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Adsorption and removal of tetracycline from water by petroleum coke-derived highly porous activated carbon

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ABSTRACT

Herein, petroleum coke (PC) derived activated carbons (ACs) were prepared via KOH activation process. The as-prepared ACs exhibited a large surface area (2800–2900 m^2/g) and total pore volume (1.4–2.1 cm^3/g). In addition, the oxygen-correlated functional groups endow the resultant ACs with an acid surface. Combining the structural characters with the surface properties, these ACs were successfully applied for the effective removal of a commonly-used antibiotics (tetracycline) from drinking water for the first time. As a typical example, the maximum adsorption capacities of 897.6, 961.5 and 1121.5 mg/g were obtained at the temperature of 303, 313 and 323 K, respectively, for tetracycline removal, which was higher than that of other reports. Furthermore, the adsorption parameters, including the initial concentration, contact time, pH of solution, ionic strength and temperature, were investigated. The adsorption isotherms and kinetics were also discussed in detail. It was observed that the adsorption isotherms were well fitted to Freundlich model, the kinetics studies implied the adsorption process was attributed to pseudo-second-order model. The above-mentioned results proved the successful application of the as-synthesized ACs for effective removal of tetracycline.

Introduction

Tetracycline (TC), as its cost effect, high quality and desirable antimicrobial activity, is widely applied in livestock industry and human therapy. It has become one of the most extensively used antibiotics all over the world [1]. According to recent statistics, about 5500 tons of TC is consumed every year in the United States and Europe [2]. However, only a small fraction of TC is metabolized or absorbed in the digestive tract and most of residuary TC is discarded to environment [3]. To our worry, TC has been frequently detected in surface water, groundwater, and even drinking water, which causes harmfulness to environment and our human health [4]. As a result, it has become a necessary task to take some effective measures to remove TC from contaminative water.

Presently, (chemical or physical) adsorption has been considered as one of most effective and facile techniques for TC removal from water [5]. Up to now, various kinds of adsorbents, including HCl-modified zeolite [6], magnetic resin (Q100) [7], alkali bio-char [8], MCM-41 impregnated with zeolite [9], La-impregnated MCM-41 materials [10], graphene oxide [11], graphene oxide functionalized magnetic particles [12], anaerobic granular sludge [13], NaOH-activated sludge, Sorbo commercial activated carbons, merck commercial activated carbons [14], activated carbon fiber modified by microwave [15], bamboo charcoal [16], multi-walled carbon nanotubes [17], nitrifying granular [18], illite [19], clays, humic substances, and clay-humic complexes [20], mesoporous BiOI microspheres [21], marine sediments [22], the red soil (RS, UdicFerrosols) [23], palygorskite [24], ITAC-Fe [25], have been developed for this purpose. Among them, activated carbon (AC) is considered as one of the most promising candidates due to its high adsorption capacity, low cost, and easy manipulation. To the best of our knowledge, the adsorption capacity of AC is mainly determined

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by the specific surface area, pore size distribution and surface functional groups [26]. To obtain AC with large surface area, well-developed pores and a variety of functional groups, the selection of raw materials plays an important role. Up to now, fossil fuels including humus [27], coal [28], pitch coke [29], have been adopted as precursors for the synthesis of ACs due to the merits of high quality, low cost and earth abundance. Among these precursors, petroleum coke (PC) is considered as a satisfactory carbon source due to its high fixed carbon content (more than 90 wt%) and low content of impurities [30]. PC, as a by-product of petrochemical engineering, is being stockpiled at a rate of more than 20,000 tons/day in Xinjiang, China. According to previous investigation, most of PC produced in Xinjiang possesses a certain contents of sulphur (1–3 wt%), making it difficult for further industrial utilization [31]. Consequently, most of PC is regarded as an industrial waste in our district. Herein, we try to re-utilize PC as precursors for synthesis of porous ACs.

As a result, this work aims to (1) synthesize highly porous ACs by activation of PC, (2) investigate the adsorption behavior of TC onto the PC-derived porous ACs. The advantages of this AC preparation method lie in easy manipulation, good reproduction, high yield and large scale production. Furthermore, the as-prepared ACs were successfully explored for TC removal from water for the first time. Impressively, the PC-derived ACs possessed desirable adsorption capacity for TC (up to 1121.5 mg/g), which is higher than that of other adsorbents reported by literatures. To further demonstrate the adsorption mechanism, the influencing factors including initial concentration, contact time, temperature, ionic strength and solution pH were investigated. In addition, the isotherms and kinetics were also studied.

