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From black liquor to highly porous carbon adsorbents with tunable microstructure and excellent adsorption of tetracycline from water: Performance and mechanism study

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ABSTRACT

In this work, we reported the successful conversion of the industrial SLS originated from black liquor to low-cost porous carbon with tunable microstructure and ultrahigh adsorption performance of tetracycline (TC) from water *via* pre-carbonation and KOH activation. Comparatively, LCA-850-4 with a very high specific surface area (2805.8 m^2/g) and pore volume (1.45 cm^3/g) showed a maximum adsorption of 1173 mg/g at 298 K, which was far higher than other reported adsorbents. LCA-850-4 exhibited excellent adsorption over a broad pH range. Kinetics and isotherm data was well fitted to the pseudo-second-order rate and Langmuir model, respectively. Thermodynamic parameters indicated a spontaneous and endothermic adsorption. The results are of importance to indicate LCA-850-4 with fast kinetics and excellent reusability possessed the huge potentials in practical pharmaceutical antibiotic wastewater treatment.

1. Introduction

Tetracyclines (TCs), as a class of pharmaceutical antibiotics, are used extensively worldwide for the treatment and/or prevention of infectious diseases for human and animals, as well as feed additives to promote growth [1]. TCs are poorly metabolized and absorbed by organic body, namely, which are excreted to the water and soil environments directly. Therefore, the long-term, widespread or improper use has resulted in TCs residuals in aquatic environments, which caused a variety of adverse effects for human health and ecosystem safe [2]. Researchers have focused on the removal of antibiotics by advanced approaches such as adsorption, electrodegradation, ozonation, biodegradation and photocatalytic degradation [3]. Among, adsorption has been proved to be the most suitable method because it is simple, low-cost, safe and effective [4]. Conventional adsorbents including activated carbon [5], clay mineral [6], chitosan particles [7], imprinted nanospheres [8] for antibiotic adsorption already could not meet current requirements. Thus, there is still an increasing demand for developing the highly efficient and low-cost adsorbent materials to remove antibiotics from wastewater.

Up to now, the research on activated carbons (ACs) is enthusiastic due to the promising candidates for energy and gas storage [9], pollutants removal [10] and supercapacitor application [11]. However, the potentiality of finding low-cost and environmental carbon sources in the light of different applications is still huge. Therefore, various cheaper resources such as agricultural by-products [12], agricultural and municipal solid wastes [13], artificially synthetic plastic wastes [14] and natural biomass [15], were attempted to fabricate ACs. Generally, ACs can be prepared *via* physical and chemical activation. The former one involves that carbon precursors are reacted with oxidizing gases, *e.g.* CO_2 and water vapor [16]. Compared to physical method, the latter one has superior advantages such as lower reaction temperature, less time, higher yields, and higher specific surface area (SSA) and pore volume (PV), commonly using KOH, H_3PO_4 or $ZnCl_2$ as chemical activating agents [5]. Especially, KOH activation is extensively used in ACs preparation, owing to the defined micropore size distribution, high PV, and an ultrahigh SSA of up to 3000 m^2/g [9,17]. Importantly, parameters including amount of KOH, activation temperature and time, heating rate and flow rates of inert gas and carbon sources play a key role in the ACs surface property and pore structure [3].

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As human understanding of environmental pollution and resource crisis deepening, renewable and biodegradable natural biopolymers have attracted more and more attention. Lignin, as the second richest natural biomass, is increasingly concerned by people in its research and application. So far, lignin is mostly applied in the form of lignin sulfonate for many aspects (*e.g.* fuel, adhesive, tanning agent and carbon precursor). Sodium lignin sulfonate (SLS), a lignin derivative, is generally produced from the black liquor, which is discharged waste from paper-making industry in large quantities and poses serious environmental concerns. Previously, some efforts have been made to achieve the conversion of SLS to ACs [18] and/or carbon fiber [19]. For example, Fu et al. [16] synthesized ACs derived from lignin *via* water vapor activation to remove methylene blue. KOH-activated lignin-based AC was performed by Babeł et al. [17] for high hydrogen electrosorption. Lignin-derived AC through CO_2 activation is applied for adsorption of sodium dodecylbenzene sulfonate, reported by Cotoruelo at al. [18]. However, until now, the conversion of SLS to porous carbons and their application still has been little studied as a main project, and particularly, there was no relevant report about the research of SLS-derived ACs for applications in antibiotic wastewater treatment.

