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Chromium removal using magnetic biochar derived from herb-residue

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ABSTRACT

Magnetic biochar prepared with *Astragalus membranaceus* residue according to the Fe^{2+}/Fe^{3+} co-precipitation method was used as an adsorbent for Cr(VI) in aqueous solutions during batch experiments. Scanning electron microscopy and energy dispersive spectroscopy results proved that the adsorbent contained substantial amounts of iron oxide and confirmed that magnetic biochar was prepared. The surface area decreased from 111.48 to 59.34 m^2/g after the adsorbent became magnetic. X-ray diffraction analysis and X-ray photoelectron spectroscopy studies further demonstrated the existence of iron oxide in the magnetic biochar and showed that oxygen-containing groups decreased after adsorption. The maximum Cr(VI) adsorption occurred at pH 2 (23.85 ± 0.23 mg/g). The adsorption data were described well by a pseudo-second-order model and the Langmuir isotherm model ($R^2 = 0.994$ and $R^2 = 0.993$, respectively). The intraparticle diffusion model results indicated that intraparticle diffusion is not the only rate-limiting step. Together, these results proved that magnetic biochar could be separated easily from water with external magnetic fields and that such a material could be used as a cost-effective adsorbent in heavy metal removal applications.

1. Introduction

Heavy metals have caused serious environmental risks and received great attention in the past several decades, especially in industrialized areas within developing countries. Heavy metals are persistent in the environment and do not biodegrade; are highly toxic for humans and other organisms [1]. Heavy metals are present in the environment in a variety of forms such free metal ions or metal-ligand complexes, and many metals accumulate in soils and sediments; humans are exposed to metals through food, the water supply, and air, and some forms of metals (*e.g.*, methylmercury) are capable of bioaccumulation [2]. Among heavy metals, chromium (Cr) is one of the most abundant and toxic metals that can be found in Earth's crust [3]. Cr is widely used in modern industrial applications such as electroplating, photography, and leather tanning [4]. There are more than 10,000 electroplating factories and the total discharge of chromium-polluted wastewater from such factories amounts to 4000 million tons every year in China [5,6]. According to the drinking water quality standards in China and the World Health Organization (WHO) guidelines [7,8], Cr(VI) concentrations should not exceed 50 µg/l in drinking water. It is particularly important to control hexavalent chromium (Cr(VI)) pollution because of its toxicity, and the drinking water standards require that new low-cost treatment technologies be used. The conventional treatment methods include adsorption with activated carbon or resins, chemical precipitation, membrane separation, ultrafiltration, and electrocoagulation [9–12]. Recently, a new and interesting method for the immobilization of metals was described whereby biochar was used to control the pollution [13].

The International Biochar Initiative defines biochar as a solid carbon-rich material obtained from a thermo pyrolysis process applied to biomass (*e.g.*, animal litter, wood, solid waste, and crop residues) under limited oxygen conditions or anaerobic conditions above 250 °C [14]. Biochar has been widely used in many studies; for example, various types of biochar were used for the adsorption of metals from wastewater (*e.g.*, Cd, Cr, Pb, and As) [15–19], sludge-based and cow manure-based biochar were used for the adsorption of atrazine [20], and plant waste-based biochar was used for the adsorption of dye [21]. However, it is not easy to separate the biochar adsorbent powder from the water solution following treatments. Previous studies have shown that modifying the adsorbents by using magnetic nanoparticles can be a useful technique to

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separate the small particles out of the water by applying an external magnetic field. These magnetic methods can be more efficient and cost-effective than the traditional centrifugation or filtration methods, especially when working with solutions containing high amounts of suspended solids or with oil-contaminated water [22]. The magnetic materials that have been used to remove pollutants from water include magnetite zeolites, which were used for the adsorption of various heavy metals, magnetite nanotubes, which were used for Zn and Pb adsorption [23], and magnetic biochar and activated carbon, which were used for the removal of Cr, Cd, and Pb [24,25].

In the current study, a magnetic biochar was prepared from *Astragalus membranaceus* herb residue, and it was used for Cr(VI) removal. Herb residues were selected as the raw material for magnetic biochar preparation to investigate a potential cost reduction pathway for handling waste in the medicinal herb industry. In particular, several million tons of hazardous waste are generated after herbal extraction every year. Therefore, converting herb waste residues into biochar adsorbent could be a practical solution for dealing with the waste in an environmentally safe manner. Adsorption experiments were carried out in batch studies to investigate the adsorption isotherms and kinetics for Cr(VI) removal. The influence of pH was also studied.

2. Materials and methods

2.1. Adsorbent preparation and characterization

Residue from a traditional herb, *Astragalus mongholicus*, was subjected to pyrolysis at 400 °C for 3 h under oxygen-limited conditions. After pyrolysis, the residues were washed with 0.1 mol/l HCl to remove the suspended ash. Magnetic biochar was prepared as described by Wang [5]. A ferric and ferrous mixed solution was prepared from ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 30 g) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$, 16.7 g) with 900 ml deionized water (DI water). Then, the Fe^{3+}/Fe^{2+} mixed solution was dropped into the biochar suspension (30 g biochar with 300 ml of DI water). The pH of the mixed biochar/Fe^{3+}/Fe^{2+} suspension was adjusted to 10.5 with a NaOH solution (10 mol/l), and the material was then stirred vigorously at 25°C for 1 h under a nitrogen atmosphere. Next, the suspension was boiled for an additional hour, and then, it was aged overnight at room temperature. Finally, the material was filtered and rinsed with DI water and ethanol several times and then dried at 50–60 °C. The ultimate filtered material was referred as *Astragalus mongholicus* magnetic biochar (MBC).

