Removal Mechanisms of Cr(VI) By Redox-Active Moieties on HNO₃ Modified Biochar Under Different pH and O₂ Conditions

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Abstract

Nitric acid (HNO_3) modified biochar (NBC) has been demonstrated to be a promising sorbent. However, the roles of their redox-active moieties (RAMs, i.e., environmentally persistent free radicals (EPFRs) and oxygen-containing function groups) in Cr(VI) removal under varying pH and O_2 conditions remain poorly understood. In this study, HNO_3 oxidation caused an obvious increase in specific surface area, porous volume, RAMs content, and surface potential of the biochar, leading to the more effective removal of Cr(VI) (with the removal rate reached 100% at pH 2.0) than that of the untreated biochar. Kinetics experiments revealed that O_2 and pH are of great importance for the reduction efficiency and rate of Cr(VI). RAMs on NBC can either directly reduce Cr(VI) (predominant pathway) or activate O_2 to produce $\cdot\text{O}_2^-$ for indirect Cr(VI) reduction. In addition, we examined the changes in the compositions of RAMs during the reaction by tuning the RAMs compositions using methanol and hydrogen peroxide. The results of electron paramagnetic resonance and X-ray photoelectron spectroscopy analysis demonstrated that the main electron donors on NBC were different at different pH values: oxygen-containing groups, e.g., $-\text{OH}$ and $-\text{C}-\text{O}-\text{C}-$, played a dominant role in reducing Cr(VI) under acidic conditions while the neutral condition was beneficial to EPFRs-dominated reduction. This study investigated the roles of the EPFRs and oxygen-containing function groups on HNO_3 modified biochar, which may provide new insights into the promoted reduction of Cr(VI) by applications of biochar.

1. Introduction

Due to industry and economic development, heavy metal contamination of soil and water has been a global challenge. In particular, chromium(Cr) poses great risks to the environment and human health because of its carcinogenicity, teratogenicity, and mutagenicity (J. Zhong et al., 2017). Chromium is released from electroplating, textile dyeing, tanneries, and other industrial processes (Arslan et al., 2010). Chromium has more complicated chemical behaviors in the environment because it exists in diverse oxidation states (i.e., trivalent Cr(III) and hexavalent Cr(VI)) (Mohan and Pittman, 2006). Cr(VI) is much more soluble, mobile, and toxic than Cr(III), and it is regarded as a priority pollutant by the U.S. EPA (Guo et al., 2012). Thus, an effective strategy to decrease the mobility and toxicity of Cr is through the adsorption-reduction method in view of its high efficiency and cost-effectiveness (Jiang et al., 2014; Wang et al., 2015).

As a carbon-rich byproduct of biomass pyrolysis, biochar is a cost-effective and environmental-friendly adsorbent with a highly porous structure and a variety of oxygen-containing functional surface groups (Yeboah et al., 2018; G. Zhang et al., 2011; Zhao et al., 2017). Although several studies have reported that virgin biochars had an adsorption and reduction effect on Cr(VI) (Choppala et al., 2016; Dong et al., 2011; Shen et al., 2012), they had relatively low sorption capacities. Therefore, surface oxidization, functionalization, and physical modification have been used to modify or activate biochar to enhance adsorption performance (Xue et al., 2012; M. Zhang et al., 2012; M.-m. Zhang et al., 2015; Y. Zhu et al., 2018). Among these modification/activation methods, chemical oxidation is a simple and effective way

to add more reactive sites (e.g., oxygen-containing functional groups) to the surface of biochar (J Jin et al., 2018). For instance, HNO_3 oxidized biochar rich in carboxyl functional groups (i.e., $-\text{COOH}$) showed remarkably greater stabilization ability for zinc, copper, and lead (Uchimiya et al., 2012). Furthermore, HNO_3 modified biochar exhibited enhanced uranium (VI) adsorption ability than the virgin biochar due to the increase in $-\text{COOH}$ content and negative surface charge (J Jin et al., 2018). However, the overall roles of HNO_3 and relative significance of potentially active components other than $-\text{COOH}$ in the sorption and reduction of Cr(VI) on biochar is still unclear.

Recently, a growing number of studies have focused on the underlying roles of redox-active moieties (RAMs) of biochar in the Cr(VI) removal process (N. Chen et al., 2021; X. Xu et al., 2019; Zhao et al., 2018; D. Zhong et al., 2018; S. Zhu et al., 2020). In addition to the well-known oxygen-containing functional groups (e.g., $-\text{OH}$, $-\text{C}-\text{O}-\text{C}$, and $-\text{C}=\text{O}$ moieties) (X. Xu et al., 2019), environmentally persistent free radicals (EPFRs) may also participate in the reduction of Cr(VI) . EPFRs, as a particular type of radicals, are formed during biomass pyrolysis and can exist in the atmosphere for hours or days (Fang et al., 2014; Odinga et al., 2020). EPFRs have been demonstrated to transfer electrons to O_2 , H_2O_2 , and persulfate to generate reactive oxygen species (ROS, i.e., $\cdot\text{O}_2^-$, H_2O_2 , $\cdot\text{OH}$) for the degradation of organic contaminants (Fang et al., 2014; Khachatryan et al., 2011). Thus, they can act as reductants to transform heavy metal ions with relatively high redox potentials (e.g., $E_0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35 \text{ V}_{\text{NHE}}$) to their less mobile and readily removed species. For example, in the study of Zhong et al. (D. Zhong et al., 2018), the active Fe_3O_4 and carbon-centered EPFRs (denoted as aromatic $\cdot\text{C}$) on the magnetic biochar composite were found to play a dominant role in the removal of Cr(VI) . Xu et al. (J. Xu et al., 2020) suggested that the phenolic hydroxyl group (i.e., Ph-OH) and EPFRs of humin can directly react with Cr(VI) as electron donors; at the same time, they can also transfer electrons to O_2 to generate superoxide radicals ($\cdot\text{O}_2^-$) to reduce Cr(VI) . Besides, the solution pH is of vital importance to the mechanisms for redox reactions between RAMs on biochar and redox-sensitive contaminants (D. Zhong et al., 2019). It has been reported that the high Cr(VI) removal performance of biochar in high-salinity water of neutral pH was mainly attributed to the presence of EPFRs rather than functional groups (Zhao et al., 2018). The latest research also found that hydrochar can reduce Cr(VI) through both direct reduction and indirect $\cdot\text{O}_2^-$ reduction pathways at pH 5.0 (N. Chen et al., 2021). However, little information is available on the effect of RAMs in the treatment of Cr(VI) over a wide environmentally relevant pH range and under oxic/anoxic conditions.