Experiments

Preparation of PC-derived ACs

Firstly, PC (obtained from Karamay refinery, 3#B) was grounded and sieved with stainless steel (the size of sieve was 200 mesh). After sufficiently mixing PC with the activating agent KOH at different mass ratios, the obtained mixture were pressed and heated in a tube furnace under the protection of nitrogen atmosphere. The heating rate was set at 5 °C/min and the activation process was carried out at 800 °C for 1 h. Finally, the activated samples were washed by 2 M HCl and deionized water, respectively, to eliminate any metal residues totally. According to the mixing mass ratios between KOH and PC (KOH/PC), the samples were named as PAC_1 (1/1), PAC_3 (3/1), PAC_4 (4/1), PAC_5 (5/1) and PAC_7 (7/1).

Characterization of PC-derived ACs

To demonstrate the structural character, the scan electron microscopy (SEM) images were recorded on the Philips XL 30 instrument with a JEOL JSM-6700F microscope. The transmission electron microscopy (TEM) technology images were taken on the FEI Tecnai G2 F20 instrument. The N_2 adsorption/desorption isotherms were carried out by the QuadraChrome adsorption instrument. The X-ray photoelectron spectrum (XPS) sweep was recorded on the ESCALAB 250 (Thermo Electron) in which the excitation of X-ray was provided by a monochromatic source of Al Kα (1486.6 eV). The elements of carbon, nitrogen and hydrogen in samples were determined by the instrument of Vario EL cube (Elementar Analysensysteme GmbH). In addition, to classify the surface groups these samples, the Bruker Vertex 70 FT-IR spectrometer was utilized to investigate sample's FT-IR spectra.

Adsorption experiments

TC was purchased from Sigma–Aldrich. Fig. S1(a,b) shows the molecular structure and estimated size of TC. For the adsorption study, a certain amount of PAC_4 was added into flasks with different concentration of TC solution, and then the flasks were shaken at 150 rpm in a thermostatic shaker bath at a selected temperature for some time. After high speed centrifugation, the supernatant of the TC solution were monitored via a UV–vis spectrophotometer (UV-1800, Shimadzu) at a fixed wavelength of λ = 355 nm. A series of experimental factors including the initial TC concentration, contact time, ionic strength and solution pH were investigated to further understand the adsorption process. The equilibrium adsorption capacity q_e (mg/g) can be calculated by the Eq. (1) as follows:

$$q_e = \frac{(C_0 - C_e)V}{1000W} \quad (1)$$

Herein C_o and C_e (mg/L) are the initial and equilibrium concentration of TC, respectively. V (mL) is the volume of the

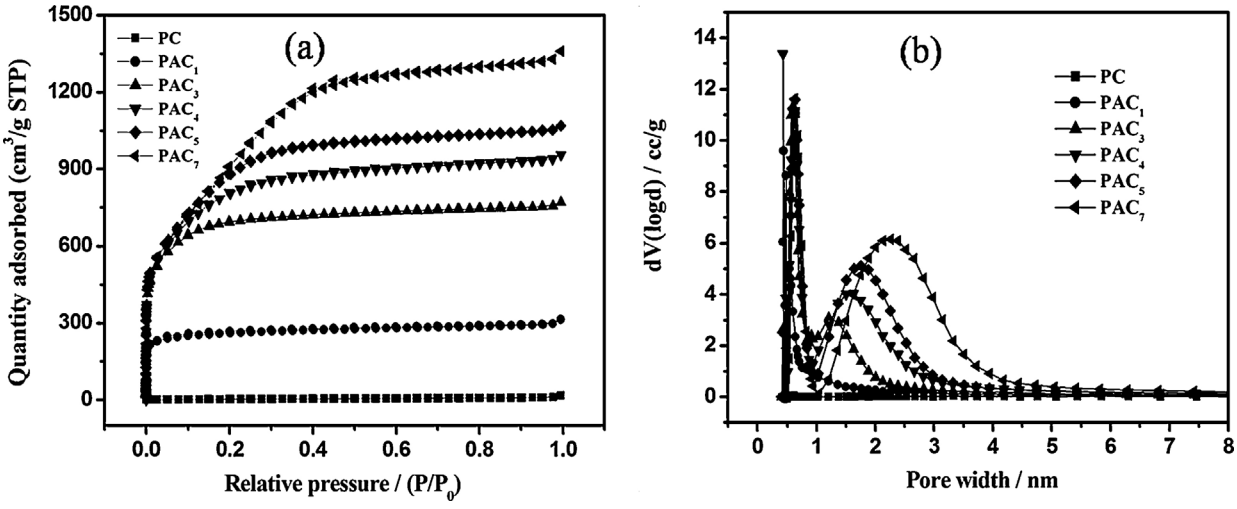

Fig. 1. (a) Nitrogen adsorption/desorption isotherms, (b) pore size distribution curves of PACs.