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Environmentally persistent free radicals mediated removal of Cr(VI) from highly saline water by corn straw biochars

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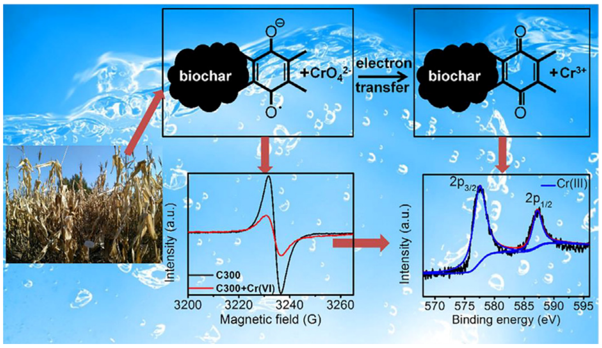
GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal ions coexisting with salts in the contaminant water are difficult to remove due to the interference of salts. Herein, biochars were pyrolyzed by corn straw at different temperatures, aiming to remove Cr(VI) in the presence of salts. Results show that biochars had surprisingly selective adsorption of Cr(VI). X-ray photoelectron and X-ray absorption near edge spectra revealed that Cr(VI) was reduced to Cr(III). All the adsorption was conducted at pH ~ 7, which differed from the previous studies that Cr(VI) could only be reduced at pH 2–4. Environmental persistent free radicals (EPFRs) on biochars were found to play the role in reducing Cr(VI) in neutral solutions, which was confirmed by electron spin resonance and free radical quenching. The biochar with EPFRs reveals a highly selective removal of Cr(VI), which has implications for the remediation of contaminated water. This work provides a new insight into biochar's properties and potential environmental applications.

1. Introduction

Heavy metal contamination of soil and water has received increasing concern because it can cause a severe threat to human health and ecosystems. Heavy metal ions are normally toxic, cumulative, and non-biodegradable. Among the most commonly presented heavy

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metals, hexavalent chromium, Cr(VI), released from textile dying, tanneries, electroplating, and metallurgical smelting of chromite ore, is highly diffusive and a well-known carcinogen. Many technologies have been applied to remove Cr(VI) from wastewater, including chemical reduction, ion exchange, ultrafiltration and so on (Ghosh and Bhattacharya, 2006; Mohan et al., 2006; Tiravanti et al., 1997; Yu et al., 2016). Adsorption is considered as a highly effective, relatively inexpensive, and easily handling method, where activated carbon, minerals, macromolecular polymers and nanomaterials are widely selected as adsorbents in the remediation of Cr(VI) containing wastewater.

Heavy metal ions in the contaminant water or soil often coexist with common salts at a relatively higher concentration, which brings difficulties in the removal of the heavy metals with a low concentration due to the interference and competitive effects. For example, tannery industrial wastewater contains about 80 g/L of NaCl (Lefebvre and Moletta, 2006), and the concentration of Cl^- in the groundwater of Yuncheng basin, China, is 1686 mg/L (Li et al., 2016a). The existence of the salts highly suppresses the removal efficiency in the treatment of heavy metal ions. To this end, the adsorbents with selective ability to trap heavy metal ions are quite intriguing to researchers (Kanel et al., 2005; Liu et al., 2008; Rapti et al., 2016). For example, zero-valent iron and Fe_3O_4/HA were found to selectively adsorb Cr(VI) or other heavy metals in the real water matrix or coexisting with salt ions (Kanel et al., 2005; Liu et al., 2008). More recently, metal organic framework composites were studied to selective adsorb Cr(VI) by chemical complexation (Rapti et al., 2016). In these studies, the surface properties of adsorbents are considered to affect the selective adsorption of heavy metal ions, although further work needs to be done on the elaboration of specific mechanisms.

Biochar, as the derivative of carbon-rich residues (e.g. wood, corn straw, grass, apricot stone), has increasingly attracted researchers' attention due to its abilities in improving soil fertility, sequestering carbon, realizing the transformation of waste and adsorbing pollutants (Chen et al., 2011; Godlewska et al., 2017; Lehmann et al., 2006). Being pyrolyzed at low temperature and free of activation agents make biochar less cost, although at the expense of high surface area, as compared to activation carbon. One of the most intriguing advantages of biochars lies in the presence of plenty of functional surface groups, such as carboxyl, hydroxyl, and phenolic functional groups, which are potential to be the sites to bind heavy metal ions (Klasson et al., 2009; Sun et al., 2014; Uchimiya et al., 2011; Zhao et al., 2017).