In this study, HNO_3 modified biochar (NBC) was employed for Cr(VI) removal over a broad initial pH range of 2.0 – 7.0 under both oxic and anoxic conditions to decipher the roles of HNO_3 and the RAM compositions in Cr(VI) removal. This study was conducted to (1) investigate the difference in the surface structural properties (i.e., functional groups, electrical properties, etc.) between NBC and untreated biochar; (2) determine direct and/or indirect pathways of NBC for Cr(VI) reduction; and (3) explore the roles of EPFRs and oxygen-containing functional groups in the reduction of Cr(VI) under the different initial pH values.

2. Materials And Methods

2.1 Biochar preparation

Corn straw was chosen as the precursor to prepare biochars. The precursor was sieved through a 0.25 mm mesh before pyrolyzing under N_2 atmosphere at 400°C for 2 h with heating rate of $10^\circ\text{C min}^{-1}$. The obtained biochar (BC) was allowed to cool down to room temperature, followed by passing through a 0.15 mm sieve. For modification, each 1.5 g sample of BC was immersed into 50 mL HNO_3 (0.8 M), mechanically shaking for 48 h. After washing with deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) to thoroughly remove the excess acid, the HNO_3 modified biochar (NBC) was dried in a vacuum oven at 60°C for 24 h and stored at 4°C in the dark for later use.

To further identify the roles of RAMs in the Cr(VI) reduction, we employed two kinds of NBC pretreatments to tune its RAM compositions, using methanol (CH_3OH) to quench the EPFRs (S. Zhu et al., 2020) or 5 w.t.% hydrogen peroxide (H_2O_2) to oxidize the RAMs (D. Zhong et al., 2019). The obtained products were labeled as $\text{NBC-CH}_3\text{OH}$ and $\text{NBC-H}_2\text{O}_2$, respectively. Details of the preparation processes are described in S2 of Supporting Information (SI).

2.2 Characterization

A series of analytical techniques were used to characterize BC and NBC. The morphology and elemental compositions of the biochar were investigated by Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX, Zeiss Sigma 300). Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Nicolet IS) and the modified Boehm titration analysis according to the method of Zhong et al. (D. Zhong et al., 2019) were conducted to analyze the functional groups of the biochar. The BET-surface area, pore size, and pore volume were determined using a Micromeritics ASAP 2020 Plus1.03 surface area and pore size analyzer. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was employed to identify the speciation of C, O, and Cr on the biochar. The surface potential of the biochar was measured by using Malvern Zetasizer Nano-ZS90 at 25°C temperature. The EPFRs in biochar samples were measured by an electron paramagnetic resonance spectrometer (EPR, Bruker MS-5000).

2.3 Adsorption experiments

As mentioned above, the removal performance of NBC under different initial pH values and O_2 conditions is still unclear. Thus, we conducted batch adsorption experiments to investigate the differences in the adsorption behavior of NBC under these conditions. In the pilot experiment, each 100 mg NBC was mixed thoroughly with 20 mL of 50 mg L^{-1} Cr(VI) solutions in every 50 mL conical flask at various pHs. The solution pHs were adjusted with 1 M NaOH or HCl solutions. The Cr(VI) removal performance by NBC at different initial pH values was shown in Fig. S1. Typical pH values (i.e., 2.0, 5.0, and 7.0) were selected for later experiments on RAMs variation and Cr(VI) removal capacity. Then the NBC and Cr(VI) solution mixture was mechanically shaken at 150 rpm at 25°C for 48 h. Each 2 mL of sample solution was taken at a specified time interval and then filtered through $0.22 \mu\text{m}$ membrane filter for the subsequent analysis.

The filtrates were then analyzed for total Cr and Cr(VI) concentrations using atomic absorption spectroscopy (AAS, PinAAcle900F) and the 1,5-diphenylcarbazide method at 540 nm (UV-2550, Shimadzu), respectively. The aqueous Cr(III) concentration was calculated based on the difference between the total Cr and Cr(VI) in solutions. The resulting solid residues were dried in a vacuum oven at 60°C for 24 h and then subjected to the characterization mentioned above.

To explore whether NBC can transfer electrons to O₂ to generate •O₂⁻, we conducted the anoxic experiments to examine the effect of active oxygen. All solutions were purged with N₂ for at least 1 h before the anoxic reactions to ensure no dissolved O₂ existed. Once the NBC and Cr(VI) solutions were mixed in every 100 mL headspace vial sealed with caps, the bottle was immediately vacuumed and filled with N₂. The adsorption experiment followed the same procedures as above, except for the absence of O₂. The removal capacities were evaluated using Eq. (1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where q_e (mg g⁻¹) is the adsorbed amount; C_0 and C_e (mg L⁻¹) are the concentration of Cr(VI) at beginning and equilibrium in the supernatant, respectively; V (mL) is the volume of solution; and m (g) is the mass of biochar.

