1, 1:2 and 1:3, respectively, were added dropwise, and the mixture was transferred into a 100-mL Teflon autoclave and kept at 180 °C for 8 h. The solid product was separated, and fully washed with deionized water until no free ions could be detected. The wet solid product was dried, ground and passed through a 200-mesh screen for further use. The raw red PAL was marked as RPAL, and the Zn-silicate adsorbents were coded as SiZn-31, SiZn-21, SiZn-11, SiZn-12 and SiZn-13 according to the different Si/Zn ratio.

2.3. Adsorption experiment

The adsorption performance of the Zn-silicate adsorbent was evaluated by a batch adsorption experiment. In a typical procedure, 10 mg of the adsorbent were fully contacted with 20 mL of aqueous solution of AMC or TC (initial concentration, 200 mg/L, pH 3.5), and then the mixture was shaken at 140 rpm in a thermostatic shaker (THZ-98A) at 30 °C for 4 h to reach adsorption equilibrium. Afterward, the adsorbents were rapidly separated from the solution by centrifugation, and the supernatant was collected. The absorbance of AMC or TC solutions before and after adsorption were measured using a UV–vis spectrophotometer (UV 765, Precision & Scientific Instrument Co., LTD, Shanghai, China), then the concentration was calculated by the absorbance using a series of standard curves. After obtaining the concentration of AMC or TC in the solution, the adsorption capacity of the adsorbents for AMC and TC can be calculated using Eq. (1).

$$q = (C_0 - C_t) \times V/m \quad (1)$$

Here, V (mL) is the volume of AMC or TC solution, C_0 (mg/L) is the initial concentration of AMC or TC solution, C_t (mg/L) is the concentration of AMC or TC at a given time (t), and m (mg) is the mass of adsorbent used.

For studying the adsorption thermodynamics, the initial concentration of AMC and TC solutions was selected in the range of 50–1000 mg/L. For studying the adsorption kinetic, the initial concentration of AMC and TC solution was fixed at 200 mg/L (pH is 3.50). After each adsorption experiment, the adsorption capacities were calculated according to the procedure described above.

Download English Version:

<https://daneshyari.com/en/article/71943>

Download Persian Version:

<https://daneshyari.com/article/71943>

[Daneshyari.com](https://daneshyari.com)