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Ultrahigh adsorption of typical antibiotics onto novel hierarchical porous carbons derived from renewable lignin *via* halloysite nanotubes-template and *in-situ* activation

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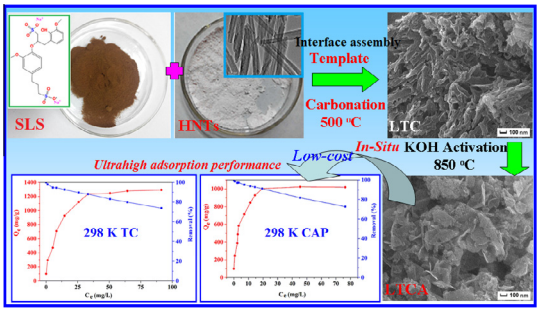
HIGHLIGHTS

- Renewable SLS and natural mineral (HNTs) were used for fabricating HPCs.
- HNTs template and KOH activation had significant impacts on adsorption properties.
- LTCA possessed ultrahigh adsorption capacity for TC (1297.0 mg/g) and CAP (1067.2 mg/g).
- Sustainable and highly performance LTCA has promising potential in various areas.

GRAPHICAL ABSTRACT



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ABSTRACT

In decade years, antibiotics residual has received considerable attention because of their detrimental effects on human health and the ecosystem, thereby resolution of this issue become a burning research project. Herein, we first prepared a novel sustainable hierarchical porous carbons (HPCs) (named LCTA) *via* the combination of halloysite nanotubes-template and *in-situ* KOH activation, using industrial by-product sodium lignin sulfonate (SLS) as biomass precursor. It was demonstrated that both HNTs template and KOH activation played a key role in the enhancements of the porosity and accessible surface. LTCA exhibited a high specific surface area of 2320 m^2/g and large pore volume of 1.342 cm^3/g. Moreover, LTCA showed an ultrahigh adsorption capacity for tetracycline (TC) of 1297.0 mg/g and chloramphenicol (CAP) of 1067.2 mg/g at 298 K, which are far higher than those adsorbents previously reported. Additionally, fast adsorption kinetics, excellent environmental adaptability and good regeneration ability make this novel HPC as a promising material for antibiotics wastewater treatment practices.

1. Introduction

With the increase of abusing antibiotics, various antibiotics including tetracycline (TC) and chloramphenicol (CAP) have been frequently detected in surface water, groundwater and even drinking water, which are mostly excreted to the external environment without metabolism through faeces [1]. The global problem of harmful antibiotics has attracted broad attention due to their detrimental impacts on human health and ecosystem. Hence, it is of great significance to develop efficient and economic methods for removal of antibiotics from wastewater. Several techniques have

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been studied for this purpose, including oxidation, adsorption, electro degradation, bio-degradation and photocatalytic degradation [2]. In particular, adsorption has been considered a promising method to remove antibiotics due to economic and environmental considerations [3]. Various adsorbents, such as natural minerals [4], metallic oxides [5], carbons [6] and molecular imprinted polymers [7] were used to remove antibiotics. Notably, carbon materials are preferred for wastewater treatment considering their high specific surface areas, abundant surface groups and high stability.

Various carbon materials (activated carbon, carbon nanotube, graphene oxide and mesoporous carbon [6,8–10]) have been investigated and serviced for eliminating antibiotics. Din et al. synthesized ordered mesoporous carbon with adsorption mount of 210 mg/g for CAP [6]. Martins et al. prepared an activated carbon with a large specific surface area from macadamia nut shells, showing an acceptable adsorption capacity of 455.8 mg/g for TC [8]. Zhang et al. investigated the adsorption of TC onto multi-walled carbon nanotubes, the result indicated the maximum adsorption capacity (Q_m) is 309 mg/g [9]. Gao et al. reported that graphite oxide (GO) exhibited a high adsorption amount for TC of 313 mg/g [10]. However, although these carbon materials demonstrated relatively good adsorption ability, unfortunately, the drawback of high cost, complicated synthesis process, low capacity and slow kinetics property limited their large-scale applications. Currently, well-design and fabrication of low-cost and highly efficient carbon materials, are highly desired yet still challenging.

Hierarchical porous carbons (HPCs) with tunable pore structure show great priority in versatile applications owing to the combined advantages of the different types of interconnected pores. Thereinto, macropores can form buffering reservoirs to minimize diffusion distances to the interior surfaces. Abundant micro- and mesopores supply larger accessible surface areas and smaller transport resistance resulting in strong adsorption ability. Tremendous efforts have been devoted to the fabrication of HPCs with macro-mesopores or meso-micropores [11]. However, the preparation and application of HPCs in the antibiotics removal have not been reported. Activation methods include chemical activation and physical activation, which are usually used to create and promote the porosity [12]. Mesoporous carbons were constructed *via* hard- or soft-template approaches. Commonly, soft-template strategy always suffers from drawbacks such as strict conditions and very precise structure-directing agents, hindering the large scale production. As for hard-template method, alternative templates and extensive carbon precursors can be arbitrarily select, however, the massive artificial silica templates (e.g., SBA-15, SBA-16 and KIT-6) are required in the synthesis process. In addition, the pore walls of templates are limited the pore sizes of as-prepared mesoporous carbons. Thus, cheap templates with especial architectures are much in demand.