To verify the contribution of RAMs in the removal of Cr(VI), 100 mg of biochars (NBC, NBC-CH₃OH, and NBC-H₂O₂) was mixed with 20 mL of 50 mg L⁻¹ Cr(VI) solutions in every 50 mL conical flask, followed by shaking at 150 rpm at 25 °C for 24 h. The content of Cr(VI) in solutions after biochar treatment was measured as described above. The Cr(VI) removal rate was calculated by Eqs. (2):

$$\text{removal rate (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

Here, C_0 and C_e (mg L⁻¹) are the concentration of Cr(VI) at the beginning and equilibrium in the supernatant, respectively.

2.4. Data analysis

All experiments were run in triplicate with well reproducible results, and the data was reported as the mean with standard deviations (SD). Error bars on the graphs represent the SD of the averages. All the results were evaluated with one-way analysis of variance (ANOVA) at a significance level of $P \leq 0.05$ using Prism 8.

3. Results And Discussion

3.1. Biochar Characterization

The difference in morphology and surface structure between BC and NBC was directly displayed in the SEM-EDX images (Fig. 1a and b). BC had an intact structure with many impurities on its surface, lacking tunnels and visible pores. In contrast, HNO₃ treated BC led to the removal of ash and alkali-metal salts (D. Zhong et al., 2018), and the corrosion made the NBC show tunnel-like structures with inner pores. Furthermore, the SEM-EDX result showed the slightly increased oxygen and nitrogen contents of NBC, which also indicated the success of HNO₃ modification.

The N₂ adsorption and desorption isotherm of BC constituted typical type IV curves with hysteresis loop of H3 (Hu et al., 2020), while that of NBC was more in line with the hysteresis loop of H4, indicating the NBC had the characteristics of microporous and mesoporous (Fig. 1e) (Zhao et al., 2018). As expected, the NBC had a larger BET surface area (27.066 m² g⁻¹) and pore volume (2.266×10⁻² cm³ g⁻¹) than those of BC (with 4.864 m² g⁻¹ BET surface area and 9.750×10⁻³ cm³ g⁻¹ pore volume). However, the average pore size of NBC (4.383 nm) was smaller than that of BC (21.435 nm) (Table S1). Density Functional Theory (DFT) model was used for further understanding the pore size distribution of BC and NBC. The results showed that the pore size of BC extended to the range of 11 nm – 100 nm (Fig. 1c), while the NBC concentrated within the limit of 11 nm (Fig. 1d), again confirming the presence of micropores and mesopores in NBC. All these differences between BC and NBC were caused by the oxidative corrosion of HNO₃, which results in the conversion of BC into the NBC of smaller pore size but the larger surface area and pore volume (Zhao et al., 2017).

The zeta potentials of BC and NBC were shown in Fig. 1f. BC was negatively charged across the pH range from 1 to 11. In comparison, the pI_{pzc} of NBC was found to be at pH 4.02. Thus, the increased surface potential of NBC may favor a weaker electrostatic attraction between the biochar and negatively charged Cr(VI) species.

To further verify the changes of functional groups on biochar before and after HNO₃ treatment, both biochars were subject to the FTIR measurement and the modified Boehm analysis (Fig. S2). The broad bands around 3407 – 3430 cm⁻¹ correspond to the stretching and vibration of –OH groups in polymeric compounds (Harikishore Kumar Reddy and Lee, 2014). The peaks around 1596 – 1612 cm⁻¹ are assigned to aromatic C=C and C=O of conjugated ketones and quinones (B. Chen et al., 2011; B. Chen et al., 2008). Transmission at 1030 – 1160 cm⁻¹ indicates the stretching/bending of oxygen-containing functional groups that correspond to C–O–C stretching/bending, alcohol –OH, and aliphatic C–O (Ahmed et al., 2016; B. Chen et al., 2008; G. Zhang et al., 2011). It was observable that these polar functional group peaks mentioned above had enhanced intensities on the NBC surface, indicating the oxidation reaction caused by HNO₃ treatment (Fig. S2a). Meanwhile, the dramatic decline of transmittance at 1380 cm⁻¹ (–CH₃) for NBC suggested decreased nonpolar aliphatic components. The titration result was in agreement with the FTIR results, which showed that the content of the Ph–OH group in the NBC increased after HNO₃ treatment (Fig. S2b). Therefore, it can be reasonably deduced that the different removal capacity between BC and NBC is mainly attributed to the changes of surface structure, surface potential, and functional groups from the HNO₃ treatment.

3.2. Effect of pH on Cr(VI) removal under the oxic condition

The time profiles of aqueous Cr species variations in the solution during Cr(VI) treatment by NBC under oxic condition are shown in Fig. 2a – c. At the solution pH 2.0, the concentration of Cr(VI) dramatically decreased from 50 mg L⁻¹ to 18.48 mg L⁻¹ during the first 2 h, and then the removal rate ultimately reached 100%. In correspondence, Cr(III) in the solution increased with the reaction time to a final concentration of 7.24 mg L⁻¹. Compared with pH 2.0, the concentration of total Cr and Cr(VI) slowly decreased to 24.53 mg L⁻¹ and 19.94 mg L⁻¹ at pH 5.0, and 35.4 mg L⁻¹ and 34.39 mg L⁻¹ at pH 7.0 within 48 h, with the increase of Cr(III) to 4.59 mg L⁻¹ and 1.01 mg L⁻¹, respectively. These results indicated that both adsorption and reduction pathways may be involved in the Cr(VI) removal process. Thus it was also significant to determine the degree of Cr(VI) reduction in the solid phases of NBC.

