



# Preparation of magnetic porous carbon from waste hydrochar by simultaneous activation and magnetization for tetracycline removal



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## HIGHLIGHTS

- A novel magnetic porous carbon with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles was prepared from hydrochar.
- Activation and magnetization of hydrochar can be simultaneously obtained.
- The as-prepared magnetic porous carbon could remove tetracycline efficiently.

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## ABSTRACT

In the present work, a novel magnetic porous carbon (MPC) with maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) particles is facilely prepared from hydrochar (a solid residue of hydrothermal carbonization of biomass) in one step through simultaneous activation and magnetization. The resultant MPC is characterized and utilized as an adsorbent for tetracycline (TC) removal from aqueous solutions. The BET surface area and micropore volume of the MPC are found to be 349 m<sup>2</sup> g<sup>-1</sup> and 0.16 cm<sup>3</sup> g<sup>-1</sup>, respectively. The adsorption kinetics data could be well described by the pseudo-second-order model, and the TC adsorption onto MPC is an endothermic and spontaneous process. The enhanced surface area of the MPC, as well as its graphite-like structure, may contribute to the adsorption capacity of TC. After adsorption, MPC could be effectively separated by applying a magnetic field.

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## 1. Introduction

Tetracycline (TC) is one of the most widely used antibiotics in the livestock industry, most of which is discharged into aquatic environments in original and metabolized forms (Zhou et al., 2012). The most dangerous effect of antibiotics in the environment is the development of multi-resistant bacterial strains that can no longer be treated with the presently known drugs (Zhu et al., 2013). Due to its potential risk and the ineffective removal by conventional water treatment, it is of great importance to explore efficient and cost-effective treatment technologies for TC removal.

Adsorption, due to its high efficiency and easy operation, is one of the most important methods for TC removal (Liu et al., 2012). Carbon-based adsorbents possess large surface areas and abundant pore structures and have shown great potential in the removal of undesirable organic pollutants from aqueous solutions (Zhou et al., 2012). These adsorbents have been verified to be very effective in TC removal, due to the capability of  $\pi$ - $\pi$  electron coupling

with TC molecules, as well as their large surface areas (Ji et al., 2009; Liu et al., 2012; Zhou et al., 2012).

Recently, magnetic carbon composites have been developed and are not only high-efficiency adsorbents for removal of pollutants from aqueous solutions, but are also easily collected magnetically after adsorption (Zhang et al., 2012). The introduction of a magnetic medium (such as maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) to carbon-based adsorbents by a pyrolysis activation (simultaneous activation and magnetization) or chemical co-precipitation reaction is an efficient method to enable the adsorbent to be efficiently separated with an external magnetic field. However, for a low surface area of carbonaceous material, co-precipitation reaction is not an efficient and facile method due to its negative effect on porosity of products (Oliveira et al., 2002). But, both an enhanced surface area and excellent magnetization property can be simultaneously obtained via a pyrolysis activation (Zhang et al., 2012). However, few studies were presented to develop this promising technology for the preparation of MPC.

Hydrochar is a by-product of hydrothermal carbonization (HTC) of waste biomass for bio-oil production (Hu et al., 2010a; Sevilla et al., 2011). As a carbon-rich, functional group abundant and pollution-free solid residue, hydrochar can be selected as an ideal

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carbon-based precursor for assembling magnetic porous carbon (MPC) (Liu et al., 2012). However, one of the main limiting factors hindering the effective exploitation of hydrochar for environmental applications is their low surface area and poor porosity (Falco et al., 2013). Hence, to enhance pollutant removal efficiency, a facile and efficient approach for the activation of hydrochar is needed to explore. To the best of the authors' knowledge, little information has been made available regarding the simultaneous activation and magnetization of hydrochar.

In the present study, a novel MPC with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles was prepared in one step with the thermal pyrolysis of ferric chloride (FeCl<sub>3</sub>) pretreated hydrochar. Nitrogen (N<sub>2</sub>) BET (Brunauer–Emmett–Teller) surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared (FTIR) and Raman spectroscopy were used to characterize the structural differences between the hydrochar and MPC. Adsorption behaviors of TC onto MPC were then investigated. The effects of the solution pH and temperature on TC adsorption were also evaluated.

The main objective of the present work was the investigation of a facile and efficient modification route of hydrochar for improvement in its performance for environmental and agricultural applications.

## 2. Methods

### 2.1. Materials

Analytical grade ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) and tetracycline (TC) were purchased from China National Medicines Corporation Ltd. and Aladdin Reagent Co., respectively. All chemical solutions were prepared using deionized water (18.2 M $\Omega$ ).

The hydrochar material was obtained from our pilot-scale HTC unit. An aqueous solution/dispersion of salix psammophila, at a concentration of 80 g L<sup>-1</sup>, was placed in a stainless steel autoclave and heated up to 573 K and then cooled with circulating water to room temperature (Sevilla et al., 2011). The resulting solid product was recovered by filtration and washed with distilled water and ethyl acetate, and finally dried at 373 K for 2 h.

