



Characterization and ciprofloxacin adsorption properties of activated carbons prepared from biomass wastes by H₃PO₄ activation



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HIGHLIGHTS

- Biomass wastes-derived activated carbon were prepared by one-step method.
- The properties of precursors were characterized by thermogravimetric analysis.
- The surface acidic functional groups were determined by NH₃-TPD.
- The characterization and adsorption properties of both carbons were compared.

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ABSTRACT

As biomass wastes, *Arundo donax* Linn and pomelo peel were used as precursors for activated carbons (ALAC and PPAC) preparation by phosphoric acid activation. The pore structure and surface acidic functional groups of both carbons were characterized by nitrogen adsorption/desorption experiment, NH₃-temperature-programmed desorption (NH₃-TPD) and Fourier transform infrared spectroscopy (FTIR). A batch of experiments was carried out to investigate the adsorption performances of ciprofloxacin under different conditions. Results showed that PPAC exhibited larger surface area (1252 m²/g) and larger portion of mesoporous, while ALAC was typical of microporous materials. Results from NH₃-TPD suggested that ALAC was characteristic of more acidic functional group than PPAC. The maximum monolayer adsorption capability was 244 mg/g for ALAC and 400 mg/L for PPAC. Kinetics studies showed intra-particle diffusion was not the unique rate-controlling step. Boundary layer resistance existed between adsorbent and adsorbate.

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1. Introduction

Activated carbon is a preferred adsorbent for the removal of pollutants from wastewater. However, its widespread use is restricted due to high costs. To decrease treatment costs, attempts have been made to find inexpensive alternative precursors for carbon preparation, such as renewable waste materials. As one kind of wetland plants, *Arundo donax* Linn are generated abundantly every year. Previous studies have reported many methods to make full use of this lignocellulosic biomass waste (Sun et al., 2013; You et al., 2016). Fruit peels have also been used for carbon preparation, such as orange peel (Fernandez et al., 2015; Nemr et al., 2009), jackfruit peel (Foo and Hameed, 2012) and pomegranate peel (Nemr et al., 2009). Pomelo peel is available from the fruit juice

processing plants as an industrial waste. Carbons produced from pomelo peel by KOH and NaOH activation have been used for the removal of anionic and cationic dyes (Foo and Hameed, 2011; Li et al., 2016).

Ciprofloxacin (CIP) is one of the extensively used fluoroquinolone antibiotics in the world. The presence of antibiotics in environments can cause serious damages to the ecosystem and human health through inducing growth of antibiotic-resistant bacteria even at low concentration (Lapworth et al., 2012). Recently, the wide occurrence of CIP in groundwater has attracted broad attentions (Yu et al., 2012). Adsorption may be an effective way to remove antibiotics like CIP due to high efficiency and good feasibility (Yu et al., 2016).

Compared with zinc chloride and hydroxides, H₃PO₄ shows advantages for producing activated carbon used for wastewater treatment (Diao et al., 2002; Li et al., 2010). (i) Precursors can be activated by H₃PO₄ at lower temperature (about 450 °C) in the atmosphere, while hydroxides at higher temperature (above

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700 °C) with the protection of inner atmosphere. (ii) H₃PO₄ has low corrosivity to the equipment and no metal residues, thus environmental friendly. (iii) Carbons prepared by H₃PO₄ activation have large particles and good sedimentation performance, which is very suitable for water treatment. (iv) H₃PO₄ activation is beneficial for the development of mesoporous, which is beneficial for larger molecules adsorption. Thus, carbons from H₃PO₄ activation are cost-effective and environmental friendly. The properties of precursors have a great effect on the physicochemical of obtained carbons. However, carbons produced from pomelo peel and *Arundo donax Linn* by H₃PO₄ activation for CIP adsorption have not been studied.

The main object of this work was to present the comparative study on physicochemical and adsorption properties of activated carbons from *Arundo donax Linn* and pomelo peel using H₃PO₄ as activating agent. CIP was chosen as adsorbate to evaluate the sorption behavior as a function of condition variables (effect of time, pH and initial concentration). The properties of activated carbons were correlated with their adsorption ability and the interaction mechanisms were also investigated.

2. Materials and methods

2.1. Chemicals

Ciprofloxacin hydrochloride (C₁₇H₁₈FN₃O₃·HCl, molecular size 13.5 × 3 × 7.4 Å) from Aladdin was used as adsorbate. With pK_{a1} = 6.1 and pK_{a2} = 8.7 for the carboxylic acid and the basic-N-moiety group, the speciation of cation (CIP⁺), zwitterion (CIP[±]) and anion (CIP⁻) were existed under different pH (Gu and Karthikeyan, 2005).