Fortunately, halloysite nanotubes (HNTs), a class of natural silicate mineral with the regular nano-tubular structure is considered as ideal candidate for hard template [13]. Furthermore, cost-saving, environment-friendly and abundant reserves of HNTs in China make them remarkably suitable for scale application. Also, carbon precursor is a key factor for developing low-cost carbons. Sodium lignin sulfonate (SLS), an industrial by-product generated in paper industry, is more enormous and available as compared with those organic carbon sources, i.e. sucrose, furfuryl alcohol, and divinylbenzene [14]. Previous significant works reported that SLS could be successfully serviced as biomass carbon precursor to fabricate desirable carbon materials[15].

Inspired by idea of sustainable eco-environment and green chemistry, the objective of this work is to design and fabricate novel HPCs from renewable SLS *via* HNTs-template method and *in-situ* KOH activation for efficiently removing TC and CAP antibiotics from wastewater. The physical/chemical characteristics of obtained HPCs were systemically investigated. Subsequently, adsorption parameters were analyzed and optimized, and adsorption performances of this advanced adsorbent were discussed by the batch adsorption. Also, the adsorption mechanism was also proposed.

2. Experimental

2.1. Materials

HNTs were purchased from Zhengzhou Jinyangguang Chinaware Co., Ltd (Henan, China). Sodium hydroxide (NaOH, AR), potassium hydroxide (KOH, AR), sodium bicarbonate ($NaHCO_3$, AR), sodium carbonate (Na_2CO_3, AR), hydrochloric acid (HCl, AR, 37 wt%) and hydrofluoric acid (HF, AR, ⩾40%) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). SLS (AR, 96%), ammonium hydroxide ($NH_3{\cdot}H_2O$, AR, 25–28%), TC (AR, 98%) and CAP (AR, 98%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of HPCs

HNTs were used as hard template to obtain porous carbon through liquid phase impregnation and carbonization. In detailed, 3.0 g of HNTs were added into 30 mL of SLS aqueous solution (30 wt.%) with ultrasonic treatment (40 kHz). The HNTs/SLS mixture was suffered a negative pressure (−0.1 MPa) about 2 h for removal of gases. Subsequently, degassing mixture was centrifuged for 1.5 h at 3000 rpm to ensure that SLS can fill in the space between HNTs or cavity, and then picked up the upper solution (SLS aqueous solution). The brown solid was dried and carbonized in a tubular furnace at 400 °C for 2 h with a heating rate of 5 °C/min under N_2 atmosphere. The milled black product was immersed in HF solution (5.0 wt.%) to remove HNTs, and washed several time with distilled water to neutral, followed by drying at 60 °C. The lignin-based template porous carbon was obtained and referred as LTC.

The mixture of LTC and KOH with a mass ratio of 1:4 by grinding was heated at 850 °C for 1 h with a ramp rate of 5 °C/min under N_2 atmosphere. The product was washed with diluted HCl (12 wt.%) to remove the impurities, after copiously rinsing with distilled water, the HPCs was dried and named as LTCA.

Meanwhile, the lignin-based carbon prepared through carbonization straightly from SLS without the additional HNTs, and the product was referred as LC. Similarly, the LC was activated under the same condition and the product was called LCA.

2.3. Characterization

The Fourier transform infrared (FT-IR) spectrometer was conducted using a Nicolet NEXUS-470 spectrophotometer with 128 scans at a 4 cm^{-1} resolution, and the ranges of spectrograms were 4000–400 cm^{-1}. Elemental analysis was measured using an element analyzer (FLASH1112A, CE, Italy). Zero point of charge (pH_{PZC}) for LTCA was measured following method described elsewhere [S1] (Supporting Information). Quantification of the surface functional groups was determined by Boehm titration [S2] (Supporting Information). Powder X-ray diffraction (XRD) analysis was taken on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 Å, 40 kV, 40 mA) and with a scan rate of 7° min^{-1}. Raman spectra were measured by a Laser Raman Spectrometer (DXR, Thermo Fisher, USA) with excitation at 532 nm incident laser light and 10 mW power. X-ray photoelectron spectroscopy (XPS) was estimated by a Kratos Axis Ultra DLD spectrometer equipped with an Al Kα X-ray source (1486.6 eV), survey scan