Journal of Hazardous Materials 305 (2016) 156–163

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Preparation of ultrafine magnetic biochar and activated carbon for pharmaceutical adsorption and subsequent degradation by ball milling

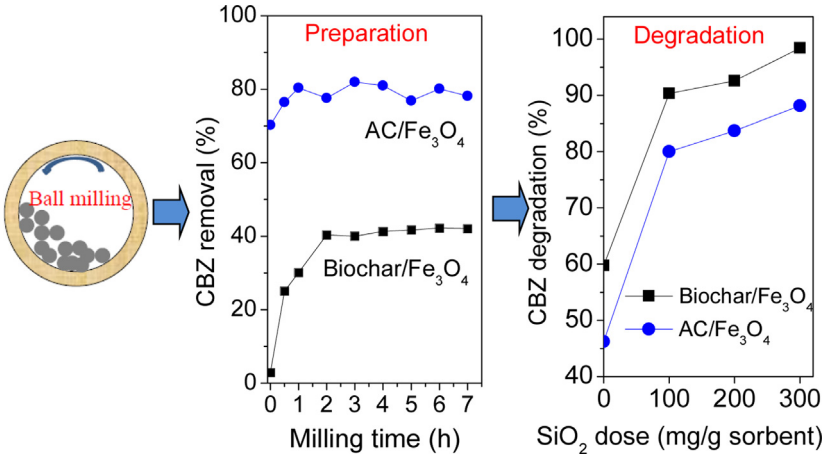
Danna Shan[a], Shubo Deng[a,*], Tianning Zhao[a], Bin Wang[a], Yujue Wang[a], Jun Huang[a], Gang Yu[a], Judy Winglee[b], Mark R. Wiesner[b]

[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China
[b] Department of Civil and Environmental Engineering, Duke University, P.O. Box 90287, Durham, NC 27708-0287, USA

## HIGHLIGHTS

- Ultrafine magnetic carbonaceous sorbents are successfully prepared by ball milling.
- Biochar/$Fe_3O_4$ exhibits fast and high sorption for carbamazepine and tetracycline.
- Ultrafine biochar/$Fe_3O_4$ and AC/$Fe_3O_4$ can be separated magnetically.
- Ball milling is effective for degradation of adsorbed CBZ/TC on the adsorbents.
- Addition of quartz sand improves the mechanochemical degradation of CBZ.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 23 July 2015
Received in revised form 27 October 2015
Accepted 23 November 2015
Available online 26 November 2015

*Keywords:*
Magnetic adsorbent
Ultrafine biochar
Activated carbon
Carbamazepine
Ball milling

## ABSTRACT

Ball milling was used to prepare two ultrafine magnetic biochar/$Fe_3O_4$ and activated carbon (AC)/$Fe_3O_4$ hybrid materials targeted for use in pharmaceutical removal by adsorption and mechanochemical degradation of pharmaceutical compounds. Both hybrid adsorbents prepared after 2 h milling exhibited high removal of carbamazepine (CBZ), and were easily separated magnetically. These adsorbents exhibited fast adsorption of CBZ and tetracycline (TC) in the initial 1 h. The biochar/$Fe_3O_4$ had a maximum adsorption capacity of 62.7 mg/g for CBZ and 94.2 mg/g for TC, while values obtained for AC/$Fe_3O_4$ were 135.1 mg/g for CBZ and 45.3 mg/g for TC respectively when data were fitted using the Langmuir expression. Solution pH values slightly affected the sorption of TC on the adsorbents, while CBZ sorption was almost pH-independent. The spent adsorbents with adsorbed CBZ and TC were milled to degrade the adsorbed pollutants. The adsorbed TC itself was over 97% degraded after 3 h of milling, while about half of adsorbed CBZ were remained. The addition of quartz sand was found to improve the mechanochemical degradation of CBZ on biochar/$Fe_3O_4$, and its degradation percent was up to 98.4% at the dose of 0.3 g quarts

* Corresponding author. Fax: +86 10 62794006.
*E-mail address:* dengshubo@tsinghua.edu.cn (S. Deng).

http://dx.doi.org/10.1016/j.jhazmat.2015.11.047
0304-3894/

sand/g adsorbent. This research provided an easy method to prepare ultrafine magnetic adsorbents for the effective removal of typical pharmaceuticals from water or wastewater and degrade them using ball milling.



## 1. Introduction

Carbonaceous materials such as activated carbon, biochar, carbon nanotubes, and graphene are widely used to remove pollutants from water or wastewater [1–3]. Activated carbon (AC) as a common adsorbent is suitable for the removal of the hydrophobic organic pollutants from water, but some macromolecular compounds such as humic acid diffuse to a limited extent into the micropores of AC, limiting the effectiveness of granular AC for these larger molecular species. Although powdered AC exhibits high adsorption loadings and rapid kinetics for organic pollutants, it must typically be separated in conjunction with several steps in conventional liquid–solid separation such as the coagulation, flocculation and sedimentation. Biochar has been considered as a promising adsorbent for different pollutants due to its low cost. Previous research has shown that biochar is an effective adsorbent for organic contaminants such as pharmaceuticals and personal care products (PPCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dyes [4–7]. Despite the versatility of biochar as an adsorbent, the commercial usage of biochar has been limited because its adsorption capacity is lower than that of AC and it is difficult to remove during the water treatment process as well. Biochar has less adsorption capacity because it is less porous and has less surface area for adsorption than AC [8].

