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An investigation into the rapid removal of tetracycline using multilayered graphene-phase biochar derived from waste chicken feather

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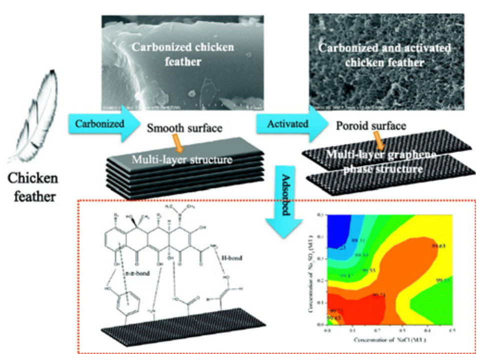
HIGHLIGHTS

- Multilayered graphene-phase biochar (MGB) is prepared by carbonization and activation of waste chicken feather.
- High surface area (1838 m^2/g) and excellent adsorbability are found with this green, economic and renewable material.
- Mechanism and Character are investigated to reveal the adsorption behavior of MGB.
- The MGB is tolerance in tough circumstances.
- Zeta potential of MGB was negative (pH < 3) and the regeneration ability was remarkable.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the removal of tetracycline (TC) using multilayered graphene-phase biochar (MGB) derived from waste chicken feather. MGB was produced through a two-stage carbonization and KOH-activation method. MGB was characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared (FT-IR), Raman spectra, Zeta potential and elemental analysis. Various chemical functional groups were demonstrated on the surface of MGB. MGB was featured by a very large BET surface area of 1838 m^2/g. A rapid equilibrium (within 30 s) and an ultrahigh removal efficiency (up to 99.65%) were obtained when MGB was used in the adsorption of TCs. The adsorption processes were temperature-dependent and the maximum adsorption capacity of MGB was 388.33 mg/g at 30 °C. The data of adsorption isotherms and kinetics were represented well by the Langmuir and Elovich models, respectively. The chemical monolayer adsorption could play an important role in this process. Furthermore, the adsorption of MGB was tolerant with wide pH, high ionic strength and even co-existing anions. Regeneration experiments indicated the removal efficiency was still satisfied (96.61%) even after four cycles. These results have important implications for the future application of animal waste-derived adsorbents in the treatment of wastewater containing antibiotic residues.

1. Introduction

The release of antibiotic residues into the aquatic environment may lead to serious problems such as the toxicity to aquatic organisms and the spreading of antibiotic resistance gene (Pouretedal and Sadegh,

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Table 1
Elemental composition of different biochars.

Raw materials	Temp. (°C)	C (%)	H (%)	O (%)	N (%)	Reference
Spruce	300	69.67	4.30	25.52	0.51	Bach et al., 2016
Birch	300	68.09	3.83	27.49	0.59	
straw	400	57.07	3.33	16.50	0.88	Zhang et al., 2015
lignosulfonate	400	33.58	1.82	27.91	3.65	
Bagasse	500	85.59	2.82	10.48	1.11	Lee et al., 2013
Cocopeat	500	84.44	2.88	11.67	1.02	
Wood stem	500	89.31	2.57	7.34	0.78	
Wood bark	500	84.84	3.13	10.20	1.83	
Cotton straw	600	43.6	5.8	49.8	0.8	Li et al., 2017
grape vine	500	73.77	3.45	21.99	0.79	Colantoni et al., 2016
sunflower husk	500	72.10	3.69	22.82	1.39	
CCF	450	66.06	3.38	16.41	14.15	Present study
MGB	750	84.77	1.10	9.85	4.28	

2014; Chen et al., 2015a; Culyba et al., 2015). It is necessary to remove such antibiotic residues thoroughly from wastewater before discharging. As one of the most widely used antibiotics, tetracycline (TC) is often found in surface water and groundwater. Due to the antibacterial characteristics, it is difficult to achieve the complete removal of TC residual through traditional biological treatment (Wu et al., 2015). As a result, there is an urgent need to develop a convenient and reliable approach to tackle environmental problems related to TC residue. Some efforts including coagulation-sedimentation and advanced oxidation have been made in removing antibiotic pollutants (Siagh et al., 2013; Yang et al., 2015; Topal et al., 2016). There is a particular interest in apply adsorption technique in practices due to its easy operation, high efficiency and low cost (Acosta et al., 2016).