The species of Cr adsorbed on NBC after 24 h were examined by XPS analysis (Fig. 2d – e). In the Cr 2p spectrum, the binding energy values at 579.5 and 588.2 eV were assigned to Cr(VI), and 576.9 and 586.5 eV to Cr(III) (Hu et al., 2020; Liu et al., 2020; Zhao et al., 2018). The XPS analysis showed that most of the absorbed Cr(VI) was converted to Cr(III) after interacting with NBC. About 89.12% of Cr adsorbed on the NBC was in the form of Cr(III) at pH 2.0, compared to 73.73% at pH 5.0 and 72.4% at pH 7.0. These results revealed that the Cr(VI) removal by NBC was a hybrid adsorption-reduction process dominated by reduction. The adsorption kinetic data was fitted to the pseudo-first-order (Eqs. (3)) and pseudo-second-order (Eqs. (4)) kinetic models to analyze the adsorption behavior of Cr(VI) on NBC.

$$q_t = q_e - q_e e^{(-k_1 t)} \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where t (h) is the time of adsorption; q_e (mg g⁻¹) and q_t (mg g⁻¹) are the removal capacity at equilibrium and time t , respectively; and k_1 (h⁻¹) and k_2 (g mg⁻¹ h⁻¹) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

The kinetic parameters calculated from the two models are presented in Table S2, and the corresponding plots are shown in Fig. S3. It can be seen that pseudo-second-order model was superior to the pseudo-first-order model in data fitting with high correlation coefficients ($R^2 = 0.922, 0.945, 0.989$ for pH 2.0, 5.0, 7.0, respectively). Therefore, the chemisorption of Cr(VI) was the determining step of the adsorption process. The rate-controlling step might be a chemical interaction involving surface chelation reaction or ion exchange between Cr anions and the polar functional groups on NBC (Ho et al., 2011; Sun et al., 2014).

The different Cr(VI) removal efficiencies by NBC at different initial pH values were primarily connected with Cr(VI) speciation in the aqueous solution and the surface charge of biochar. At solution pH 1.0 – 6.8,

Cr(VI) ions are present as $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , which have more negative adsorption free energy than that of CrO_4^{2-} (predominant form at $\text{pH} > 6.8$) (Huang et al., 2016). Under the solution $\text{pH} < \text{pH}_{\text{pzc}}$ (4.02), the hydrated surface of NBC was protonated and positively charged, which resulted in a remarkable electrostatic attraction between the NBC and the anionic Cr(VI). Besides, a lower pH can produce a higher redox potential of Cr(VI)/Cr(III), which is conducive to the reduction of Cr(VI) by NBC (Mohan et al., 2006). Therefore, the removal efficiency of NBC under oxic condition at pH 2.0 could reach 97.54% within 24 h (Fig. S4). Nevertheless, when the solution $\text{pH} > \text{pH}_{\text{pzc}}$, the hydrated surface of NBC was deprotonated and negatively charged with the increasing pH values, which inhibited the Cr(VI) adsorption owing to the electrostatic repulsion between the NBC and Cr(VI) anions. Meanwhile, the OH^- can compete with Cr(VI) ions for the available adsorption sites on the surface of NBC at a higher pH (Ahmadi et al., 2016). The removal efficiencies of NBC at pH 5.0 and 7.0 reduced to 50.00% and 23.83% (Fig. S4). For the pristine BC, there was almost nil Cr(VI) removal at pH 5.0 and 7.0 due to its negatively charged surface (Fig. S4).

3.3. Direct and indirect reduction of Cr(VI) by NBC

In the Cr(VI) reduction system, the reducing agent can either directly transfer electrons to Cr(VI) (direct reduction pathway) or transfer electrons firstly to O_2 to produce $\cdot\text{O}_2^-$ then to Cr(VI) (indirect reduction pathway) (J. Xu et al., 2020). To further confirm this point of view, we conducted the anoxic experiments in the pH range of 2.0 to 7.0 and analyzed the concentrations of solution Cr species (Fig. 2a – c). As shown in Fig. 2a – c, the variation trend of total Cr, Cr(VI), and Cr(III) in the solution under anoxic condition was the same as that under oxic condition, but the specific Cr concentrations were different. The removal efficiency and rate of NBC under anoxic conditions were lower than that under oxic conditions. The overall removal rate of Cr(VI) by NBC was reduced by 5.74% (pH 5.0) and 8.97% (pH 7.0) in the absence of O_2 , respectively, compared to the oxic condition (Fig. 3a). Besides, Cr(VI) removal rate constants under oxic conditions were 1.12-fold (pH 2.0), 1.22-fold (pH 5.0), and 4.46-fold (pH 7.0) higher than those at the corresponding pH values under anoxic conditions (Fig. 3b). These results confirmed that the contribution of indirect reduction to Cr(VI) removal increased with the increasing initial pH values. Besides, competitive adsorption of O_2 and Cr(VI) may happen on the NBC surface. The increasing pH converted NBC's surface charge from positive to negative, which not only weakened the electrostatic adsorption between the NBC and the anionic Cr(VI) but also inhibited the direct electron transfer from the NBC to Cr(VI). Thus, O_2 could preferentially be adsorbed on the NBC surface to accept the electrons, leading to the generation of $\cdot\text{O}_2^-$ for indirect Cr(VI) reduction. Hence, we concluded that NBC could reduce Cr(VI) by indirect pathway, and it was strongly dependent on the pH values. It is worth noting that NBC can still directly reduce Cr(VI) in the absence of O_2 with the removal capacities of 100% (pH 2.0), 56.67% (pH 5.0) and 28.43% (pH 7.0) (Fig. 3a), indicating that the direct reduction dominated the Cr(VI) removal process of NBC under varying pHs.