To improve the separation properties of these carbonaceous adsorbents, researchers developed iron-enhanced composites that can be separated magnetically. Magnetic particles such as Fe, $Fe_2O_3$ and $Fe_3O_4$ are typically added to the adsorbents via either chemical co-precipitation or pyrolysis activation [5,9–11]. Although co-precipitation reaction is simple, it may decrease or block adsorbent pores, making some surfaces unavailable for adsorption [10]. While pyrolysis activation is effective, the reaction favors the formation of $Fe_2O_3$ which yields materials with relatively low magnetic properties [5].

High energy ball milling is another technique that can prepare ultrafine powders, and this technique has been shown to effectively produce magnetic materials [12–16]. Compared with conventional AC, submicron-sized (0.72 μm) AC prepared by ball milling exhibited higher sorption of bisphenol A and carbamazepine in drinking water [17]. For biomedical applications, Ramanujan et al. developed magnetic adsorbents for theophylline through milling the activated carbon with iron particles [12]. Ball milling can also be used to degrade chemical species. Mechanochemical degradation has been used to treat wastes such as aromatic compounds, halogenated compounds and pharmaceuticals [18–24]. Unlike traditional degradation methods which use oxidizing agents, milling utilizes the mechanical energy to activate chemical reactions, suggesting possible merit as an eco-friendly process [25]. However, the coupling of adsorption and subsequent mechanochemical degradation of contaminants has not been studied to date.

In this study, we used ball milling method to both prepare the ultrafine magnetic biochar/$Fe_3O_4$ and AC/$Fe_3O_4$ materials and to subsequently degrade pharmaceutical contaminants on spent adsorbents. To evaluate the sorption capacity of these two adsorbents, CBZ and TC, two of the most frequently detected pharmaceuticals in wastewater [26,27], were selected as target adsorbates. The magnetic hybrid adsorbents were optimized and characterized. The adsorption of CBZ and TC on the adsorbents was evaluated, and the degradation of the adsorbed pharmaceuticals by ball milling was also investigated.

## 2. Materials and methods

### 2.1. Materials

Coconut, pinenut and walnut shells were obtained from a local market in Beijing. Coal powder and coconut based granular activated carbon were purchased from Zhengzhou Yedao Environmental Protection Co. (China). The biochar and activated carbon were all crushed and sieved into the particle size of about 150–200 mesh (75–100 μm). Iron powder (Fe), ferric oxide (α-$Fe_2O_3$) and magnetite ($Fe_3O_4$) were purchased from Sinopharm Chemical Reagent Co., and milled for 2 h before use. The two typical pharmaceuticals including carbamazepine (CBZ, purity = 97%, water solubility = 121 mg/L; $pK_{a1}$ = 2.3, $pK_{a2}$ = 13.9; MW = 236) and tetracycline (TC, purity = 98%, water solubility = 170 mg/L; $pK_{a1}$ = 3.3, $pK_{a2}$ = 7.7, $pK_{a3}$ = 9.7 and $pK_{a4}$ = 12; MW = 444), were purchased from J & K Scientific Co. (Beijing, China). Other chemicals including potassium permanganate ($KMnO_4$) and quartz sand ($SiO_2$) were obtained from Beijing chemical Works. All solvents (methanol, acetic acid, hydrochloric acid, acetonitrile and formic acid) used in this study were HPLC grade (J.T. Baker Inc., USA). All chemical solutions were prepared in ultrapure water produced by a Milli-Q system (Millipore, USA).

### 2.2. Preparation of magnetic biochar and activated carbon

For biochar preparation, coconut, pinenut and walnut shells were first heated to 500 °C in a tubular furnace for 1.5 h under nitrogen atmosphere. The magnetic biochar and AC were obtained by ball milling in a planetary ball mill (Nanjing University Instrument Co., China) with stainless steel vials (80 mL) and balls (diameter = 5.60 mm, 120 g in each vial). The biochar (coconut, pinenut, walnut shells based or coal powder based biochar) and iron or iron oxides (Fe, α-$Fe_2O_3$ or $Fe_3O_4$) were first mixed at a mass ratio of 3:1 (total 3 g), and then the mixture was added into the vials. The ratio of the balls to the powdered mixture (biochar and iron or iron oxides) ($C_R$) was 40:1. The ball mill equipment was then operated at a speed of 550 rpm for 6 h in ambient air and the rotation direction altered every 0.5 h. The final magnetic materials including biochar/Fe, biochar/$Fe_2O_3$, biochar/$Fe_3O_4$, AC/Fe, AC/$Fe_2O_3$, and AC/$Fe_3O_4$ were obtained. The milling time was optimized in the range of 1–7 h for the preparation of magnetic biochar and AC.

### 2.3. Adsorbent characterization

Adsorbent particle size was characterized by a laser particle analyzer (Mastersizer 2000, UK). The microscopic features of the magnetic adsorbents were observed by the field emission scanning electron microscopy (FE-SEM, JEOL JSM-6301F, Japan) equipped with an energy-dispersive X-ray analyzer. The pore size distribution and specific surface area were determined by nitrogen adsorption at 77 K on a gas sorption analyzer (Autosorb iQ, Quantachrome Co., USA). The magnetic strength of the adsorbents was