



Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge



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HIGHLIGHTS

- The adsorption effect of Cr(III) on biochar is stronger than that of Cr(VI).
- Surface functional groups contribute weakly to adsorption.
- The main mechanism of adsorption involves surface precipitation and ion-exchange.
- Reduction operation is helpful to improve chromium removal.

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ABSTRACT

In this work, static equilibrium experiments were conducted to distinguish the adsorption performance between the two valence states of chromium on biochar derived from municipal sludge. The removal capacity of Cr(VI) is lower than 7 mg/g at the initial chromium concentration range of 50–200 mg/L, whereas that of Cr(III) higher than 20 mg/g. It indicates that Cr(III) is much easier to be stabilized than Cr(VI). No significant changes in the biochar surface functional groups are observed before and after the adsorption equilibrium, demonstrating the poor contribution of organic matter in chromium adsorption. The main mechanism of heavy metal adsorption by biochar involves (1) surface precipitation through pH increase caused by biochar buffer ability, and (2) exchange between cations in solution (Cd^{2+}) and in biochar matrix (e.g. Ca^{2+} and Mg^{2+}). The reduction of Cr(VI) to Cr(III) is necessary to improve removal efficiency of chromium.

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1. Introduction

Chromium is a common heavy metal pollutant with different species of varying valence states. In recent years of the cosmopolitan process of industrialization and urbanization, the industry of tannery and electroplating has discharged a large amount of hazardous chromium into water, air and soil (Belay, 2010; Deveci and Kar, 2013; Mohan et al., 2011; Montanes et al., 2014; Wang et al., 2014). Trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are two common major species of chromium. Trace Cr(III) is essential for mammals, but detrimental when present in excess. Meanwhile, Cr(VI) with significantly higher solubility and mobility than Cr(III) is extremely dangerous because of its toxic, carcinogenic, allergenic, and irritant effects, especially causing damage of liver, lung and kidney (Dayan and Paine, 2001;

Kimbrough et al., 1999; Mohan and Pittman, 2006; Saha et al., 2011).

Conventional treatment methods to reduce or minimize the amount, concentration and dangers of chromium include coagulation, chemical precipitation, ion-exchange, membrane separation, electrolysis and electrodialysis. Despite their high efficiency and utility, these techniques also have some disadvantages that limit the application, such as considerable toxic waste production, high cost, and huge energy consumption (Mohan and Pittman, 2006). Adsorption is a promising process because of its operational simplicity and economic efficiency. The use of low-cost and effective adsorbents is crucial in adsorption (Wang et al., 2013). Biochar derived from biomass via oxygen-limited pyrolysis is an alternative to activated carbon (AC), which is the most commonly used adsorbent.

The behavior of Cr(III) and Cr(VI) on adsorbents must be comparatively evaluated to optimize the technique design and procedure, and efficiently remove Cr. Previous studies investigated the above two chromium species on the traditional adsorptive

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Table 1
Main properties of BC900.

Property	Value	Property	Value
Ash content percentage (wt.%)	88.07 ± 0.56	pH (S/L = 1:10)	12.15
C (wt.%)	15.92 ± 2.74	pH _{PZC}	10.17
H (wt.%)	0.11 ± 0.11	Cation exchange capacity (cmol·kg ⁻¹)	247.51 ± 7.49
O/wt.%	2.439 ± 0.575	BET surface area (m ² ·g ⁻¹)	67.603
N (wt.%)	0.53 ± 0.07	Average pore size (nm)	3.840
Ca (g·kg ⁻¹)	69.56	Pore volume (cm ³ ·g ⁻¹)	0.09855
Mg (g·kg ⁻¹)	17.52		

material AC (Mohan and Pittman, 2006). For Cr(VI) adsorption on AC, (1) the optimal pH is neutral or even acidic, which compensates for Cr(VI) ionization in the high pH and OH⁻ ion competition in the low pH, and also attributes to the tendency to reduction reaction; (2) the rate controlling step varies with pH, with an external mass transfer at initial pH 11 and an inter-particle control mechanism at initial pH 6; and (3) Cr(VI) reduction to Cr(III) partially occurs (Di Natale et al., 2015; Duranoğlu et al., 2012; Sun et al., 2014; Wu et al., 2008). In general, the efficiency increases with increasing pH for Cr(III) adsorption, because Cr(OH)₃ precipitates when the pH is high enough, and at acid condition, the optimal pH is approximately 6 because of chemical speciation; in addition, the rate controlling step is a function of initial Cr(III) concentrations and equilibrium temperatures, i.e. particle diffusion in high