3.4. Roles of RAMs on NBC in Cr(VI) reduction

3.4.1. Roles of EPFRs

We speculated that the Cr(VI) reduction capacity of NBC might be related to EPFRs, and therefore used the EPR technique to investigate the changes in EPFRs on biochars. Both BC and NBC had the broad singlet EPR signals, which confirmed the presence of free radicals in both biochars. Besides, the EPFRs content of NBC was about twice that of BC (Fig. 4a). It was reported that EPFRs with g-factors below 2.0030 are attributed to carbon-centered EPFRs (e.g., cyclopentadienyls), those of 2.0030 – 2.0040 are for carbon-centered radicals with an adjacent oxygen atom (e.g., phenoxy-derived species), and > 2.0040 for oxygen-centered radicals (e.g., semiquinone-type radicals) (Odinga et al., 2020). The g-factors of BC and NBC were 2.0057 and 2.0054, respectively. Hence, both were characteristic of oxygen-centered EPFRs, namely, semiquinone-type EPFRs. Semiquinone-type EPFRs are reported to participate in redox transformation of contaminants, such as As(III) oxidation (D. Zhong et al., 2019) and Cr(VI) reduction (Zhao et al., 2018). Therefore, the EPFRs on NBC may directly and/or indirectly donate electrons to reduce Cr(VI) to Cr(III), accompanied by forming quinone groups on the biochar.

To investigate the effect of EPFRs in the biochar/Cr(VI) systems in depth, EPFRs were recorded before and after the Cr(VI) treatment under varying pHs (i.e., 2.0, 5.0, and 7.0) and O₂ (i.e., anoxic and oxic) conditions. As illustrated in Fig. 4b, the intensity of EPR signals under oxic and anoxic conditions decreased with decreasing solution pH, consistent with the residual Cr(VI) concentration in the solution (Fig. 2a – c). This is in accordance with the previous result (D. Zhong et al., 2018) that EPFRs could directly transfer electrons to reduce Cr(VI), and more Cr(VI) could be reduced by EPFRs at a lower pH. At the same time, these EPFRs of NBC under anoxic and oxic conditions were consumed to different extents. EPFRs were consumed to a lesser extent under anoxic conditions than under oxic conditions. Yet, the removal efficiency was the opposite, further validating that the semiquinone-type EPFRs could participate in electron transfer to O₂ for the indirect Cr(VI) reduction. These results demonstrated that semiquinone-type EPFRs may be directly and indirectly responsible for the Cr(VI) reduction, and there was high dependence of Cr(VI) reduction by EPFRs on the solution pH and O₂.

To further investigate the role of EPFRs on Cr(VI) transformation, methanol was used to scavenge surface EPFRs before treating Cr(VI). As seen in Fig. 4a, the EPR measurement of the NBC after the methanol treatment revealed a pronounced decrease in EPFRs concentration. Meanwhile, the removal capacity of NBC-CH₃OH was reduced by 5.83% (pH 2.0), 13.06% (pH 5.0), and 43.26% (pH 7.0) in the presence of O₂ when compared to the NBC, respectively (Fig. 5). Therefore, the decrease of EPFRs on NBC-CH₃OH led to an apparent suppression of the removal efficiency of Cr(VI), and the contribution of EPFRs to Cr(VI) removal increased with the increasing initial pH values. This observation agreed with the previous finding that EPFRs probably act as the reductants to reduce Cr(VI) in the neutral condition instead of hydroxyl or catechol groups on the biochar (Zhao et al., 2018). Likewise, the removal capacity of NBC-CH₃OH under oxic condition increased by approximately 4.80% (pH 2.0), 14.16% (pH 5.0), and 82.70% (pH 7.0) when compared with that under anoxic condition, respectively (Fig. 5). It further demonstrated that EPFRs could transfer electrons to O₂ for the indirect Cr(VI) reduction, and the contribution of indirect reduction increased with the increasing initial pH values.

3.4.2. Roles of oxygen-containing functional groups

According to the above analysis of the role of EPFRs on Cr(VI) reduction, we speculated that oxygen-containing functional groups on NBC may also play similar roles in Cr(VI) reduction by direct and/or indirect pathways. As shown in Fig. 6a, significant changes in FTIR spectra of the NBC before and after the reaction with Cr(VI) were observed. For example, FTIR spectra showed decreases of the peak assigned to -OH ($3407 - 3430 \text{ cm}^{-1}$) and C-O-C ($1030 - 1160 \text{ cm}^{-1}$) groups after reacting with Cr(VI), suggesting that they may be the key regulators for Cr(VI) reduction. The peaks representing aromatic C-H bending vibrations ($800 \pm 10 \text{ cm}^{-1}$) also became inconspicuous after the reaction. Besides, the slight red shift of C=C/C=O ($1596 - 1612 \text{ cm}^{-1}$) occurred mainly due to the complexation of the -COOH group with Cr (J. Xu et al., 2020). Although the involvement of oxygen-containing functional groups in the Cr(VI) reduction can not be determined by using FTIR alone (e.g., complexation also affects the FTIR peak and positions), these results still indicated that the -OH , C-O-C , and C=O were involved in the Cr(VI) reduction to some extent.

The content of acidic functional groups (Ph-OH and -COOH) on NBC was determined by a modified Boehm titration method before and after adsorbing Cr(VI) at different conditions. Before reacting with Cr(VI), it is worth noting that the methanol used in this study had little impact on the content of Ph-OH and -COOH groups of the $\text{NBC-CH}_3\text{OH}$ (Fig. 6b), again proving that the decrease of EPFRs on $\text{NBC-CH}_3\text{OH}$ was responsible for the reduced removal efficiency of Cr(VI) (Fig. 5). However, after Cr(VI) treatment, the Ph-OH content of NBC sharply decreased (Fig. 6c). In contrast, the -COOH content increased correspondingly, which suggested that the Ph-OH may be oxidized to the -COOH group by transferring electrons to Cr(VI) (Fig. 6d). Meanwhile, the consumption of the Ph-OH group at pH 2.0 and 5.0 was greater than that at pH 7.0, indicating that more Ph-OH group participated in reducing Cr(VI) under acidic conditions.

