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Novel N-doped hierarchically porous carbons derived from sustainable shrimp shell for high-performance removal of sulfamethazine and chloramphenicol

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ABSTRACT

In this research, shrimp shell, as an abundant, environmental-friendly and renewable biomass source, was successfully converted into novel N-doped hierarchically porous carbons (N-HPCs) *via* a simple self-template carbonization and KOH activation. The physical–chemical properties of N-HPCs were characterized by FT-IR, SEM, TEM, Raman, BET and elemental analysis. The optimum N-HPCs (named N-HPC-850-2) exhibited the highest specific surface area (3171 m^2/g) and total pore volume (1.934 cm^3/g), and was used to effectively eliminate sulfamethazine (SMZ) and chloramphenicol (CAP) from water. Batch adsorption results showed increasing temperature was in favor of adsorption and the N-HPC-850-2 had a high adsorption affinity toward two antibiotics over a broad pH range. Adsorption isotherm data were fitted with Langmuir model very well, with the maximum monolayer adsorption capacity of 699.3 and 742.4 mg/g for SMZ and CAP at 318 K, respectively. The pseudo-second-order rate model described adsorption kinetics data well and adsorption processes were governed predominately by intra-particle diffusion and film diffusion. The thermodynamic parameters indicated the spontaneous and endothermic adsorption. Importantly, the N-HPC-850-2 adsorbent also exhibited a good regeneration capacity. Here, we provided a promising approach to prepare low-cost and high-performance biomass-based N-HPCs for fast and highly efficient removal of antibiotics from aquatic system.

1. Introduction

Pharmaceutical antibiotics can selectively inhibit or kill microorganisms and are widely used in human and animal medicine to control infectious diseases and/or in livestock farming to improve feed efficiency [1,2]. However, the majority of antibiotics cannot be absorbed and are excreted as original or metabolized forms in feces and urine [3]. Also, antibiotics are unavoidably discharged into environments *via* domestic wastewater effluent and improper disposal of expired drugs, which cause huge potential danger to human, including acute and/or chronic toxic effects and microorganism antibiotic resistance [4]. Among, Chloramphenicol (CAP) and Sulfonamides (SAs) are two commonly applied antibiotics. Sulfamethazine (SMZ) is the most frequent (about 50% percentage) among the SAs detected in the various environment samples [5]. CAP and SMZ are ubiquitous in surface, groundwater, wastewater and even drinking water. For example, it was reported that the detected concentrations of CAP in municipal sewage, the Nanming River and the sediment of Nanming River of Guiyang City, China were up to 47.4 μg/L, 19.0 μg/L and 1138 ug/kg, respectively [6]. Furthermore, they cannot be effectively removed in the sewage treatment plants. It is very necessary and important to develop and evaluate high-performance, low-cost and sustainable adsorbents to eliminate antibiotic wastewaters.

Biochar pyrolyzed from biological resource has recently attracted many attentions, because of its large specific surface area, high porosity, hydrophobicity, low cost, stability and abundant precursor [7]. Previous studies revealed that biochar showed strong adsorption affinity toward various organic and inorganic pollutants [8]. Adsorption ability of biochar is mainly determined by its physical–chemical properties such as elemental composition, surface chemistry and structure characteristics, which are usually controlled by preparation conditions including calcination temperature and time, heating rate and inert gas flow. The choice of the precursors commonly depends on the availability, cost and the presence of heteroatoms (*e.g.* N, B or P). The exploration of new,

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available, economic and renewable biomass sources resulting in high-performance carbons has intensified, especially considering the potential large-scale applications in water treatments.

Shrimp shell, an industrial by-product and food waste in daily life, mainly contains crude protein, crude fat, calcium protein and chitin (polysaccharide), which can be an ideal candidate for converting into carbon materials by a simple pyrolysis [9]. Unfortunately, such biochars exhibit poor adsorption capacity due to their relatively low porosity and surface area. Generally, the introduction of micropores into the resultant biochars can be achieved by physical or chemical activation, allowing high performance for environmental application [10]. Meanwhile, $CaCO_3$ presented in shrimp shell can be properly used as hard templates to leave the corresponding pores. Therefore, shrimp shell is an ideal biomass for the preparation of N-doped hierarchically porous carbons (N-HPCs), which show the advantages of different types of pores and enhance surface hydrophilicity. To our best knowledge, there is rare report about the utilization of N-HPCs for eliminating antibiotic from water to date, particularly shrimp shell as precursor.

The aim of this work is to fabricate novel N-HPCs using shrimp shell as renewable biomass, *via in-situ* self-template pyrolysis and chemical activation, and verify the efficiency of shrimp shell-derived N-HPC in removing two heavily used antibiotics, CAP and SMZ. The physical, chemical and structural information were characterized in detail. The batch method was explored to determine adsorption isotherms, kinetics and reusability. Influencing factors including activation temperature, KOH/biochar mass ratio, solution pH, temperature and contact time were also examined.

