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Removal of aqueous Cr(VI) by a magnetic biochar derived from *Melia azedarach* wood

Xin Zhang[a,b], Lei Lv[d], Yingzhi Qin[a], Min Xu[a], Xianbin Jia[c], Zhihua Chen[a,*]

[a] School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Xinxiang 453007, China
[b] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, China
[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China
[d] Sinosteel Wuhan Safety & Environmental Protection Research Institute Co., Ltd., Wuhan No.1244, Heping Road, Qingshan District, Wuhan 430081, China

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ABSTRACT

Magnetic biochar (MMABC) prepared from *Melia azedarach* wood was used for aqueous Cr(VI) removal. MMABC was a mesoporous material with S_{BET} 5.219 m^2/g and superparamagnetic magnetization 17.3 emu/g contributed by the contained Fe_3O_4. The MMABC showed higher removal efficiency (99.8%) than biochar under conditions of dosage 5 g/L, pH = 3.0, and Cr(VI) concentration 10 mg/L. The saturation magnetization (16.1emg/g) of MMABC still remained after adsorption. According to FTIR and Raman results, the benzene-ring adjacent carbonyl did not showed obvious positive effects on Cr(VI) removal. A potential mechanism and corresponding apparent kinetic model indicated the Cr(VI) removal process by MMABC followed adsorption-reduction-adsorption steps. Cr(VI) was firstly adsorbed on surface and subsequently reduced to Cr(III), which was further adsorbed on MMABC surface. *Langmuir* isotherm (with maximal adsorption capacity of 25.27 mg/g) and pseudo second-order kinetic model were suitable for adsorption step.

1. Introduction

Hexavalent chromium (Cr(VI)) is a wastewater contaminant that mainly discharge from industrial procedures of chromium mining & smelting, metal processing, dyeing, manufactures of chromium salt, electroplating, and leather, etc. (Selvi et al., 2001). Cr(VI) is a high toxic, carcinogenic, mutagenic and teratogenic agent to living organisms (Selvi et al., 2001). For many decades, great efforts have been made to remove effluents' Cr(VI) by means of adsorption, chemical precipitation, electrocoagulation, ion exchange, membrane separation, reduction and biosorption methods, etc. (Alvarado et al., 2013; Duan et al., 2017b; Owlad et al., 2009). Adsorption is considered as a simple, high-efficient (Demirbas, 2008), and low-cost (Mohan et al., 2014) method benefits from various adsorbents that can be derived from solid waste with "dealing with waste by waste" significances.

Biochar is an activated-carbon like adsorbent (Chen et al., 2015a; Liu et al., 2015) commonly derived (or by-produced) from biomass pyrolysis that has poly-generated potentials on energy recoveries (biofuels) (Chen et al., 2014; Chen et al., 2016). Different kinds of biomass were pyrolyzed to biochar, which had been demonstrated appropriate to adsorb heavy metal ion and organic pollutant (Inyang et al., 2016; Mohan et al., 2014; Qiu et al., 2009). The functionalization (or modification) of biochar is attractive to enhance adsorption capacities of contaminants. Many functionalization ways such as surface decoration (Liu et al., 2015; Yan et al., 2015), inorganics compound (Zhang et al., 2013a; Zhang et al., 2013b), molecules grafting (Shi et al., 2017), magnetization (Chen et al., 2011; Han et al., 2016; Wang et al., 2015a; Wang et al., 2015b; Yap et al., 2017) etc. had been reported. Among these functionalization ways, magnetization is fascinating since corresponding products (magnetic biochar, MBC) show strong paramagnetism and high saturation properties, which give advantages on high efficient solid-liquid separations (avoiding slurry production during water treatment plants running), as well as contaminant adsorb capacities improvements (Essandoh et al., 2017; Wang et al., 2015b; Zhang et al., 2013a).

Many biochar derived from different biomass had been used for aqueous Cr(VI) adsorptions (Chen et al., 2015a; Deveci & Kar, 2013; Han et al., 2016; Zhou et al., 2016). It was believed that Cr(VI) adsorption was influenced by effluent's pH value, which dominated the rate control steps of adsorption, Cr(VI) ionization, and Cr(VI) reduction to trivalent Cr(III) (Chen et al., 2015a; Zhou et al., 2016). High pH value reduced Cr(VI) adsorption efficiency since the abundant OH^- led to $Cr(OH)_3$ generation and hindered the chromium ions to transfer and interact with surface functional groups (Chen et al., 2015a). Inversely,

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[*] Corresponding author.
E-mail address: chenzhihua@htu.edu.cn (Z. Chen).