To further elucidate the role of the oxygen-containing functional group in the transformation of Cr(VI), H_2O_2 treatment was used to oxidize the reduced functional groups on the NBC surface. After the H_2O_2 oxidation, neither the EPFRs intensity nor the content of Ph-OH of biochar was restored to its original level as depicted in Fig. 4a & 6b. The removal efficiencies of Cr(VI) after $\text{NBC-H}_2\text{O}_2$ treatment for 24 h under different conditions are shown in Fig. 5. The removal capacities of $\text{NBC-H}_2\text{O}_2$ under anoxic conditions still reached 73.88% (pH 2.0), 22.23% (pH 5.0), and 5.97% (pH 7.0), suggesting that the oxygen-containing functional groups could directly participate in the Cr(VI) reaction without O_2 . Under oxidic conditions, the removal capacities increased to 78.00% (pH 2.0), 27.07% (pH 5.0), and 12.23% (pH 7.0), hence the oxygen-containing groups can also transfer electrons to O_2 for the indirect Cr(VI) reaction.

Compared with NBC in the presence of O_2 , the reduction of removal capacity of $\text{NBC-H}_2\text{O}_2$ gradually increased in the order of pH 2.0 (20.04%) < pH 5.0 (46.43%) < pH 7.0 (48.66%). Thereby, the higher Cr(VI) removal efficiency deciphered the greater contribution of oxygen-containing groups in the lower pH. It is also apparent that the removal capacity of $\text{NBC-H}_2\text{O}_2$ was much lower than that of $\text{NBC-CH}_3\text{OH}$ at pH 2.0

and pH 5.0 (Fig. 5). Noteworthy the EPFRs content of NBC-H₂O₂ was higher, but the content of the Ph-OH group was lower than that of NBC-CH₃OH (Fig. 4a & 6b). Therefore, the Ph-OH group plays a dominant role in reducing Cr(VI) under acidic conditions. On the contrary, the Cr(VI) removal capacity of the NBC-H₂O₂ was getting closer to that of NBC-CH₃OH at pH 7.0, again proving that a neutral condition was more favorable for EPFRs-dominated reduction of Cr(VI).

The transition of oxygen-containing functional groups of biochar at varying pH values for Cr(VI) reduction was also investigated by XPS. From the O 1s spectrum (Fig. 7a), the peaks around 531 eV, 532 eV, 532.9 eV, and 533.5 eV were typically signals of -COOH, C=O, C-O-C, and C-OH & O-H, respectively (Liu et al., 2020). After reacting with Cr(VI), the proportion of C-OH & O-H and C-O-C groups in biochar decreased, along with increases in the percentage of -COOH and C=O. This may be ascribed to the oxidation of the C-OH & O-H and C-O-C groups by Cr(VI) and subsequent formation of the -COOH and C=O groups. This result can be further consolidated by the XPS C1s spectra (Fig. 7b). The binding energies at 284.2, 285.6, 287.9, and 289 eV corresponded to the C-C, C-O (phenol and alcohol), C=O, and -COOH groups, respectively (Liu et al., 2020). A relative decrease in the C-O content coupled with the increases in the -COOH and C=O content were observed after reaction with Cr(VI). Therefore, these characterization results suggested that C-O in the form of phenol, alcohol, or ether probably donated electrons to Cr(VI) coupled with the formation of the -COOH and C=O groups, which was consistent with FTIR and titration analysis (Fig. 6). Correspondingly, the Cr(III) species in the NBC increased with decreasing pH (i.e., 72.4% at pH 7.0, 73.7% at pH 5.0, and 89.12% at pH 2.0), suggesting the formed -COOH and C=O groups would complex with Cr(III). Besides, the increasing initial pH led to the decreasing contents of -COOH & C=O groups and the absorbed Cr(III) on the NBC (Fig. 2, 6d, and 7), which again supported that less Cr(VI) reduction will occur in the neutral pH because of the reduced contribution of oxygen-containing groups (Liu et al., 2020; Y. Zhu et al., 2018). Therefore, it can be reasonably deduced that oxygen-containing functional groups, including the -OH and C-O-C groups, acted as electron-donating moieties and played a dominant role in reducing Cr(VI) under acidic conditions, and the resultant -COOH and C=O groups participated in Cr(III) complexation.

4. Conclusion

In this work, corn straw biochar was modified by HNO₃ to prepare NBC with semiquinone-type EPFRs and oxygen-containing functional groups. We systematically investigated the key roles of these two redox-active moieties (RAM) in the Cr(VI) removal at varying initial pH and O₂ levels from water. HNO₃ oxidation induced the increase of BET surface area, pore volume, and RAM content, and changed zeta potentials of biochar to improve Cr(VI) adsorption. The results indicated that the initial pH values and O₂ are the decisive factors for the Cr(VI) removal efficiency and rate. Most of the Cr adsorbed on the biochar existed in the form of Cr(III) after reduction. Both EPFRs and oxygen-containing functional groups in the NBC can directly and indirectly (activation of O₂ to produce •O₂⁻ for reduction) reduce Cr(VI), where the direct reduction dominates the Cr(VI) removal and the contribution of indirect reduction increases with the increasing pH value. The neutral condition was more favorable for EPFRs-dominated reduction of Cr(VI).

Furthermore, oxygen-containing functional groups, especially –OH and C–O–C groups, played a dominant role in reducing Cr(VI) under acidic conditions, and the formed –COOH and C=O groups could be involved in complexation with Cr(III). This study provides a better understanding of the removal of Cr(VI) by RAMs in the biochar.

Declarations

Ethics approval and consent to participate

Consent for publication

Not applicable

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

All authors contributed to the study conception and design:

Xiyan Yin: Conceptualization, Experiment, Writing-Original Draft, Formal analysis; Jia Wen: Formal analysis, Supervision, Funding acquisition, Project administration; Zhuangzhuang Xue: Validation, Writing - Review & Editing, Formal analysis; Cuiliang Yang: Validation, Writing - Review & Editing; Yangfang Li: Data curation; Li Yuan: Data curation.