Brunauer–Emmett–Teller surface area (S_{BET}) analyzes, X-ray diffraction (XRD) analyzes, magnetic analyzes, scanning electron microscope-energy dispersive spectrometer (SEM-EDS) analyzes, and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure of the magnetic biochar. The S_{BET} was evaluated according to the surface area and porosity analyzer (ASAP 2020, Micromeritics, Norcross, USA). The XRD measurements were performed with a Shimadzu XRD F-7000 by using Cu Kα (k = 1.54 Å) radiation at 40 kV and 30 mA; samples were scanned from 5–90 °C with a scanning speed of 6 °C/min. The magnetic properties were assessed by using a SQUID-VSM vibrating sample magnetometer (Quantum Design, San Diego, USA). Scanning electron microscopy (SEM, KYKY-2800B, China) and energy dispersive spectroscopy (EDS) with an Oxford INCA EDS detector were used to study the surface morphologies and EDS data of MBC. Surface analysis of MBC before and after Cr(VI) adsorption was conducted by using XPS (Thermo Fisher Scientific, K-Alpha, USA) with a monochromated Al Kα source and a spot size 400 µm in diameter.

Table 1
Textural properties of biochar and magnetic biochar (MBC).

	S_{BET} (m^2/g)	S_{mic} (m^2/g)[a]	V_T (cm^3/g)[b]	V_{mic} (cm^3/g)[c]
Biochar	111.48	50.43	0.095	0.0258
MBC	59.34	4.298	0.119	0.0019

[a] S_{mic}: micropore surface area calculated by using the t-plot method.
[b] V_T: total pore volume.
[c] V_{mic}: micropore volume calculated with the t-plot method.

2.2. Cr(VI) adsorption experiments

The Cr(VI) solution (500 mg/l) was prepared with potassium dichromate ($K_2Cr_2O_7$, guaranteed reagent). All the working solutions were prepared fresh daily and stored at 4 °C. The effect of pH on Cr(VI) adsorption onto MBC was evaluated over a pH range from 1 to 7, with an initial concentration of 50 mg/l Cr(VI) and 2 g/l MBC. The initial pH was adjusted by using HCl or NaOH solutions. For these tests, 0.05 g of MBC were added to 50 ml glass tubes containing 25 ml of the Cr(VI) solutions adjusted to different pH values. The kinetic experiments were also carried out with Cr(VI) concentrations of 50 mg/l and a MBC dosage of 2 g/l; for these tests, a constant pH of 2 was used. The solutions were filtered through 0.22 µm membrane filters at different time intervals. Adsorption isotherm experiments were conducted with 25 ml Cr(VI) solutions (5–500 mg/l) and 0.05 g MBC (2 g/l) at 25 °C. The concentration of Cr(VI) was analyzed with the 1,5-diphenylcarbazide method by using an ultraviolet (UV) spectrophotometer at 540 nm [26]. All experiments were performed in triplicate.

3. Results and discussion

3.1. MBC characterization

The S_{BET} was measured with N_2 adsorption at 77 K according to the BET method. The S_{BET} and textural properties are listed in Table 1. According to the BET results, the S_{BET} of MBC decreased from 111.48 to 59.34 m^2/g after magnetic modification. A decrease in S_{BET} of MBC versus unmodified biochar was also reported by Wang [5], and this was due to the iron oxide that formed on the biochar surface.

Fig. 1 shows the SEM images and EDS results for the biochar. The SEM micrographs of biochar (Fig. 1A) clearly demonstrated that porous materials are present in the biochar while the MBC surface is blocked. The EDS and magnetic analysis of MBC (Figs. 1C and 2) showed that the MBC contained substantial amounts of iron oxide, which likely consisted of iron oxide particles that formed on the surface of the MBC [5].

In order to study the structure and phase composition characteristics of MBC, XRD analyzes were carried out, and the XRD patterns of MBC are shown in Fig. 3. The sharp iron oxide peaks suggest the presence of crystallinity in the MBC phases. The peaks at 30.16 (220), 35.5 (311), 43.16 (400), and 62.78 (531) were assigned to Fe_3O_4 (magnetite, PDF number 01-019-0629) in MBC, and these corresponded to the four indexed (220), (311), (400), and (531) planes of magnetite. The peak at 57.12 was also assigned to Fe_3O_4 (magnetite, PDF number 01-088-0315). The peaks at 27.9 (205), 43.3 (012), and 50.1 (2112) were assigned to iron oxide, Fe_2O_3 (maghemite-Q, PDF number 01-025-1402) in MBC. These results demonstrated the existence of iron oxide in the magnetic biochar and confirmed that magnetic biochar was prepared.

Binding energy of iron, oxygen, and carbon was studied with XPS analyzes. The XPS spectra of Fe, C, and O are shown in Fig. 4. The Fe $2p_{3/2}$ functional groups were characterized according to previously published studies, and the results in this study were consistent with those in the former studies [27,28]. The values

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