2.2. Synthesis of activated carbons

Activated carbons were prepared using the following simple method. *Arundo donax Linn* and pomelo peel were precursors for activated carbons. The dried and clean precursor was ground and sieved. Particles with sizes lower than 0.35 mm (45 mesh) diameter were used. After immersing in 85 wt.% H₃PO₄ solution at a ratio of 1:2.5 (g precursor/g H₃PO₄), which was the optimum impregnation ratio used for lignocellulosic biomass activation (Huang et al., 2014), the wet sample was soaked for 10 h. Then, the samples were transferred into a muffle furnace with widely used preparation conditions by H₃PO₄ activation (temperature of 450 °C and activation time of 60 min). After cooling to room temperature, the obtained carbons were washed with tap water and afterward deionized water repeatedly until the pH of the filtrate became steady. Then, the adsorbents were filtered, dried and crushed. Particles with sizes between 0.074 and 0.15 mm (100–200 mesh) were stored in a desiccator for further experiments.

2.3. Characterization methods

SDT Q600 equipment was used to obtain thermo gravimetric analysis (TGA) information. The two samples (the compounds of *Arundo donax Linn* and H₃PO₄, pomelo peel and H₃PO₄) were heated at a rhyme of 5 °C/min in N₂ atmosphere.

The pore structure of carbons was performed on a surface area analyzer at 77 K (Micromeritics, ASAP 2020). Prior to N₂ adsorption/desorption, the samples were degassed at 200 °C under vacuum for 5 h. The surface area (S_{BET}) was determined by the Brunauer–Emmett–Teller (BET) model from relative pressures (P/P₀) in the range of 0.01–0.1 with correlation coefficient high than 0.9999. The total pore volume (V_t) was obtained by single point adsorption of N₂ at a high relative pressure (~0.99). Micropore area (S_{mic}) and micropore volume (V_{mic}) were determined by t-plot method. Mesoporous area

(S_{meso}) and mesoporous volume (V_{meso}) were calculated using BJH model. Eq. (4) V/S_{BET} was used to calculate the average pore width. The pore size distribution was auto-generated by applying the density functional theory (DFT) method to the N₂ adsorption isotherms using the software supplied by ASAP 2020.

The NH₃-temperature-programmed desorption (NH₃-TPD) was tested on a Micromeritics Autochem 2920 instrument in a quartz reactor with a TCD as detector. The sample (0.10 g) was pretreated with Ar gas at 200 °C for 1 h to remove free and weakly adsorbed gas. After cooling down to 100 °C, 10% NH₃/Ar mixture gas of 20 mL/min was introduced and the catalyst was purged for 3 h. After adsorption, pure Ar was introduced. The sample was then heated up to 500 °C at a heating rate of 5 °C/min. Surface oxygenated groups on carbon decomposed upon heating, releasing CO and/or CO₂. To deduct the produced gas, TPD without NH₃ adsorption process was carried out. The NH₃-TPD results of activated carbon were recorded by deducting TPD results.

The types of surface functional groups of both activated carbons were also recorded with Nicolet 6700 FTIR Spectrometer (Thermo Fisher). The spectra were recorded from 4000 to 400 cm⁻¹ and the resolution was 4 cm⁻¹.

2.4. Adsorption experiments

Batch adsorption experiments were performed by contacting 0.1 g of the adsorbents with 100 mL of CIP solution. To obtain adsorption isotherms, initial CIP concentrations in the range of 100–800 mg/l at natural solution pH were tested. The flasks were sealed and placed in an oscillator at a speed of 125 rpm with a temperature control of 298 K until equilibrium was reached. To study the effect of adsorption time, samples with an initial concentration of 350 mg/g were withdrawn at predefined time and analyzed to determine the residual liquid-phase CIP concentration. The effect of pH on CIP adsorption was evaluated by adjusting the pH values of the solutions (initial concentration of 350 mg/L) using concentrated HCl or NaOH to the designated values. The solution was filtered using a syringe with 0.45 μm filter membrane and then determined by UV–Vis spectrophotometer (UV-752, Shanghai) at 275 nm.

2.5. Data analysis

To determine the adsorption kinetics of CIP onto both carbons, the experimental data at various contact time corresponding to the adsorption capacity of CIP was fitted with three kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion model. The linear expression of pseudo-first-order (Eq. (1)), pseudo-second-order (Eq. (2)), and intra-particle diffusion models (Eq. (3)) are expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$q_t = k_{pi} t^{1/2} + C \quad (3)$$

where k_1 (min⁻¹) is the rate constant of the pseudo-first-order model, k_2 (g/(mg min)) is the rate constant of second-order model, k_{pi} (mg/g min^{1/2}) is the diffusion rate constant of intra-particle model, C gives an idea about the thickness of boundary layer, q_e and q_t (mg/g) are the amount of CIP adsorbed at equilibrium and at time t (min).

Adsorption isotherm was used to evaluate the characteristic of the adsorption process between liquid and solid phases when the adsorption reached equilibrium. Four commonly used isotherm

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