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lower pH value was preferred attributed to an increasing in protonation during Cr(VI) adsorption (Chen et al., 2015a; Deveci & Kar, 2013; Zhou et al., 2016). Cr(VI) adsorption capacity increased with effluent temperature since the favorable endothermic (thermodynamic) reactions (Inyang et al., 2016; Yang et al., 2017). Moreover, biochar surface is rich in active functional groups such as hydroxyl, carbonyl, phenol, quinone, and aliphatic, etc (Jindo et al., 2014). The distribution of these functional groups is highly depended on pyrolytic temperature, in addition to used biomass types. It was pointed out by Zhou et al. (Zhou et al., 2016) that surface carboxyl and hydroxyl groups were in favor of Cr(VI) adsorption. The surface richer carboxyl and hydroxyl groups were obtained from lower pyrolysis temperature (300 °C) rather than higher temperature (450 °C and 600 °C) (Zhou et al., 2016). Since the Cr (III) was retained in solution, Zhou et al. (Zhou et al., 2016) indicated that the mechanism of Cr(VI) removal included adsorption and reduction stages: (1) Cr(VI) ions were adsorbed to biochar surface via electrostatic attractions; (2) the adsorbed Cr(VI) was reduced to Cr(III) and then discharged into the solution. The MBC have been prepared and utilized for Cr(VI) removal by several studies. Yang et al. (Yang et al., 2017) prepared a pinewood derived MBC under 700 °C pyrolytic temperature, showing a maximal adsorption capacity of 52.1 mg/g at 40 °C. The MBC derived from *eucalyptus* leaf (pyrolysis under 400 °C) showed a 97.11% efficiency for Cr(VI) removal from electroplating wastewater (Wang et al., 2014). The post-adsorption MBC still retained its original magnetic separation performance (Wang et al., 2014). A MBC was prepared by Duan S et al. (Duan et al., 2017a) using co-pyrolysis of iron sludge and cotton stalk blends under 500 °C. After magnetization, the MBC showed excellent adsorption capacity (67.44 mg/g) compared with primitive biochar (40.91 mg/g) (Duan et al., 2017a). However, the potential mechanism of Cr(VI) removal using MBC, even the related adsorption-reduction process via kinetics have not been reported.

Melia azedarach (MA) tree is an important source for paper pulp, logistics packing-case, furniture production since its fast-growing capacity. Annually, large amount of MA residues (wood, sawdust, bark, branch) is generated (such as in Guangxi Province, China), which is a potential feedstock for MBC preparation with environmental significances. Our study aims to use MA wood to prepare a MBC adsorbent for Cr(VI) removal via pyrolysis. The characterizations, Cr(VI) removal capacity, potential adsorption mechanism, kinetics were investigated.

2. Materials and methods

2.1. Magnetic biochar preparation

Air-dried *Melia azedarach* (MA) chips was obtained from Guiping City, Guangxi province (China). Wood chips was further crushed and sieved into 0.177–0.25 mm (i.e. 80–60 mesh) size. $Fe(NO_3)_3\ 9H_2O$ (analytical reagent) was dissolved in 300 ml deionized water and impregnated with MA via Fe/C (mol/mol) = 0.07 ratio at 120 °C (oil-bath with Silicone oil) for 4 h. The MA feedstock after impregnation was subsequently dried in air- cyclic oven at 100 °C for 24 h to obtain magnetic biochar precursor (MAFeN007). The raw MA, and MA without $Fe(NO_3)_3\ 9H_2O$ impregnation but hot water treated (120 °C) for 4 h (denoted as MA120), were used for parallel experiments.

The conditions (400 °C, 1h) for magnetic MA biochar (MMABC) preparation was referenced to Wang et al. (Wang et al., 2014). 10 g precursor was firstly contained in a quartz funnel and inserted in a stainless steel tube, followed by down-stream nitrogen (99.99% purity with 100 ml/min flow) aerification for 10 min to eliminate intra-tubal air. Afterwards, precursor was heated from room temperature to 400 °C in rate of 10 °C/min and maintained for 1 h. Once the intra-tubal temperature balanced to room temperature, MMABC was extracted and stored in vacuum (0.01 atm). Biochar derived from MA and MA120 (signed as MABC and MABC120, respectively) were obtained in a same programmed temperature.