In recent years, environmentally persistent free radicals (EPFRs) have attracted increasing attentions in respect of their adverse impacts on health (Lomnicki et al., 2008; Wang et al., 2018). EPFRs are formed during the pyrolysis of biomass in the presence of metal oxides via a mechanism of chemisorption followed by electron transfer (Lomnicki et al., 2008). They are relatively stable, and exist in the atmosphere for hours and days (Fang et al., 2014). It had been reported that semiquinone type EPFRs can induce O_2 to form $O_2^{\cdot -}$ (Khachatryan et al., 2011). Thereafter, EPFRs were used to degrade *p*-nitrophenol and activate H_2O_2 to produce $^{\cdot}OH$ for the degradation of 2-chlorobiphenyl (Fang et al., 2014; Yang et al., 2016). Until now, more attentions were focused on the effects of EPFRs to generate reactive oxygen species (ROS), with the aim of degrading organic pollutants (Fang et al., 2013; Yang et al., 2016). To the best of our knowledge, no work has reported about the effect of biochar-based persistent free radicals in the treatment of heavy metals. As EPFRs can transfer electrons to oxygen, H_2O_2, and persulfate to induce Fenton reactions (Fang et al., 2013; Fang et al., 2014; Khachatryan et al., 2011; Yang et al., 2016), they can, in principle, act as reductants to react with heavy metal ions with a relatively higher redox potentials (e.g. CrO_4^{2-}), such that the reducible heavy metal ions with a less mobility can be produced and readily removed.

In this paper, environment-friendly biochars pyrolyzed from corn straw, were chosen to remove Cr(VI) in the presence of the competitive ions at a relatively higher concentration, with the aim to study the selective adsorption capacities of corn straw biochars on Cr(VI). Fourier Transform Infrared (FTIR) spectroscopy, X-ray photoelectron spectra (XPS), X-ray absorption near edge spectra (XANES) and electron spin resonance (ESR) were applied to elucidate the selective adsorption and removal mechanisms of Cr(VI) on the biochars. ESR was used to quantify biochar-based EPFRs and their effects on the removal of Cr (VI). By introducing H_2O_2 and C_2H_5OH as the competitive scavengers, the role of EPFRs in the removal of Cr(VI) was further investigated and elucidated.

2. Materials and methods

2.1. Biochar preparation

Corn straw was selected as the precursor to prepare biochars. The precursor was crushed and sieved through a 0.25 mm mesh. Then, it was put into a stainless steel reactor (10.5 cm in height and 6.5 cm in diameter) with a lid and heated in a muffle furnace at 300 °C, 500 °C and 700 °C for 2 h. The products were allowed to cool at room temperature, followed by washing with 1 M HCl (36%-38%, Sinopharm Chemical Reagent Co., Ltd.) and 3 M HF (40%, Sinopharm Chemical Reagent Co., Ltd.) solution to remove the ash materials. After drying in an oven at 105 °C for 24 h, the biochars were lightly ground and homogenized before passing through a 210 µm sieve. The biochars pyrolyzed at 300 °C, 500 °C, and 700 °C were labeled as C300, C500, and C700, respectively. Some biochars were further immersed into different concentrations of HNO_3 (2, 6, 10, 14 M) to activate the surface of biochars. After shaking for 48 h, the solid products were washed with deionized water until the pH was ~7, and then oven-dried at 105 °C for 24 h. C500 treated by 14 M HNO_3 was referred as 14 M-C500.

2.2. Adsorption experiments

Adsorption isotherms were measured through a batch equilibrium experiment. The ratio of solid adsorbents to solution used for the adsorption experiment and selective adsorption experiment was 50 mg/20 mL. Cr(VI) solution were prepared by analytical grade $K_2Cr_2O_7$ (99.8%, Sinopharm Chemical Reagent Co., Ltd.) at different concentrations ranging from 25 to 950 mg/L, which were then mixed with 50 mg of biochars. The mixtures were shaken at room temperature (RT) for 24 h. Afterwards, the mixtures were centrifuged at 5000 rpm and filtered through 0.45 µm membrane for Cr(VI) analysis with ICP-OES (OPTIMA 8300, USA). All samples were run in triplicate.

For selective adsorption experiment, Cr(VI) at different concentration (1, 2, and 5 mg/L) was mixed with high concentrations of Cl^- (180, 1800, 3600, and 9000 mg/L). For other salt ions (NO_3^-, SO_4^{2-}, HPO_4^{2-}, F^-, HCO_3^- and CO_3^{2-}), 5 mg/L of each salt were mixed with 5 mg/L of Cr(VI). The other experiment procedures were the same as the adsorption isotherm experiment. All samples were run in triplicate.

In order to study the removal efficiency of Cr(VI) by the biochars pretreated with H_2O_2 and ethanol, the biochars were immersed into 25 mL of H_2O_2 or ethanol at different concentrations and shaken for 12 h. The solid products were then collected, thoroughly washed with deionized water and oven-dried for 24 h. For immersing time series experiments, the biochars were mixed with 25 mL of 40 mM H_2O_2 and 0.1 mM ethanol, respectively. All the adsorption was conducted at pH ~ 7.

2.3. Data analysis

The adsorption amounts of Cr(VI) on the biochars were calculated by the following equation:

$$q_e = V(C - C_e)/m \tag{1}$$

For the selective adsorption experiments, the removal efficiency, *R* %, was calculated as followed: