Magnetic biochar combining adsorption and separation recycle for removal of chromium in aqueous solution
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ABSTRACT
Biochar has been developed in recent years for the removal of contaminants such as Cr (VI) in water. The enhancement of the adsorption capacity of biochar and its recyclable use are still challenges. In this study, magnetic biochar derived from corncobs and peanut hulls was synthesized under different pyrolysis temperatures after pretreating the biomass with a low concentration of 0.5 M FeCl₃ solution. The morphology, specific surface area, saturation magnetization and Fourier transform infrared spectroscopy (FT-IR) spectra were characterized for biochar. The magnetic biochar performed well in combining adsorption and separation recycle for the removal of Cr (VI) in water. The Cr (VI) adsorbance of the biochar was increased with the increase in pyrolysis temperature, and the magnetic biochar derived from corncobs showed better performance for both magnetization and removal of Cr (VI) than that from peanut hulls. The Langmuir model was used for the isothermal adsorption and the maximum Cr (VI) adsorption capacity of corncob magnetic biochar pyrolyzed at 650 °C reached 61.97 mg/g. An alkaline solution (0.1 M NaOH) favored the desorption of Cr (VI) from the magnetic biochar, and the removal of Cr (VI) still remained around 77.6% after four cycles of adsorption-desorption. The results showed that corncob derived magnetic biochar is a potentially efficient and recoverable adsorbent for remediation of heavy metals in water.

Key words | adsorption, biochar, hexavalent chromium, magnetic separation, recycle

INTRODUCTION
Chromium is a heavy metal widely used in the leather, electroplating and dyeing industries (Ghosh 2009). It has been reported that the concentration of Cr (VI) in wastewater produced by many industries is mainly from 0.1 to 200 mg/L, and some were estimated to be even more than 3,000 mg/L (Owlad et al. 2009; Wang et al. 2014). Because of the improper discharge of wastes, the amount of chromium spread in the water and soils is threatening the ecological environment and human health (Naz et al. 2016). Chromium mainly exists in the form of trivalent Cr (III) and hexavalent Cr (VI), and Cr (VI) is generally considered to be highly soluble, active, toxic and bioavailable (Qi et al. 2015; Zhang et al. 2015). Cr (VI) is a powerful epithelial irritant and a confirmed human carcinogen, and is also toxic to many organisms (Kotas & Stasicka 2000). Thus, many kinds of adsorbents have been developed to remove Cr (VI), such as active carbon, biomass, clay, polymeric resins, biopolymers, etc. (Kimbrough et al. 1999; Kalidhasan et al. 2016; Mohan & Pittman 2006; Sud et al. 2008). In recent years, biochar has been successfully used for the removal of contaminants, including arsenic, lead, cadmium, sulfonamides, etc. (Mohan et al. 2007; Zhang et al. 2013a; Agrafioti et al. 2014; Kumari et al. 2014). It was also introduced for Cr (VI) remediation in water (Wang et al. 2014; Han et al. 2016).

Biochar is a carbon-rich solid material that is produced by pyrolysis of biomass under high temperature and oxygen-limited conditions (Lehmann et al. 2006). The raw material of the feedstock is low-cost and environment-friendly, and biochar is attractive as an efficient adsorbent with its large surface area, powerful ion exchange ability and abundant functional groups (Lehmann et al. 2008; Beesley & Marmiroli 2011). However, we have to face the challenges of the enhancement of the adsorption capacity of biochar and its recyclable use (Chen et al. 2011; Zhang et al. 2013b; Wang et al. 2014; Han et al. 2016).

Magnetic separation has been considered as a recovery and pollution-control process for wastewater treatment, separation of mining wastes and purification of drinking
water (Ponder et al. 2000; Wu & Qu 2005). Magnetic separation processes for ferromagnetic materials or ferrous particles have been used extensively in the past years (Ebner et al. 1999; Svoboda & Fujita 2003; Luo & Nguyen 2017). The contaminants in aqueous solution were adsorbed by feasible sorbents and then removed using magnetic separation, which was considered to have a low energy cost and to be economic (Terashima et al. 1986; Hu et al. 2007; Li et al. 2010).

Considering iron oxide, like maghemite (γ-Fe₂O₃), is a good adsorbent (Wang & Lo 2009) and the stable magnetic property favors the recycling collection after use, magnetic biochar is the ideal economic composite, combining iron oxides and biomass for the removal of pollutants in water. For examples, Chen et al. (2011) immersed biomass of orange peel in Fe (II) and Fe (III) solutions with NaOH added and then pyrolyzed it to get a magnetic biochar for adsorbing naphthalene, p-nitrotoluene and phosphate simultaneously. A synthesized magnetic biochar from oak bark by alkaline precipitation of Fe (II)/Fe (III) showed enhanced adsorption of Pb (30.20 mg/g), Cd (7.40 mg/g) (Mohan et al. 2014a), and corn stover magnetic biochar removed 4.11 mg/g fluoride (Mohan et al. 2014b). The magnetic biochar from eucalyptus leaf residue also effectively removed heavy metals of Cr (>97%) and coexisting Ni (100%) and Cu (100%) in artificial and actual electroplating wastewater, in which the Cr (VI) concentration was ~200 mg/L (Wang et al. 2014). Wang et al. (2015) treated biomass of pine wood with natural mineral hematite and the adsorption of arsenic by the produced magnetic biochar reached 428.7 mg/kg, which was almost twice that of unmodified biochar. Zhang et al. (2015b) proposed a simple one-step synthesis of magnetic biochar using directly pyrolysis of cottonwood pretreated with 2 M FeCl₃·6H₂O solution, and increased the adsorption capacity of arsenic to 3,147 mg/kg.

In our recent study (Han et al. 2016), magnetic biochar derived from peanut hulls was prepared in a similar way to Zhang et al. (2015b). The removal of Cr (VI) was 1–2 orders of magnitude higher compared to intrinsic peanut hull biochar (Han et al. 2016). However, the regeneration and reuse after several cycles of this composite are not investigated. In addition, direct pyrolysis of biomass pretreated with 2 M FeCl₃ would cause a more acid atmosphere, which might be a potential risk of corrosion to the apparatus, and it was necessary to reduce the concentration of the FeCl₃ solution. Furthermore, different feedstock affects the reactivity of biochar, and the corncob biomass was found to be more active (Hao et al. 2013), but the adsorption performance of corncob magnetic biochar has not been explored before.

Accordingly, we focused on the following issues in the present study: (1) magnetic biochar derived from corncobs and peanut hulls was synthesized after using a low concentration of 0.5 M FeCl₃ solution to pretreat the biomass; (2) the adsorbance of Cr (VI) on magnetic biochar under different pyrolysis temperature was compared; (3) thermodynamic adsorption-desorption experiments were conducted to evaluate the adsorption capacity and recycle efficiency of magnetic biochar.

### MATERIALS AND METHODS

#### Chemicals and materials

The raw materials of corncobs and peanut hulls were obtained from an agricultural field in Tangshan, Hebei province in Northern China. Potassium dichromate (K₂Cr₂O₇), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and acetone were purchased from Sinpharm Chemical Reagent Co. Ferric chloride hexahydrate (FeCl₃·6H₂O) and 1,5-diphenylcarbazide were obtained from Aladdin Chemical Reagent Co. and Aesar Alfa, respectively. All the chemicals were analytical grade and used without further purification, and solutions were prepared using deionized water (18.3 MΩ·cm).

#### Preparation of magnetic biochar

The biomass of corncobs or peanut hulls was washed with deionized water, dried in the oven at 80 °C, and ground into particles. Then, 10 g of biomass particles were immersed in 80 mL FeCl₃ solution (0.5 M), which was much lower than the 2 M of FeCl₃ used in our previous experiments (Han et al. 2016). The mixtures were stirred well for 0.5 h, and then dried in the oven at 70 °C for 0.5 h. As-received pretreated biomass was pyrolyzed in the oxygen-free furnace (Tianjin Zhong Huan Experimental Electric Furnace Co., Ltd) with 100 mL/min nitrogen flow at a heating rate of 5 °C min⁻¹. After maintaining the desired peak temperature (450, 550, 650 °C) for 2 hours and cooling down naturally, the produced magnetic biochar was rinsed several times with deionized water and then dried, crushed and sieved. The 0.5 ~ 1 mm sized samples were collected in a sealed bottle before use. For convenience, we used the symbols ‘CMBC-450 °C’ and ‘PMBC-450 °C’ to denote magnetic biochar derived from corncobs and peanut hulls pyrolyzed at 450 °C, respectively.
Characterization and analysis

The morphology and elements of the samples were characterized using field emission scanning electron microscopy (SEM) (Zeiss Merlin VP Compact) with an energy dispersive spectrometer (EDS). The saturation magnetization was determined with a superconducting quantum interference device magnetometer (MPMS SQUID-VSM). Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by FT-IR Spectrometer (PerkinElmer). The Brunauer–Emmett–Teller (BET) surface area was measured with a Quadrasorb Station 1 analyzer (Quantachrome Instruments). The Cr (VI) concentration was determined by UV-visible spectrophotometer (UV-1750 Shimadzu) at the wavelength of 540 nm, based on Cr (VI) chromogenic reaction with 1, 5-diphenylcarbazide in aqueous solution (APHA 1995).

Adsorption experiments

Adsorption batch experiments were conducted for removal of 40 mL Cr (VI) solution (200 mg/L) by 0.1 g magnetic biochar particles with the size of 0.5 mm in size, in 50 mL centrifuge tubes at 160 r/min and 25 °C. A little of the suspension was withdrawn at time intervals, filtered through a 0.22 μm membrane. The concentration of Cr (VI) in the filtrate was measured and the adsorption capacity of the biochar was calculated as follows:

\[ Q_e = \frac{C_0 - C_e}{M} \times V \]

where \( Q_e \) (mg/g) is the Cr (VI) adsorption capacity of the biochar when adsorption reaches equilibrium, \( C_0 \) (mg/L) is the initial concentration of Cr (VI) in solution, \( C_e \) (mg/L) is the equilibrium concentration of Cr (VI), \( V \) (L) is the volume of the solution, and \( M \) (g) is the mass of biochar.

An adsorption isotherm was carried out by adding 0.1 g magnetic biochar into 40 mL Cr (VI) solution at various initial concentrations (20, 50, 100, 200, 250, 300, 400 mg/L) at 160 r/min and 25 °C. After 7 days, when it reached equilibrium, the Cr (VI) adsorption on biochar was analyzed.

Desorption and recycle experiments

According to the preliminary research, the magnetic biochar derived from corncobs at 650 °C (CMBC-650 °C) showed a higher adsorption capacity than others (different biomass and pyrolysis temperature), and it was selected for desorption and recycle experiments. After adsorption in 40 mL Cr (VI) solution (100 mg/L) for 3 days, CMBC-650 °C was separated with a magnet, washed and dried, then put in 50 mL centrifuge tubes with 40 mL extract at 160 r/min and 25 °C for 2-day desorption. The leachate was measured and the performance of desorption was compared in 0.1 M NaOH, 0.1 M Na2CO3, 0.1 M HNO3, and DI water. Such circular adsorption-desorption of Cr (VI) on magnetic biochar was conducted four times to evaluate the recycle efficiency.

RESULTS AND DISCUSSION

Characterization of magnetic biochar

The morphology characteristics of corncob and peanut hull-derived magnetic biochar (CMBC and PMBC) prepared in different temperature conditions was shown in SEM images (Figure 1). Lots of pores were formed from the pyrolysis of the cell wall, resulting in the large specific area. And there were many inerratic particles (of regular shape) distributed on the surface of the biochar. The EDS spectra of CMBC-650 °C (Figure 2) indicated the presence of iron in particles, and the γ-Fe2O3 modified biochar was successfully synthesized, which is accordance with our previous study (Han et al. 2016). The iron oxide particles were micro-sized, and the higher temperature favors the more numerous and bigger crystals of γ-Fe2O3, comparing CMBC/PMBC-450 °C with CMBC/PMBC-650 °C (Figure 1).