2. Experimental

2.1. Materials

Shrimp shell was purchased from Yongheng Fish Meal Co. Ltd (Wenzhou, China). CAP (AR, ≥ 98%) and SMZ (AR, ≥ 98%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Potassium hydroxide (KOH, AR, ≥ 90%), concentrated hydrochloric acid (HCl, AR, 37%) and concentrated ammonia ($NH_3{\cdot}H_2O$, AR, 25∼28%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received.

2.2. Instruments

Fourier transform infrared (FT-IR) spectroscopy was carried out on a Nicolet NEXUS-470 spectrophotometer (U.S.A.). Laser Raman Spectrometer (DXR, Thermo Fisher, USA) was used to identify the degree of graphitization. Element analyzer (FLASH 1112A, Italy) was used to analyze elemental percentage. The morphology was observed by transmission electron microscope (TEM, JEM-2100, JEOL, Japan) and scanning electron microscope (JSM-7001F, JEOL, Japan). The specific surface area and porosity were determined by N_2 adsorption–desorption isotherm measured at 77 K in a Micromeritics Nove 2000e apparatus (Quantachrome Corp., USA).

2.3. Preparation of N-HPCs

Shrimp shell was held at 400 °C for 2.0 h with a heating rate of 5 °C/min under N_2 in a tubular furnace (SK-G06123K, Tianjin Zhonghuan Lab Furnace Co., Ltd, China). The product was washed by HCl of 1.0 mol/L to remove impurities, then washed with water and finally dried at 80 °C. The shrimp shell-derived biochar was denoted as C-400.

KOH and C-400 were mixed and ground uniformly at the different mass ratios (0:1, 1:1 or 2:1). The mixture was heated to activation temperature with a heating rate of 5 °C/min under N_2, held at 700 °C (800 or 850 °C) for 1 h and then cooled to RT. The product was washed with hot deionized water and HCl (0.5 mol/L), washed with water and dried overnight to obtain N-HPCs. The N-HPCs at different conditions were denoted as N-HPC-*T*-*x*, here *T* represents temperature, and *x* is the mass ratios of KOH and C-400.

2.4. Adsorption experiments

To select an optimum adsorbent, 3.0 mg of the four N-HPCs was added into centrifuge tube containing 10 ml of CAP (SMZ) solutions with the different initial concentrations (100, 150 and 200 mg/L), respectively. The tubes were placed in water baths at 298 K for 12 h. The mixture was filtered through 0.22 μm membrane and the free CAP (SMZ) concentrations were analyzed using UV–vis spectrophotometer at the maximum wavelength of 278 nm for CAP and 262 nm for SMZ. The adsorption amount at equilibrium Q_e (mg/g) was calculated as follow:

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

where C_0 and C_e (mg/L) are the initial and equilibrium antibiotic concentrations, respectively. *V* (L) is the solution volume and *m* (g) is the mass of adsorbent.

To investigate pH effect, 3.0 mg of N-HPC-850-2 was added into 10 ml of 200 mg/L CAP (SMZ) solutions with different solution pH of 3.0–9.0, respectively. Except for the pH effect study, adsorption experiments were carried out at the initial solution pH for SMZ and CAP. The removal ratio of CAP (SMZ) was obtained by the following equation:

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Adsorption isotherm test: 3.0 mg of N-HPC-850-2 was added into centrifuge tube containing 10 ml of CAP (SMZ) solutions with the initial concentrations ranging from 20 to 280 mg/L. Adsorption was carried out in water baths at 298, 308 and 318 K for 12 h, respectively. Similarly, adsorption kinetics of CAP (SMZ) by N-HPC-850-2 was performed at 298, 308 and 318 K by measuring the free CAP concentrations in the supernatants at the different contact time intervals. The adsorption amount at time *t* (Q_t, mg/g) was calculated as follow:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

where C_t (mg/L) is the free concentration at *t* time.

To study the regeneration of N-HPC-850-2, NaOH aqueous solution (0.2 mol/L) was used as the regeneration reagent to remove adsorbed antibiotics. Adsorption of reused adsorbent (3.0 mg) toward 10 ml of SMZ (150 mg/L) and CAP (150 mg/L) was performed at 298 K, respectively.

All the adsorption experiments were conducted in triplicate and the average values were reported with the relative error of less than 5%.

3. Results and discussion

3.1. Characterization

Figs. 1 and 2 show SEM and TEM images of C-400 and N-HPC-850-2, respectively. In Fig. 1a, b, C-400 had an irregular bulk shape in several microns and the surface appeared to be smooth, without visible porous structure. After activation process, N-HPC-850-2 displayed an abundant porous structure with the uneven surface, the particle size of which became relatively small. Meanwhile, some thin carbon sheets were presented in SEM image of N-HPC-850-2. TEM was used to study the microstructure of carbons. There were no obvious pores in Fig. 2a for C-400 with smooth surface. Clearly,