### 2.2. Synthesis of magnetic porous carbon

The preparation of the MPC from the hydrochar material was carried out as follows: the hydrochar material (20 g) was immersed into the prepared FeCl<sub>3</sub> solution (26.7 g FeCl<sub>3</sub> in 120 mL of water) for 12 h, and then the hydrochar material was separated by filtration and dried at 353 K for 2 h under air. The obtained material was pyrolyzed at the temperature of 973 K for 1 h under nitrogen (N<sub>2</sub>) flow of 1 L min<sup>-1</sup> at a heating rate of 4 K min<sup>-1</sup>. The carbonized sample was washed with 0.1 M of hydrochloric acid (HCl) and water. The prepared material, denoted as MPC, was milled and sieved to obtain particles in powder form (<0.15 mm).

### 2.3. Characterization of the samples

Nitrogen gas sorption isotherms and textural properties of the hydrochar and MPC were determined by the Quantasorb SI instrument (Quantachrome, USA). The surface area was calculated using the BET method with relative pressures of 0.06–0.2, and the total pore volume was determined from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.99. The micropore volume was obtained through a *t*-plot analysis. Magnetic measurement was carried out

at 300 K by a vibrating sample magnetometer (VSM) with a maximum magnetic field of  $\pm 4000$  Oe.

The microscopic features of the hydrochar and MPC were characterized by SEM (XL300, Philips) equipped with an energy-dispersive X-ray (EDX, Link 300) analyzer and TEM (H-600, Hitachi). The power XRD patterns were recorded on the X'Pert PRO system equipped with a Cu K $\alpha$  radiation (40 kV, 40 mA) over the  $2\theta$  range of 10–80°. The surface functional groups of hydrochar and MPC were determined by FTIR spectroscopy using a Nicolet (Nexus 470) spectrometer. The spectra were performed at 4 cm<sup>-1</sup> resolution with a 400–4000 cm<sup>-1</sup> scan range. Raman spectra were recorded by the LabRam-1B spectrometer with He–Ne laser operating at a wavelength of 514 nm, and the curve fitting were performed with the combination of Gaussian line shapes that gave the minimum fitting error.

XPS experiment was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. Binding energies was calibrated by setting C to 1s at 284.6 eV.

The measurement of pH of zero point charges (pH<sub>PZC</sub>) of the MPC sample was determined with the following procedure:

- (1) A 25 mL sodium chloride (NaCl, 0.01 M) solution was placed into 60 mL glass bottle. The initial solution pH was adjusted to successive initial values between 2.0 and 12.0, and 0.05 g of the MPC sample was added to the glass bottle.
- (2) The glass bottle was filled with N<sub>2</sub> to eliminate the effect of carbon dioxide (CO<sub>2</sub>) on the pH change, and then shaken at 313 K.
- (3) The final solution pH was measured after a desired contact time of 48 h.
- (4) The difference between the final pH and the initial pH, denoted as  $\Delta$ pH, was plotted against the initial pH. The solution pH at which the curve crosses the line of  $\Delta$ pH = 0 was taken as the pH<sub>PZC</sub> of sample (Liu et al., 2011, 2012).

### 2.4. Batch adsorption experiments

Adsorption kinetics of TC on MPC were performed by placing 0.05 g of MPC in a glass bottle containing a 50 mL TC solution on a shaker at 298 K, with initial TC concentrations of 10, 30, 50 mg L<sup>-1</sup>. Samples were taken and then subjected to filtration through a 0.22  $\mu$ m nylon membrane filter at appropriate time intervals. The TC concentrations were determined using an ultraviolet–visible (UV–vis) spectrophotometer (UV–vis 4802, Unicop Instruments Co. Ltd., Shanghai) at a wavelength of 360 nm.

Equilibrium isotherm experiments were performed at 303 K over the initial TC concentration range from 5 to 80 mg L<sup>-1</sup>. The glass bottles were shaken for 5 days, this period having been previously determined by kinetics experiments.

The amount of TC adsorbed on the adsorbent at equilibrium ( $q_e$ , mg g<sup>-1</sup>) was calculated using the following equation (Eq. (1)):

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

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of TC (mg L<sup>-1</sup>),  $m$  is the mass of adsorbent (g), and  $V$  is the volume of reaction solution (L).

To examine the effect of pH on TC adsorption onto the MPC, TC adsorption was carried out with different aqueous solutions (pH = 3.1, 4.9, 5.9, 7.0, 8.1, 9.1 and 10.1), and, the solution pH was adjusted with NaOH or HCl (0.1 M) solutions. The TC concentration and temperature of adsorption were fixed at 30 mg L<sup>-1</sup> and 298 K, respectively.

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