It is worth noting that magnetization is a significant factor for the use of recyclable biochar (Wang et al. 2015). The magnetic hysteresis loop of CMBC pyrolyzed at 650, 550, and 450 °C is illustrated in Figure 3, indicating that the higher pyrolysis temperature contributes to the magnetic properties. According to the saturation magnetization of biochar (Table 1), the various feedstocks affected the magnetization, and CMBC-650 °C showed the better magnetic performance. It was due to that corncob particles could adsorb more ferric ion than peanut hulls in solution and then more γ-Fe2O3 was formed and loaded on CMBC at a higher pyrolysis temperature. Besides, the value of the saturation magnetization of PMBC-450 °C in this study is 11.27 emu/g, which is capable of separation by a magnet (Figure 3), suggesting a successful approach to prepare magnetic biochar in a low concentration of FeCl3 solution (0.5 M).

The functional groups of the biochar and magnetic biochar were determined by FT-IR and the spectra are...
shown in Figure 4. The broad peak around 3,444 cm\(^{-1}\) represented a bonded hydroxyl group. The peaks at 2,922 and 2,854 cm\(^{-1}\) were assigned to C-H stretching, and 1,630 and 1,398 cm\(^{-1}\) corresponded to C=O stretch of carboxylate. The peak of 1,082 cm\(^{-1}\) was the signal of C-O, while 788 cm\(^{-1}\) was an aromatic group. From Figure 4(a), the peaks of intrinsic biochar CBC were stronger and sharper than PBC, indicating corncob biochar was more active. As shown in Figure 4(b), magnetic biochar of CMBC-650 \(^\circ\)C was also measured by FT-IR before and after Cr (VI) adsorption. According to that, the Fe-O vibration peak was broad at
around 580 cm\(^{-1}\) \((\text{Chen et al. 2014})\), the small peak at 574 cm\(^{-1}\) was newly observed to be the Fe-O bond, suggesting the \(\gamma\)-Fe\(_2\)O\(_3\) particles were loaded on biochar. The weak signals of the C-H, C=O, and C-O peaks changed after Cr (VI) adsorption, indicating the associated working \((\text{Dong et al. 2014})\).

Cr (VI) adsorption experiments

The performance of Cr (VI) adsorption on different magnetic biochars is compared in Figure 5(a). The corncob derived magnetic biochar could adsorb more Cr (VI) than peanut hulls. The adsorption capacity increased with the rise in pyrolysis temperature, consistent with our previous study \((\text{Han et al. 2016})\). The higher temperature favored the crystallization and location of \(\gamma\)-Fe\(_2\)O\(_3\), and expanded the specific surface area from 19.33 m\(^2\)/g (CMBC-450 \(\degree\text{C}\)) to 211.95 m\(^2\)/g (CMBC-650 \(\degree\text{C}\)).

Isothermal adsorption was conducted on CMBC-650 \(\degree\text{C}\) as illustrated in Figure 5(b). The Langmuir and Freundlich equations were used as follows to fit the data.

\[
\text{Langmuir: } q_e = \frac{KQC_e}{1 + KC_e} \tag{2}
\]

\[
\text{Freundlich: } q_e = K_fC_e^{n} \tag{3}
\]

where \(q_e\) is the amount of Cr (VI) adsorbed at equilibrium (mg/g); \(K\) and \(K_f\) represent the Langmuir bonding term related to interaction energies (L/mg) and the Freundlich affinity coefficient (mg\(^{1-n}\)L\(^n\)/g), respectively; and \(C_e\) is the equilibrium solution concentration (mg/L) of the Cr (VI). Langmuir was the preferred model \((R^2 = 0.997)\), as listed in Table 2. The maximum Cr (VI) adsorption capacity \((Q)\) of CMBC-650 \(\degree\text{C}\) was 61.97 mg/g, and such high adsorbance suggested the low concentration of 0.5 M Fe\(^{3+}\) was a feasible choice for biomass pretreatment, considering the trade-off between consumption and efficiency.

