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

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Abstract

Ball milling was used to prepare two ultrafine magnetic biochar/Fe₃O₄ and activated carbon (AC)/Fe₃O₄ hybrid materials targeted for use in pharmaceutical removal by adsorption and mechanochemical degradation of pharmaceutical compounds. Both hybrid adsorbents prepared after 2 hours 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 hour. The biochar/Fe₃O₄ had a maximum adsorption capacity of 62.7 mg/g for CBZ and 94.2 mg/g for TC, while values obtained for AC/Fe₃O₄ 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 hours 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/Fe₃O₄, and its degradation percent was up to 98.4% at the dose of 0.3 g quartz 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.

Keywords

Magnetic adsorbent; Ultrafine biochar; Activated carbon; Carbamazepine; 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)

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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 ($0.72\ \mu\text{m}$) 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 ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) were purchased from Sinopharm Chemical Reagent Co., and milled for 2 hours before use. The two typical pharmaceuticals including carbamazepine (CBZ, purity = 97%, water solubility = 121 mg/L; $\text{p}K_{\text{a}1} = 2.3$, $\text{p}K_{\text{a}2} = 13.9$; MW = 236) and tetracycline (TC, purity = 98%, water solubility = 170 mg/L; $\text{p}K_{\text{a}1} = 3.3$, $\text{p}K_{\text{a}2} = 7.7$, $\text{p}K_{\text{a}3} = 9.7$ and $\text{p}K_{\text{a}4} = 12$; 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 hours 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, $\alpha\text{-Fe}_2\text{O}_3$ 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 hours in ambient air and the rotation direction altered every 0.5 hour. 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 hours 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 analyser (Autosorb iQ, Quantachrome Co., USA). The magnetic strength of the adsorbents was measured by a vibrating sample magnetometer (VSM, Lakeshore 730T, USA). A zeta potential instrument (Delsa Nano C, Beckman Coulter, USA) was used to determine the surface electrical properties of the materials used.

2.4. Sorption experiments

In the screening and optimization of magnetic adsorbent preparation experiments, 20 mg of adsorbents was mixed with 100 mL of CBZ solution (pH = 6.0) in 250 mL conical flasks, and the flasks were then shaken at 170 rpm and 25°C for 48 hours in a shaker. The sorption behaviors of CBZ and TC on the biochar/Fe₃O₄ and AC/Fe₃O₄ were quantified in terms of sorption kinetics, sorption isotherm and pH effect experiments carried out in 250 mL flasks containing 100 mL of CBZ or TC solution, using a dose of biochar/Fe₃O₄ or AC/Fe₃O₄ of 0.2 g/L. All flasks were shaken at 170 rpm and 25°C. In the sorption kinetics and isotherm experiments, the initial solution pH values were adjusted to 6.0 before the adsorbents were added into the solution, and no pH adjustment was conducted in the sorption process since the pH values before and after the sorption experiments were similar (6.0±0.3). The initial concentrations of CBZ and TC were 30 mg/L in the kinetic and pH effect on sorption experiments, while their initial concentrations were set in the range of 5-60 mg/L in the sorption isotherm experiments. In the investigation of pH effect on CBZ and TC sorption, initial solution pH was adjusted to 4.0-9.0 using HCl or NaOH solution (0.1 mol/L), and no pH adjustment was conducted in the adsorption process.

2.5. Mechanochemical degradation experiments via ball milling

Adsorbents for ball milling degradation experiments were prepared by sorption studies of 1.0 g/L biochar/Fe₃O₄ or AC/Fe₃O₄ in 50mg/L CBZ or TC (pH=6) solutions for 48 hours. Spent adsorbents were magnetically collected from sorption experiments and dried at 50°C for 3 hours. The dried adsorbents were milled for different lengths of time with either no milling agent or with Fe₃O₄, Fe, KMnO₄ and quartz sand (SiO₂). The ball milling conditions were C_R (120:1), rotational speed of 550 rpm, and rotation direction was altered every 0.5 hour.