2.2. Batch adsorption experiment

Desirable concentration (5mg/L, 10 mg/L, 30 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L) of Cr(VI) solutions were prepared by diluting the stock solution (1000 mg/L), which was obtained by dissolving 2.8287 g $K_2Cr_2O_7$ (analytical reagent) in 1000 ml deionized water. Certain mass of MMABC was added to 100 ml Cr(VI) solution and shaken mechanically at 120 rpm under room temperature (25 °C). The solid-liquid separations at different time were realized using injected Cellulose-Acetate membrane filter (< 0.45 μm). The Cr(VI) and Cr(III) concentrations were measured according to PRC National Standard (GB/T 7467-1987) using visible light spectrophotometry (V-5800H, METASH) at $\lambda = 540$ nm after diphenylcarbazide ($C_{13}H_{14}N_4O$) colorations. The removal efficiency (η, %) and adsorbing capacity (q_t, mg/g) was respectively calculated by:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$q_t = \frac{(C_0 - C_t)\cdot V}{m} = \frac{\eta\cdot C_0\cdot V}{100m} \tag{2}$$

where C_0 and C_t denoted initial and current concentration of Cr(VI), mg/L, respectively; m, the mass of adsorbent, g; V, the solution volume, L. The separated MMABC after adsorption were further air-cyclic dried under 100 °C for 12 h aimed to perform further characterizations.

2.3. Sample characterizations

The proximate and ultimate analysis of MA was carried out via PRC National Standard (GB/T 212-2008), and CHNS/O analyzer (Vario Micro cube, Elementar), respectively. Inorganic elements contained in ash were detected using X-ray fluorescence (XRF) microprobe (EAGLE III, EDAX Inc.).

Thermo-analysis (TG/DSC) were experimented for MA, MA120, $Fe(NO_3)_3\ 9H_2O$ crystal, MAFeN007 to contrastively study the weight loss behaviors during pyrolysis by using a TG/DSC analyzer (STA449C, NETZSCH). 5–10 mg samples was contained in an α-alumina crucible (another empty one was used for tare) and heated (10 °C/min) from room temperature to 700 °C under anoxic pyrolytic atmosphere maintained by nitrogen (100 ml/min flow).

BET specific surface areas (S_{BET}) was determined by nitrogen adsorption technique (−196 °C) in a Surface Area and Porosimetry system (BK112-T, JWGB). The functional groups were analyzed using FTIR (NEXUS 470) and Laser Confocal Raman Microspectroscopy system (RTS-EX, TEO) in wavenumber and Raman Shift range of 400–4000 cm^{-1} and 50–3000 cm^{-1}, respectively. Chemical valences and semi-quantitative of C1s, O1s, Fe2p, Cr2p were analyzed by X-ray Photoelectron Spectroscopy (XPS) system (ESCALAB250Xi, Thermo Fisher Scientific) referencing binding energy of C1s at 285.0 eV. X-ray Diffraction (XRD) patterns were analyzed by using X'Pert PRO diffractometer (PANalytical B.V.) by scanning 2θ from 10° to 80° with a 2°/min rate. Magnetic hysteresis loops of materials (1–10 mg) were measured using Multi-functional Magnetic Measurement system (VersaLab, Quantum Design).

pH dependent point zero charge (pH_{PZC}) was measured according to pH shift method (Gatabi et al., 2016): 10 ml of 0.01 M NaCl solutions (NS) were firstly adjusted to desirable pH value ($pH_{initial}$, ranged from 3 to 10 in step-size of 1) by 0.1 M NaOH and 0.1 M HCl; then, 30 mg of MMABC were added to NS and shaken mechanically for 48 h at 250 rpm (25 °C). The final pH (pH_{final}) was measured and differential to $pH_{initial}$ obtained the ΔpH, which were further plotted against with $pH_{initial}$. The pH_{PZC} value was obtained at $\Delta pH = 0$ using cubic spline interpolation method.