As a widely used adsorbent, activated carbon is usually made from the pyrolysis of plant-derived biomass, including leaves, branches, barks, seeds and rinds (Nethaji et al., 2013; Zhou et al., 2015; Tripathi et al., 2016; Maneerung et al., 2016; He et al., 2016). There is also an increasing interest in biochar derived from animal biomass. For example, the chicken feathers (CFs) are produced in thousands of tonnes annually (Chen et al., 2015b). However, most CFs are usually burned or dumped to landfilled, which might lead to further environmental pollution (Reddy, 2015). Although the hydrolysis/pyrolysis of CFs have been reported in some previous studies, the knowledge regarding their carbonization and activation is still very limited (Senoz et al., 2012; Wang et al., 2013; Giraldoa and Moreno-Piraján, 2013; Kluska et al., 2016; Zhang et al., 2016). The feather fiber is constituted with multilayer "beta sheets", which is featured by micro-coiled helix (alpha spiral) of polypeptide. Overlapped with each other, the beta sheets are linked by disulfide bond and/or van der Waals forces. However, this structure could be easily rebuilt at high temperatures. As a result, there is a potential space

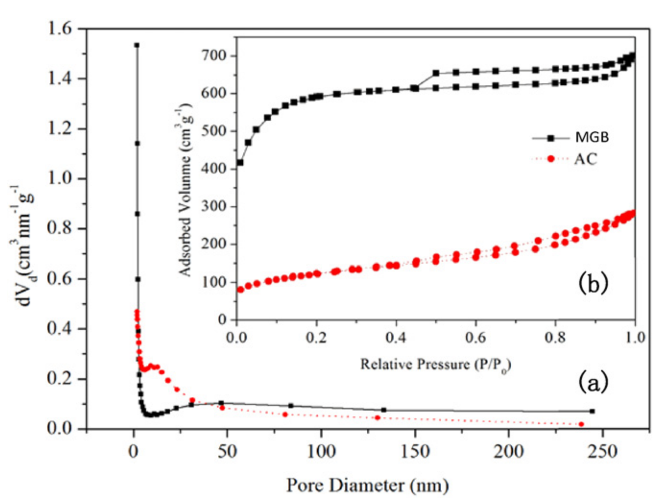

Fig. 1. (a) Adsorption and desorption isotherms (b) pore size distribution of MGB and AC.

in formulating CFs with multilayered porous structures and high specific surface area (Senoz et al., 2012; Kluska et al., 2016; Wang et al., 2013; Giraldoa and Moreno-Piraján, 2013; Zhang et al., 2016).

In this study, a two-stage carbonization and KOH-activation method was developed to produce multilayered graphene-phase biochar (MGB) derived from CFs. The physiochemical characteristics of CFs were explored. Batch adsorption and regeneration experiments were undertaken to investigate the adsorption performance of tetracycline onto MGB. In addition, the corresponding adsorption kinetics and thermodynamics were also studied with the consideration of some influencing factors such as adsorbent dosage, pH, ionic strength and co-existing anions. The results would have important implications for the future application of animal waste-derived adsorbents in the treatment of wastewater containing antibiotic residues.

2. Materials and methods

2.1. Chemicals and materials

All of the reagents used in this study are analytical grade. TC (USP, 99% in purity) was purchased from Adamas reagent Co., Ltd. AC was purchased from Tianjin Fengchuan Chemical Corporation, China. Chicken feathers (CFs) were collected from the poultry market of Twins Trees, Hohhot, China. Deionized water was deployed in stock solutions and other solutions.

2.2. Preparation of MGB

CFs had been washed with deionized water twice before they had been dried at 60 °C in oven for 24 h. Afterwards, CFs were tidied and loaded into a tube furnace. Argon atmosphere were delivered into the tube continuously (60 cm^3/min) during these two stages. In the first stage, CFs were heated at 220 °C (rising rate of 10 °C/min) for 8 h. It is helpful for the crosslinking and reformulating processes between the beta sheets (Senoz et al., 2012; Kluska et al., 2016). In the second stage, the heating temperature was risen from 220 °C to 450 °C (with a ramp of 10 °C/min) and kept for 1 h. The carbonized CFs (CCFs) were delivered after a natural cooling down. Thereafter, CCFs were washed with ethanol (95%) and deionized water and dried at 80 °C in oven for no $<$12 h. Thenceforth, the levigated CCFs were blended with the same weight of KOH. After being dissolved and/or dispersed with water and ethanol in a corundum boat, the mixture was dried at 110 °C in oven for 24 h. Afterwards, the loaded corundum boat was placed in tube furnace again and heated at 800 °C for 1 h in argon atmosphere. MGB was achieved at last. It was washed with HCl (0.1 mol/L) and distilled water (until pH $\approx$ 7) alternately before dried at 110 °C for 24 h.

Table 2
Specific surface area values of various absorbents.

Adsorbent	Raw material	Activating agent	Surface area (m^2/g)	Reference
MGB	Chicken feather	KOH	1838.86	Present study
Commercial AC	Wood	–	412.50	Present study
Biochar	Vine wood	KOH	13.40	Pouretedal and Sadegh, 2014
AC	Tyre	KOH	814.00	Acosta et al., 2016
AC	Char	N_2	776.46	Maneerung et al., 2016
Biochar	Macadamia nut shells	NaOH	1524.00	Martins et al., 2015
Biochar	Cork Powder Waste	KOH	>1300.00	Cardoso et al., 2008