2.6. Measurement of CBZ, TC and their intermediates

To measure the concentration of CBZ and TC in solution after the sorption experiments, samples were taken from the solution and then filtered through a 0.22 µm nylon membrane. A UV-vis spectrophotometer (DR5000 Hach, USA) was used to determine the concentrations of CBZ at a maximum absorbance wavelength of 284nm and TC at a maximum absorbance wavelength of 276 nm.

In the degradation experiments, methanol and water solutions of 20% acetic acid and 1% hydrochloric acid were used to extract CBZ and TC, respectively. CBZ and TC were extracted from the milled adsorbents by sonicating a 0.2g/L mixture of the adsorbent and solvent for 0.5 hour. Afterwards, the samples were centrifuged at 3000 rpm for 15 min and filtered through a 0.22 µm nylon membrane. The concentrations of CBZ and TC in the extracts were analyzed by a high-performance liquid chromatography (HPLC, Ultimate 3000, DIONEX Co., USA) followed by a tandem mass spectrometer equipped with electrospray ionization (ESI-MS-MS, API3200, AB Sciex, USA). Data processing was performed with Analyst 1.5TM software package (Applied Biosystems, MA, USA).

To separate the intermediates of CBZ and TC, chromatographic separation was performed on a XBridge C18 column (3.0mm × 150mm, 3.5µm, Waters, USA). The column

temperature was 30°C for CBZ and 40°C for TC. The gradient elution with a flow rate of 0.4 mL/min was used to analyze the intermediates. The injection volume was 10 µL in a ChemStation data acquisition system. For CBZ detection, the mobile phase consisted of water (A) and methanol (B). For TC detection, the mobile phase consisted of water with 0.1% formic acid (A) and acetonitrile (B).

The mass spectrometer was operated using ESI source in positive ion mode. The ESI-MS-MS parameters, including declustering potential, entrance potential, collision energy, collision cell entrance potential, and collision cell exit potential were optimized before analysis. Multi-reaction monitoring (MRM) mode was applied to test the concentrations of residual CBZ and TC on the prepared adsorbents and full scan mode to explore the intermediates.

3. Results and discussion

3.1. Selection of biochar and magnetic materials

Four common precursors including coconut shell, pinenut shell, walnut shell and coal powder were used to prepare different biochar. Coconut shell based biochar exhibited the highest adsorbed amount of 89.6 mg/g for CBZ among the four biochars (Fig. 1a), and as a result, coconut shells were selected to prepare magnetic biochar and activated carbon in the following experiments. To produce the hybrid adsorbents with magnetic properties, Fe, Fe₂O₃ and Fe₃O₄ were used to prepare composites with biochar and activated carbon. The adsorbed amounts of CBZ on these adsorbents are shown in Fig. 1b. Composites prepared with Fe₃O₄ had the highest adsorption of CBZ for both the biochar and the activated carbon, and Fe₃O₄ was selected to prepare the magnetic adsorbents in the following study. Another benefit to use Fe₃O₄ composites is that Fe₃O₄ has relatively high magnetism (Fe ~ 215 emu/g, Fe₃O₄ ~ 80 emu/g and α-Fe₂O₃ < 0.2 emu/g) [28,29], so magnetic biochar/Fe₃O₄ and AC/Fe₃O₄ can be easily separated from solution.

3.2. Effect of ball milling time on adsorbent size and adsorption capacity

Before ball-milling the hybrid adsorbents, biochar, AC, and Fe₃O₄ were milled for 7 hours, and their median diameters (D50) decreased significantly within initial 1 hour, and reached about 0.2 µm after 2 hours of milling (Fig. S1). Similarly, the D50 values of biochar/Fe₃O₄ and AC/Fe₃O₄ after 2 hours of milling were also about 0.2 µm, and kept almost constant with increasing milling time (Fig. 2).