Meanwhile, all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

References

1. Ahmadi M, Kouhgard E, Ramavandi B (2016) Physico-chemical study of dew melon peel biochar for chromium attenuation from simulated and actual wastewaters. Korean J Chem Eng 33:2589–2601

2. Ahmed MB, Zhou JL, Ngo HH, Guo W, Chen M (2016) Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour Technol* 214:836–851
3. Arslan G, Edeballi S, Pehlivan E (2010) Physical and chemical factors affecting the adsorption of Cr(VI) via humic acids extracted from brown coals. *Desalination* 255:117–123
4. Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour Technol* 102:716–723
5. Chen B, Zhou D, Zhu L (2008) Transitional Adsorption and Partition of Nonpolar and Polar Aromatic Contaminants by Biochars of Pine Needles with Different Pyrolytic Temperatures. *Environ Sci Technol* 42:5137–5143. <https://doi.org/https://pubs.acs.org>
6. Chen N, Cao S, Zhang L, Peng X, Wang X, Ai Z, Zhang L (2021) Structural dependent Cr(VI) adsorption and reduction of biochar: hydrochar versus pyrochar, *Sci Total Environ*, 783 <https://doi.org/10.1016/j.scitotenv.2021.147084>
7. Choppala G, Bolan N, Kunhikrishnan A, Bush R (2016) Differential effect of biochar upon reduction-induced mobility and bioavailability of arsenate and chromate, *Chemosphere*. 144:374–381
8. Dong X, Ma LQ, Li Y (2011) Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *J Hazard Mater* 190:909–915
9. Fang G, Gao J, Liu C, Dionysiou DD, Wang Y, Zhou D (2014) Key role of persistent free radicals in hydrogen peroxide activation by biochar: implications to organic contaminant degradation. *Environ Sci Technol* 48:1902–1910
10. Guo J, Lian J, Xu Z, Xi Z, Yang J, Jefferson W, Liu C, Li Z, Yue L (2012) Reduction of Cr(VI) by *Escherichia coli* BL21 in the presence of redox mediators. *Bioresour Technol* 123:713–716
11. Reddy HK, Lee D (2014) Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. *Colloids Surf A Physicochem Eng Asp* 454:96–103
12. Ho YS, Ng JCY, McKay G (2011) Kinetics of Pollutant Sorption by Biosorbents. *Review, Separ Purif Method* 29:189–232
13. Hu X, Wen J, Zhang H, Wang Q, Yan C, Xing L (2020) Can epicatechin gallate increase Cr(VI) adsorption and reduction on ZIF-8?, *Chem Eng J*, 391 <https://doi.org/10.1016/j.cej.2019.123501>
14. Huang X, Liu Y, Liu S, Tan X, Ding Y, Zeng G, Zhou Y, Zhang M, Wang S, Zheng B (2016) Effective removal of Cr(vi) using β -cyclodextrin–chitosan modified biochars with adsorption/reduction bifunctional roles. *RSC Adv* 6:94–104
15. Jin J, Li S, Peng X, Liu W, Zhang C, Yang Y, Han L, Du Z, Sun, Wang K (2018) HNO₃ modified biochars for uranium (VI) removal from aqueous solution. *Bioresour Technol* 256:247–253
16. Jiang W, Cai Q, Xu W, Yang M, Cai Y, Dionysiou DD, O'Shea KE (2014) Cr(VI) adsorption and reduction by humic acid coated on magnetite. *Environ Sci Technol* 48:8078–8085
17. Khachatryan L, Vejerano E, Lomnicki S, Dellinger B (2011) Environmentally persistent free radicals (EPFRs). 1. Generation of reactive oxygen species in aqueous solutions. *Environ Sci Technol*

18. Liu N, Zhang Y, Xu C, Liu P, Lv J, Liu Y, Wang Q (2020) Removal mechanisms of aqueous Cr(VI) using apple wood biochar: a spectroscopic study. *J Hazard Mater* 384:121371
19. Mohan D, Pittman CU Jr (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J Hazard Mater* 137:762–811
20. Mohan D, Singh KP, Singh VK (2006) Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. *J Hazard Mater* 135:280–295
21. Odinga ES, Waigi MG, Gudda FO, Wang J, Yang B, Hu X, Li S, Gao Y (2020) Occurrence, formation, environmental fate and risks of environmentally persistent free radicals in biochars. *Environ Int* 134:105172
22. Shen YS, Wang SL, Tzou YM, Yan YY, Kuan WH (2012) Removal of hexavalent Cr by coconut coir and derived chars—the effect of surface functionality. *Bioresour Technol* 104:165–172
23. Sun Z, Liu Y, Huang Y, Tan X, Zeng G, Hu X, Yang Z (2014) Fast adsorption of Cd(2)(+) and Pb(2)(+) by EGTA dianhydride (EGTAD) modified ramie fiber. *J Colloid Interface Sci* 434:152–158
24. Uchimiya M, Bannon DI, Wartelle LH (2012) Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *J Agric Food Chem* 60:1798–1809
25. Wang T, Zhang L, Li C, Yang W, Song T, Tang C, Meng Y, Dai S, Wang H, Chai L, Luo J (2015) Synthesis of Core-Shell Magnetic Fe₃O₄@poly(m-Phenylenediamine) Particles for Chromium Reduction and Adsorption. *Environ Sci Technol* 49:5654–5662
26. Xu J, Dai Y, Shi Y, Zhao S, Tian H, Zhu K, Jia H (2020) Mechanism of Cr(VI) reduction by humin: Role of environmentally persistent free radicals and reactive oxygen species. *Sci Total Environ* 725:138413
27. Xu X, Huang H, Zhang Y, Xu Z, Cao X (2019) Biochar as both electron donor and electron shuttle for the reduction transformation of Cr(VI) during its sorption. *Environ Pollut* 244:423–430
28. Xue Y, Gao B, Yao Y, Inyang M, Zhang M, Zimmerman AR, Ro KS (2012) Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests, *Chem Eng J*, 200–202673-680. <https://doi.org/10.1016/j.cej.2012.06.116>
29. Yeboah S, Lamptey S, Cai L, Song M (2018) Short-Term Effects of Biochar Amendment on Greenhouse Gas Emissions from Rainfed Agricultural Soils of the Semi-Arid Loess Plateau Region, *Agronomy*, 8 <https://doi.org/10.3390/agronomy8050074>
30. Zhang G, Zhang Q, Sun K, Liu X, Zheng W, Zhao Y (2011) Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. *Environ Pollut* 159:2594–2601
31. Zhang M, Gao B, Yao Y, Xue Y, Inyang M (2012) Synthesis, characterization, and environmental implications of graphene-coated biochar, *Sci Total Environ*, 435–436567–572 <https://doi.org/10.1016/j.scitotenv.2012.07.038>