Herein, the main objective is to convert the starting material SLS to highly porous carbons with tunable microstructure *via* a pre-carbonation and KOH activation and then application for highly efficient adsorptive removal of TC antibiotic from the aquatic environment. Importantly, optimum conditions were specially chosen to obtain an ultrahigh TC adsorption performance. A series of characterizations were conducted to reveal the structure and surface property of these carbon materials. The influences of various parameters including initial TC concentration, contact temperature, solution pH and adsorption time on adsorption process and adsorption isotherm, kinetics and thermodynamics nature were also investigated.

2. Material and methods

2.1. Materials

The SLS (96%) and TC (USP Grade) used in experiments were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China) without further purification. Potassium hydroxide (KOH, AR), hydrochloric acid (HCl), sodium hydroxide (NaOH, AR), calcium chloride ($CaCl_2$, AR) and sodium chloride (NaCl, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received.

2.2. Preparation method

The preparation procedure was described in detail as follows: SLS was heated at 500 °C for 2.0 h with a heating rate of 5.0 °C/min in a tubular furnace (SK-G06123K, Tianjin Zhonghuan Lab Furnace Co., Ltd, Tianjin, China) under N_2 flow. Subsequently, the black products were washed with ethanol and distilled water and named LC. KOH activation was performed with various weight ratios of LC/KOH (1/0-4) in a nickel crucible at different activation temperatures of 700, 800 and 850 °C for 1.0 h with a heating rate of 5 °C/min, respectively. After cooling down, the product was treated with HCl (8%, v/v) to remove impurities, washed with distilled water to neutral and dried at 60 °C for 12 h. The SLS-based activated porous carbon was referred as LCA-*T*-*x*, *T* and *x* represent activation temperature and mass ratio of KOH/LC, respectively.

2.3. Characterization

Surface chemical property was analyzed with Fourier transformed infrared spectroscopy (FTIR, Nicolet NEXUS-470, USA). Raman spectroscopy was carried out on a Laser Raman spectrometer (DXR, Thermo Fisher, USA). Scanning electron microscope (SEM, JSM-7001F, JEOL, Japan) and transmission electron microscope (TEM, JEM-2100, JEOL) were performed for determining the morphology and structure. Elemental analysis was used an element analyzer (FLASH1112A, Italy). N_2 adsorption–desorption isotherms were measured at 77 K with an Autosorb-iQC apparatus (Quantachrome Corp., USA). The Brunauer–Emmet–Teller equation (BET) method was used to calculate the SSA. The micropore volume and surface area were determined with the *t*-plot analysis and the pore size distributions were determined by the DFT method.

2.4. Batch adsorption experiments

2.0 mg of each LCA-*T*-*x* adsorbent was used to adsorb TC molecule from 10 mL of aqueous solution (200 mg/L) for 24 h at 298 K, and the results showed the LCA-850-4 was optimum for further investigation. To investigate adsorption kinetics, batch experiments was conducted by adding 2.0 mg of LCA-850-4 into the TC solutions (10 mL) with the different initial concentrations of 50, 100 and 150 mg/L at 298, 308 and 318 K for different designated interval time, respectively. To study adsorption equilibrium property, different initial concentrations (50–350 mg/L) at three different temperatures for 24 h were adopted. The concentration of free TC in supernatant was tested by UV–vis spectrophotometer (UV-2450, Shimadzu, Japan) at a wavelength of 357.0 nm and the amount of TC adsorbed was calculated by the following equations:

$$Q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

$$Q_t = \frac{V(C_0 - C_t)}{M} \quad (2)$$

where C_o and C_e (mg/L) are the initial concentrations, respectively. C_t (mg/L) is the remaining antibiotic concentration at time t (min). V (mL) is the solution volume and W (mg) is the weight of adsorbent.

In the pH and ionic concentration effect experiments, the initial pH values of TC solutions (250 mg/L) were adjusted in the range of 3.0–8.0 using dilute NaOH or HCl solutions, different Na^+ and Ca^{2+} concentration in the range of 0–100 mmol/L were dissolved in the TC solutions (200 mg/L). The percentage removal (%) was calculated according to the following equation.

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (3)$$

The adsorption–desorption cycle experiments were carried out to estimate reusability. 0.2 mol/L NaOH aqueous solution was used as the regeneration reagent to remove adsorbed TC from carbon solid. Then this LCA-850-4 was used to adsorb TC from fresh solution again. The cycle procedure was conducted for four times.

2.5. Adsorption behavior analysis

The pseudo-first-order and pseudo-second-order rate model [20] were used to simulate the adsorption kinetics data and given as below:

$$\ln(Q_1 - Q_t) = \log Q_1 - k_1 t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_2^2} + \frac{1}{Q_2} t \quad (5)$$

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