The effect of the mill time length on the adsorption of CBZ is presented in Fig. 3. The mill time length did not influence the removal of CBZ on the AC/Fe₃O₄. However, longer mill times increased the biochar/Fe₃O₄ removal of CBZ from 2.9% (no milling) to about 40.4% (2 hours of milling). Since the CBZ molecules were mainly adsorbed in the micropores of AC, ball milling had a little effect on the sorption of CBZ on the AC/Fe₃O₄. In contrast, biochar does not have many micropores, and CBZ sorption on biochar is hypothesized to primarily take place on the biochar surface. Since ball milling significantly decreased the size of the biochar/Fe₃O₄ composite and increased the surface area for adsorption, resulting in the CBZ removal increased by about 37%. Since CBZ removal plateaued after 2 hours of

milling, a mill time length of 2 hours was used to prepare the biochar/Fe₃O₄ and AC/Fe₃O₄ in the following experiments. The magnetism of the biochar/Fe₃O₄ and AC/Fe₃O₄ adsorbents was tested show that the adsorbents can be easily removed from solution. The magnetic adsorbents exhibited a saturation magnetization (Ms) of 19.0 emu/g for biochar/Fe₃O₄ and 20.8 emu/g for AC/Fe₃O₄ (Fig. S2), and both adsorbents were easily separated from solution with a permanent magnet after the sorption process (Fig. 3, inset).

To study the individual contributions of Fe₃O₄, biochar and AC to CBZ removal, these materials were milled under the same conditions as the biochar/Fe₃O₄ and AC/Fe₃O₄ composites and used to remove CBZ from an aqueous solution (Fig. S3). Separate sorption experiments of 50mg/L Fe₃O₄, 150 mg/L biochar, 150 mg/L AC, 200 mg/L biochar/Fe₃O₄ and 200 mg/L AC/Fe₃O₄ were conducted. The removal of CBZ by biochar/Fe₃O₄ (36.9%) was lower than that by biochar (46.8%), but higher than Fe₃O₄ (13.9%), indicating that biochar played a dominant role in the sorption of CBZ on the biochar/Fe₃O₄. The lower removal of CBZ by the biochar/Fe₃O₄ composite may be due to the presence of Fe₃O₄ on the surface of the composite. Similarly, the AC also had more contributions to CBZ removal than Fe₃O₄, but the removal percent of CBZ by AC/Fe₃O₄ was lower than that by AC, possibly due to the occupation of Fe₃O₄ on AC surfaces or pores.

3.3. Characterization of biochar/Fe₃O₄ and AC/Fe₃O₄ adsorbents

SEM and SEM-EDS were used to characterize the adsorbent particle size and the distribution of Fe₃O₄ (Fig. 4). The images show that the median diameters of the hybrid adsorbents are around 200 nm (Fig. 2) and that these particles form micron-sized aggregates (Fig. 4a and b). To evaluate the distribution of Fe₃O₄ in the composites, SEM-EDS mapping was employed to characterize the biochar/Fe₃O₄ and AC/Fe₃O₄. As shown in Fig. 4c and d, nano-particles of Fe₃O₄ (white area) were dispersed fairly homogeneously into the biochar or activated carbon. Since the mass ratio of biochar/AC:Fe₃O₄ was 3:1 and Fe₃O₄ density was higher than carbonaceous materials, Fe₃O₄ is hypothesized to be dispersed on the surface of biochar or activated carbon, making the hybrid adsorbents easy separation by a magnet.

The pore size distribution and specific surface area of biochar, AC, biochar/Fe₃O₄, and AC/Fe₃O₄ after 2 hours of milling are shown in Fig. 5 and Table 1. The specific surface area of biochar/Fe₃O₄ increased to 365 m²/g, which is much higher than that of the pristine biochar, while the particles size of biochar/Fe₃O₄ dramatically decreased from about 84 μm to 210 nm (Fig. S1 and Fig. 2). It is notable that the total pore volume of biochar/Fe₃O₄ increased remarkably, and about 0.42 cm³/g of pore volume was attributed to the pores above 2 nm, indicating that some Fe₃O₄ particles were crushed into the biochar and produced more pores. In contrast, the AC/Fe₃O₄ obtained after 2 hours of milling had lower specific surface area and pore volume than the pristine AC, suggesting that some pores in AC may be blocked by the nano Fe₃O₄ produced in the milling process. Since the inner pores in AC are responsible for CBZ sorption, pore blockages by Fe₃O₄ could significantly decrease the adsorption capacity.