Cr (VI) desorption and magnetic biochar recycle

Different desorption reagents, including 0.1 M NaOH, 0.1 M Na\(_2\)CO\(_3\), and DI water and 0.1 M HNO\(_3\), were used in the present study to confirm the Cr (VI) desorption efficiency of 44.6%, 20.0%, 1.1%, 3.9%, respectively, as shown in Figure 6(a). It indicated that alkalinity enhanced the Cr (VI) desorption, in accordance with the others \((\text{Dong et al. 2011})\). When the pH value was low, the iron oxide particles on the adsorbents were protonated and bonded well with the Cr (VI) anion by electrostatic attraction; while in an alkaline solution, OH\(^-\) was more competitive on the active sites of \(\gamma\)-Fe\(_2\)O\(_3\) particles, and some of the Cr (VI) was repulsive and released back to aqueous solution \((\text{Huang & Li 2009})\). Compared to the reported desorption efficiency (>90%) of Cr (VI) on iron oxides by 0.1 M NaOH \((\text{Hu et al. 2005})\), only 44% of the Cr (VI) was desorbed from magnetic biochar in present study. The same solution of 0.1 M NaOH could have more positive effects.
on Cr (VI) desorption from iron oxides. The possible reason was that the adsorbance of Cr (VI) on iron oxides and magnetic biochar was 19.2 mg/g \cite{Hu}, and 61.97 mg/g, respectively. On the other hand, the bonds of Cr (VI) with chemical functional groups on magnetic biochar were hard to break, and similar results were reported by Dong \cite{Dong} regarding a desorption efficiency of 47% of Cr (VI) on biochar.

The recycle of CMBC-650°C for Cr (VI) adsorption used 0.1 M NaOH as a desorption reagent, and the results are shown in Figure 6(b). The adsorption-desorption experiments were conducted for four cycles, and the adsorption capacity was 83.2%, 80.7%, 76.7%, 77.6%, respectively. After four cycles, the adsorption capacity of CMBC-650°C still kept a high level, attributed to the bonding sites of the magnetic biochar not being destroyed. Interestingly, the loaded Cr (VI) was not fully desorbed (44%), but the removal efficiency was not influenced, which was due to the initial concentration of 100 mg/L Cr (VI) being lower than its saturated adsorbance. The results showed that the corncob derived magnetic biochar is a preferred recyclable candidate for removal of Cr (VI) in aqueous solution.

**CONCLUSIONS**

The magnetic biochar derived from corncobs and peanut hulls was synthesized under different pyrolysis temperatures and used for the removal of Cr (VI) in water. The saturation magnetization of the magnetic biochar was measured, and the biochar was easily separated by a magnet, indicating the successful use of a low concentration of FeCl$_3$ solution (0.5 M) to pretreat the biomass. The magnetization and Cr (VI) adsorbance of biochar were increased with the increase in the pyrolysis temperature. And the magnetic biochar derived from corncobs showed better performance for both magnetization and removal of Cr (VI) than that from peanut hulls.
Thermodynamic adsorption indicated that Langmuir was the proper model to describe the isotherms, and the maximum Cr (VI) adsorption capacity of the corncob magnetic biochar pyrolyzed at 650°C was calculated as 61.97 mg/g. The adsorbed Cr (VI) on magnetic biochar could be desorbed in alkaline solution, and the removal of Cr (VI) still remained at around 77.6% after four cycles of adsorption-desorption using 0.1 M NaOH as a desorption reagent. Therefore, the corncob derived magnetic biochar pyrolyzed at relatively high temperature is a potential candidate for an efficient and recoverable adsorbent for remediation of heavy metal pollution.

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