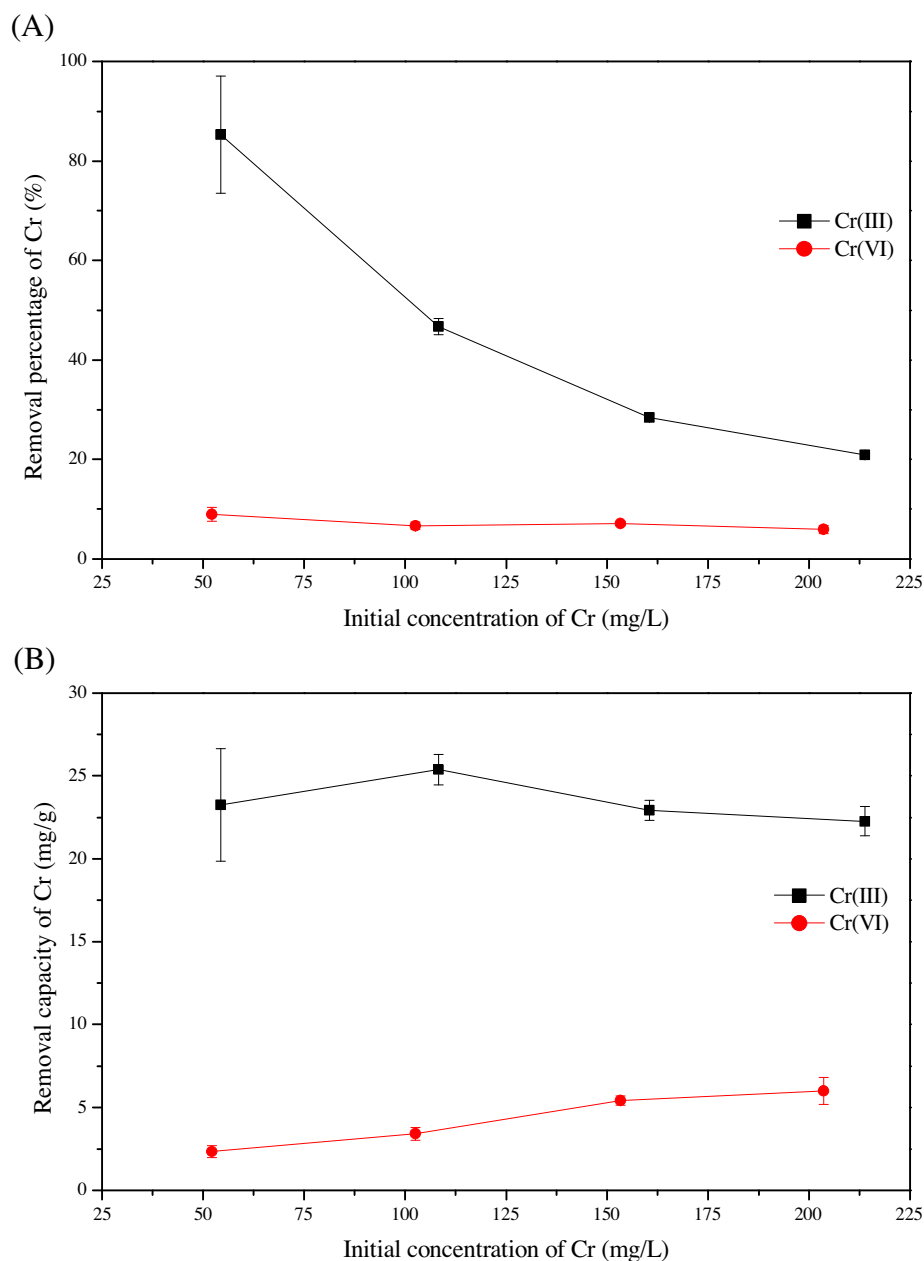


Fig. 1. Removal percentage and removal capacity of Cr(III) and Cr(VI) adsorption onto BC900. Equilibrium conditions: 50 mg BC900, 25 mL solution, no K⁺ stock solution added, 25.0 ± 1.0 °C, overnight. (A) Removal percentage versus initial Cr concentration; (B) removal capacity versus initial Cr concentration.

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