3.4. Sorption kinetics and isotherms of CBZ and TC

The sorption kinetics of CBZ and TC on the biochar/Fe₃O₄ and AC/Fe₃O₄ are illustrated in Fig. 6a. Both adsorbents exhibited fast adsorption of CBZ and TC in the first hour. The adsorption of CBZ on biochar/Fe₃O₄ was very fast, and the sorption equilibrium was almost achieved within 2 hours while the sorption equilibrium took almost 10 hours with AC/Fe₃O₄. In contrast, the sorption equilibrium of TC on the biochar/Fe₃O₄ was reached by approximately 20 hours, and the equilibrium on the AC/Fe₃O₄ was not obtained within 36 hours. The longer sorption equilibration times for TC with the adsorbents are probably due to the large molecular size of TC. The ultrafine biochar/Fe₃O₄ and AC/Fe₃O₄ had faster adsorption of CBZ and TC than traditional porous adsorbents [5,30-32]. The faster adsorption of the CBZ and TC on the biochar/Fe₃O₄ surface is due to the sorption of the contaminant on the surface of the adsorbent rather than in the micropores.

The sorption isotherms of CBZ and TC on the biochar/Fe₃O₄ and AC/Fe₃O₄ are shown in Fig. 6b, and the widely used Langmuir and Freundlich models were adopted to describe the experimental data. The fitting curves and model parameters are presented in Fig. 6b and Table S1. According to the correlation efficient (R^2) obtained, the adsorption data of CBZ and TC on AC/Fe₃O₄ were fitted better by the Langmuir model, while the Freundlich model described the adsorption of CBZ and TC on the biochar/Fe₃O₄ better, which may be related to their adsorption on both magnetite and carbonaceous materials. It has been reported that the magnetite nanoparticles can adsorb chlorotetracycline (CTC) through the formation of Fe-O bonds between CTC and Fe atoms [33]. Researchers have also shown that oxytetracycline (OTC) can bond with Fe₃O₄ through -CONH₂, -OH and -N(CH₃)₂ groups [34]. These reactive amide and hydroxyl functional groups are also present in TC and CBZ and could be causing surface complexation with Fe₃O₄. The carbonaceous materials such as activated carbon can also adsorb TC and CBZ through hydrophobic interaction and π - π interaction [35-36]. The complex adsorption interactions of TC and CBZ on the hybrid biochar/Fe₃O₄ and AC/Fe₃O₄ made the conventional models ineffective for all data.

According to the Langmuir fitting, the maximum sorption capacities (q_m) of CBZ on the biochar/Fe₃O₄ and AC/Fe₃O₄ were 62.7 and 135.1 mg/g, respectively, while the q_m values of TC on the biochar/Fe₃O₄ and AC/Fe₃O₄ were 94.2 and 45.3 mg/g, respectively. Since CBZ (0.9 nm) has a smaller molecular diameter than TC (1.4 nm), CBZ molecules diffuse more easily into the porous AC, resulting in the higher q_m on the AC/Fe₃O₄ than on the biochar/Fe₃O₄. For the larger TC, the biochar/Fe₃O₄ had higher q_m value than AC/Fe₃O₄. It is clear that the biochar/Fe₃O₄ obtained by ball milling was favorable for the removal of macromolecular pharmaceuticals, while the AC/Fe₃O₄ was suitable for the removal of small molecules.