32. Zhang M-m, Liu Y-g, Li T-t, Xu W-h, Zheng B-h, Tan X-f, Wang H, Guo Y-m, Guo F- (2015) y., Wang, S.-f., Chitosan modification of magnetic biochar produced from *Eichhornia crassipes* for enhanced sorption of Cr(VI) from aqueous solution, *RSC Advances*, 5 46955-46964. <https://doi.org/10.1039/c5ra02388b>
33. Zhao N, Yin Z, Liu F, Zhang M, Lv Y, Hao Z, Pan G, Zhang J (2018) Environmentally persistent free radicals mediated removal of Cr(VI) from highly saline water by corn straw biochars. *Bioresour Technol* 260:294–301
34. Zhao N, Zhao C, Lv Y, Zhang W, Du Y, Hao Z, Zhang J (2017) Adsorption and coadsorption mechanisms of Cr(VI) and organic contaminants on H₃PO₄ treated biochar, *Chemosphere*. 186:422–429
35. Zhong D, Jiang Y, Zhao Z, Wang L, Chen J, Ren S, Liu Z, Zhang Y, Tsang DCW, Crittenden JC (2019) pH Dependence of Arsenic Oxidation by Rice-Husk-Derived Biochar: Roles of Redox-Active Moieties. *Environ Sci Technol* 53:9034–9044
36. Zhong D, Zhang Y, Wang L, Chen J, Jiang Y, Tsang DCW, Zhao Z, Ren S, Liu Z, Crittenden JC (2018) Mechanistic insights into adsorption and reduction of hexavalent chromium from water using magnetic biochar composite: Key roles of Fe₃O₄ and persistent free radicals. *Environ Pollut* 243:1302–1309
37. Zhong J, Yin W, Li Y, Li P, Wu J, Jiang G, Gu J, Liang H (2017) Column study of enhanced Cr(VI) removal and longevity by coupled abiotic and biotic processes using Fe(0) and mixed anaerobic culture. *Water Res* 122:536–544
38. Zhu S, Huang X, Yang X, Peng P, Li Z, Jin C (2020) Enhanced Transformation of Cr(VI) by Heterocyclic-N within Nitrogen-Doped Biochar: Impact of Surface Modulatory Persistent Free Radicals (PFRs). *Environ Sci Technol* 54:8123–8132
39. Zhu Y, Li H, Zhang G, Meng F, Li L, Wu S (2018) Removal of hexavalent chromium from aqueous solution by different surface-modified biochars: Acid washing, nanoscale zero-valent iron and ferric iron loading. *Bioresour Technol* 261:142–150

Figures

Figure 1

SEM-EDX patterns of (a) BC and (b) NBC; N₂-DFT pore size distribution of (c) BC and (d) NBC; (e) N₂ adsorption/desorption isotherms for BC and NBC; and (f) Zeta potentials of both materials.

Figure 2

Changes in the concentrations of total Cr, Cr(VI) and Cr(III) after NBC addition under different initial solution pH of (a) 2.0, (b) 5.0, and (c) 7.0 (sampling time was 0.5, 1, 2, 4, 8, 18, 24, 36, and 48 h); High resolution XPS Cr 2p spectra of NBC after reaction with 50 mg L⁻¹ Cr(VI) at pH (a) 2.0, (b) 5.0, and (c) 7.0 for 24 h, respectively.

Figure 3

(a) Time profiles of 50 mg L⁻¹ Cr(VI) removal with NBC (Cr(VI) removal efficiencies within 48 h were shown in brackets) and (b) the corresponding rate constants under oxic and anoxic conditions at

different initial pH values.

Figure 4

(a) EPR spectra of BC, NBC, NBC-CH₃OH, and NBC-H₂O₂; (b) EPR spectra of NBC before and after reacting with Cr(VI) under varying pHs (i.e., 2.0, 5.0, and 7.0) and O₂ (i.e., oxic and anoxic) conditions.

Figure 5

Removal efficiency of 50 mg L⁻¹ Cr(VI) by the different biochars under oxic and anoxic conditions at initial pH (a) 2.0, (b) 5.0, and (c) 7.0 for 24 h, respectively (the bars are standard errors; letters in the figures indicate significant differences (P < 0.05)).

Figure 6

(a) FTIR spectra; (b) Ph-OH and -COOH contents of different biochars; changes in (c) Ph-OH content and (d) -COOH content of NBC before and after reaction with 50 mg L⁻¹ Cr(VI) after 24 h (the bars are standard errors; letters in the figures indicate significant differences ($P < 0.05$)).

Figure 7

XPS spectra of (a) O 1s and (b) C 1s before (NBC) and after reacting with 50 mg L⁻¹ Cr(VI) under varying pH for 24 h.

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