3.5. Effect of solution pH on CBZ and TC sorption

The effect of solution pH on the sorption of CBZ and TC by the magnetic adsorbents was also studied (Fig. 7a). The percentage of CBZ removed by the two hybrid adsorbents was consistent throughout a pH range of 4.0-9.0, and the percentage of TC removed decreased slightly as the solution pH increased from 4.0 to 9.0. The zeta potentials of biochar, AC, biochar/Fe₃O₄ and AC/Fe₃O₄ were negative at pH 4.0-9.0 (Fig. 7b), and they decreased with

increasing solution pH. The stable removal of CBZ through the pH range of 4-9 was expected since CBZ molecules have a neutral charge within this range (pK_a values of 2.3 and 13.9 for the $-\text{CONH}_2$ group) [37-39], and no electrostatic interactions were expected between the CBZ and the negatively charged adsorbents. Since TC was expected to have a negative charge (pK_a values of 3.3, 7.7, 9.7 and 12 [40]), electrostatic repulsion of the adsorbents with anionic TC may have caused the reduction in sorption of TC at higher pHs (Fig. 7a). Interestingly, the sorption of TC to positively charged Fe_3O_4 [33] was tested separately, and the TC adsorption decreased at higher pHs despite the predicted electrostatic attraction. Despite slight changes in sorption capacity for TC, the solution pH generally had little effect on the sorption of CBZ and TC for either of the magnetic adsorbents, and the adsorbents had relatively high sorption capacity for CBZ and TC in a wide range of pH values.

3.6. Degradation of adsorbed CBZ and TC via ball milling

Fig. 8 shows the percent degradation of CBZ and TC adsorbed on the biochar/ Fe_3O_4 and AC/ Fe_3O_4 after ball milling for different periods of time. The breakdown of CBZ progressed slowly during the degradation test, and by the end of the 6 hour test, 59.7% of the CBZ on the biochar/ Fe_3O_4 and 46.2% of the CBZ on the AC/ Fe_3O_4 had been degraded. The TC was broken down more quickly, and about 99% of the TC on both adsorbents had been degraded within 3 hours. HPLC-MS/MS analysis (Fig. S4) was conducted to measure the concentration of TC intermediates as the degradation occurred, but the TC intermediates were not detected since the concentration of TC was very low. The degradation of CBZ and TC was greater on the biochar/ Fe_3O_4 adsorbent than the AC/ Fe_3O_4 adsorbent. This response is attributed to the adsorption of the CBZ and TC on the surface of biochar rather than in the microporous of the AC since ball milling has been shown to be more effective at degrading compounds at the adsorbent surface. TC was also better degraded by ball milling than CBZ because the large molecular diameter of TC molecules prevented the compound from diffusing into the adsorbent micropores. The smaller CBZ particles were able to diffuse into the adsorbent micropores, which reduced their exposure to the ball milling.

Ball milling was very effective for the degradation of TC on the adsorbents, but considerably less effective in degrading adsorbed CBZ. To increase the degradation efficiency, different milling reagents including Fe_3O_4 , Fe, KMnO_4 , and SiO_2 were added in the ball milling process. The percent of CBZ degraded by milling with 300mg additive/g on the biochar/ Fe_3O_4 is shown in Fig. S5. It can be seen that KMnO_4 and quartz sand were the most effective additives for the enhanced degradation of CBZ. Since quartz sand is more cost-effective, it was selected for use in the following experiments. Adding quartz sand to the ball milling increased the degradation of CBZ on both biochar/ Fe_3O_4 and AC/ Fe_3O_4 to 98.4% and 88.2% respectively (Fig. 9). The enhanced degradation by the addition of quartz sand is due to both the energy of collision and the friction between Fe_3O_4 and quartz sand and possibly due to free radicals produced on quartz sand surface as well [41].

The degradation of the CBZ during the quartz sand ball milling was analyzed by tracking the CBZ degradation intermediates using HPLC-MS/MS. The concentrations of the five main intermediates (A, B, C, D and E) are presented in Fig. 10, and the spectra with their peaks

are included in Fig. S6. The concentration of CBZ decreased with increasing milling time, and about 2.5% of CBZ was remained after 3 hours of milling. The concentration of intermediate A reached a maximum after 2 hours of milling while the maximum concentrations of intermediates B, C, D and E were found at 3 hours. After 6 hours of milling, the CBZ was almost completely degraded, and intermediates A, B, and C were present at less than 2%, while the intermediates D and E were present at 9.1% and 11.6% respectively. From this work we have shown that after 6 hours of ball milling, the spent magnetic biochar/Fe₃O₄ should be relatively environmentally benign.

4. Conclusions

Ultrafine magnetic biochar/Fe₃O₄ and AC/Fe₃O₄ were successfully prepared by simple ball milling of Fe₃O₄ with biochar and AC. The resulting hybrid contained Fe₃O₄ particles that were uniformly dispersed throughout the carbonaceous matrix, yielding adsorbents approximately 200 nm in mean diameter after 2 hours of milling. The biochar/Fe₃O₄ and AC/Fe₃O₄ adsorbents were effective for CBZ and TC removal from aqueous solution, and can be separated magnetically. The biochar/Fe₃O₄ had the fast and high adsorption for CBZ and TC because the adsorption mainly occurred on the adsorbent surfaces, avoiding the slow diffusion of large molecules in porous materials. Moreover, the adsorbed CBZ and TC on the surface of biochar/Fe₃O₄ was more easily degraded by mechanochemical ball milling than the CBZ and TC in the AC/Fe₃O₄. After 3 hours of ball milling, the TC adsorbed on the biochar/Fe₃O₄ and AC/Fe₃O₄ was degraded by 99% and 97% respectively. Ball-milling was less effective for the degradation of CBZ adsorbed on the biochar/Fe₃O₄ and AC/Fe₃O₄, but CBZ degradation was improved to 98.4% and 88.2% respectively with the addition of 300 mg SiO₂/g adsorbent. This study indicates that ball milling is not only a simple and economical method to prepare effective magnetic adsorbents for pharmaceutical removal from water, but also an effective technique to degrade the adsorbed pollutants on the spent adsorbents, reducing their environmental risk.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Sorption of CBZ on different biochars (a) and magnetic carbonaceous adsorbents (b)

Fig. 2. Particle sizes of biochar/Fe₃O₄ and AC/Fe₃O₄ at different milling time

Fig. 3. Effect of milling time on the sorption of CBZ on biochar/Fe₃O₄ and AC/Fe₃O₄ (inset plot showing the magnetic separation biochar/Fe₃O₄ and AC/Fe₃O₄ after CBZ sorption)

Fig. 4. SEM images of biochar/Fe₃O₄ (a) and AC/Fe₃O₄ (b) after 2 h milling as well as Fe₃O₄ distribution (bright image) in biochar/Fe₃O₄ (c) and AC/Fe₃O₄ (d)

Fig. 5. Pore size distribution of biochar, biochar/Fe₃O₄, AC and AC/Fe₃O₄ in the range of 1.1 nm - 2.1 nm (a) and 2.2 nm - 35.9 nm (b) ($dV(D)$: the derivative of pore volume (V) with respect to pore size (D))

Fig. 6. Sorption kinetics (a) and isotherms (b) of CBZ and TC on the biochar/Fe₃O₄ and AC/Fe₃O₄ (q_e : adsorbed amount at equilibrium; C_e : equilibrium concentration)

Fig. 7. Effect of solution pH on the sorption of CBZ and TC on biochar/Fe₃O₄ and AC/Fe₃O₄ (a), and zeta potentials of biochar, AC, biochar/Fe₃O₄ and AC/Fe₃O₄ (b)

Fig. 8. Degradation of CBZ (a) and TC (b) adsorbed on biochar/ Fe_3O_4 and AC/ Fe_3O_4 after ball milling for different time

Fig. 9. Effect of quartz sand dose on the degradation of CBZ on biochar/Fe₃O₄ and AC/Fe₃O₄ after 6 h ball milling

Fig. 10. Change of CBZ and its intermediates after milling of the CBZ adsorbed biochar/ Fe_3O_4 with quartz sand for different time

Table 1
Surface area and pore volume of biochar, biochar/Fe₃O₄, AC and AC/Fe₃O₄

Sample	Specific surface area (m ² /g) ^a	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g) ^b
Biochar	30.9	0.042	0.030
Biochar/Fe ₃ O ₄	365	0.54	0.12
AC	994	0.45	0.35
AC/Fe ₃ O ₄	486	0.38	0.17

^aThe specific surface area was calculated by the BET method.

^bThe pore volume was calculated by the DFT method.