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Sorption and Reduction of Hexavalent Chromium from Aqueous Solutions by Surface Modified Biochars

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The surface of wheat straw-based biochar was modified by a pretreatment using H₃PO₄. Biochars with different surface characteristics were obtained and characterized. Their reducing and sorption capacities for aqueous Cr(VI) were evaluated. The removal of Cr(VI) was enhanced with an increase in biochar surface acidity. The sorption performance was related to the equilibrium concentration. Oxygen-containing groups were involved in Cr(III) complexation, some of which were formed due to Cr(VI) oxidation. The competitive sorption of proton was evident for over protonated biochars at low range. Biochar porosity also played a role. The influences of other factors were also discussed.

Keywords hexavalent chromium; biochar; sorption; reduction

INTRODUCTION
Chromium is widely used in a variety of industries such as leather tanning, textile dyeing, metal plating, and wood preservation. Chromium is considered as a major pollutant which causes severe environmental and public health problems. In aqueous phase, chromium exists primarily in two states: Cr(III) and Cr(VI). The hexavalent form is considered to be much more hazardous (1).

In recent years, the potential of biochar to remediate water and soil contamination has attracted much attention. Biochar is a carbon-enriched material obtained from biomass through pyrolysis. It has exhibited strong affinity for various heavy metals such as Cu²⁺, Cd²⁺, and Pb²⁺ (2-4). The surface characteristics of biochar are crucial in determining its performance for heavy metal removal. Uchimiya et al. (5,6) found that the existence of surface functional groups on biochar was favorable for heavy metal retention.

It is well established that the removal of Cr(VI) from aqueous solution by biomass involves the sorption of Cr(VI) anion, the reduction of Cr(VI) to Cr(III) and the binding of Cr(III) on surface (7-9). Park et al. (10) used a protonated brown seaweed to treat Cr(VI) and observed its complete reduction to Cr(III). Although the removal of Cr(VI) using various biomass has been extensively explored, studies on the effectiveness of biochar are still limited (11,12). Some aspects such as the effects of biochar physicochemical characteristics, the involvement of electrostatic force and proton, and the conversion of Cr(VI) on biochar surface are not well understood.

In previous studies, biochars were commonly prepared through direct pyrolysis (13,14), which required high temperature. Chemical pretreatment has the potential to lower pyrolysis temperature, and meanwhile modify the surface characteristics of biochar, which has not been explored before. In this study, biochars were prepared by treating the precursor in H₃PO₄ solution before pyrolysis. Based on previous studies (15,16), phosphoric acid was able to endow carbon materials with an acidic surface. By varying the dosage of H₃PO₄, biochars with different surface characteristics were obtained. The sorption and reduction behaviors of Cr(VI) using them were then investigated. This study is aimed to:

1. test the effectiveness of the surface modified biochars (SMBs);
2. investigate the influences of biochar surface characteristics on Cr(VI) reduction and sorption;
3. explore the effects of parameters including initial Cr(VI) concentration, pH and temperature; and
4. determine the mechanisms governing Cr(VI) removal.

METHODS
Reagents and Materials
The chemical reagents used in this study were all of analytical grade. A stock solution with a Cr(VI) concentration of 353.5 mg/L was prepared from potassium dichromate, which was diluted to obtain solutions with desired concentrations.

Preparation of Biochars
Wheat straw was collected from Wuqiao county, Hebei province, China. The material was washed several times with
distilled water, and cut into pieces with a length of 10-20 mm. 2.0 g wheat straw was soaked firstly in 50 mL solution with various H$_3$PO$_4$ dosages (0, 1, 2, 3 and 4 mL, purity > 85%) for 24 h. The treated material was then dried at 105°C for 2 h and heated in a muffle furnace at 250°C for 2 h. The products were washed repeatedly with deionized water to a constant conductance, ground into powder and sieved to size range from 125 to 600 μm. The resulting biochars, denoted as BC-0, BC-1, BC-2, BC-3, and BC-4 based on the dosage of H$_3$PO$_4$ added, were stored in a desiccator for further use.

Characterization Methods

The surface physical characteristics of biochars were characterized with a Micromeritics ASAP 2020, using N$_2$ as the adsorbate at 77 K. The surface area ($S_{BET}$) was obtained using the BET equation, the total pore volume ($V_T$) was estimated at a relative pressure of 0.99. The pore size distribution was analyzed based on the density functional theory (DFT).

The FTIR analysis was conducted with a Nicolet Nexus 670. The samples were mixed with KBr powder and the mixture was pressed into pellets. The spectra were recorded from 4000 to 400 cm$^{-1}$ and 32 scans were taken at the resolution of 4 cm$^{-1}$.

The XPS analysis was conducted using a PHIL700 ESCA system equipped with a Al Kα X-ray source (1486.6 eV) under a vacuum pressure < 10$^{-6}$ Pa. Pass energy was set as 187.85 and 32.35 eV for survey and high-resolution spectra, respectively. The spectra were calibrated by taking the graphitic peak as 284.6 eV. Cr-laden biochars were also characterized using FTIR and XPS. For their preparation, 0.2 g biochar was mixed with 100 mL Cr(VI) solution (180 mg/L) at pH 1.8 for 72 h, then filtered and dried at 80°C overnight.

The pH$_{pzc}$ values were determined by a mass titration method proposed by Noh and Schwarz (17). The total P content of biochar was analyzed with a molybdate-antimonyascorbic acid method after H$_2$SO$_4$-H$_2$O$_2$ digestion (18).

Removal of Cr(VI) by Biochar

Removal of Cr(VI) from aqueous solution was conducted by batch mode in stoppered flasks. Unless otherwise stated, 0.100 g biochar and 50 mL solution were mixed and shaken in a thermostatic shaker bath at 120 rpm. In equilibrium studies, solutions with different initial Cr(VI) concentrations were added at 25°C. Solution pH was adjusted to 1.8 by the addition of 1 mol/L HCl. The equilibrium time was set as 120 h hours based on preliminary experiments. After treatment, water samples were filtrated with 0.45 μm membrane filters, followed by the analysis of Cr species. The uptake of total Cr by per unit mass of biochar at equilibrium, $q_e$ (mg/g), was calculated by the following equation:

$$q_e = V \cdot \frac{([\text{Cr(VI)}]_0 - [\text{Cr}])}{m}$$

where $[\text{Cr(VI)}]_0$ is the initial concentration of Cr(VI) (mg/L), $[\text{Cr}]$ is the equilibrium concentration of total Cr (mg/L), $V$ is the volume of solution (L), $m$ is the weight of biochar (g).

In kinetic studies, 0.10 g biochar and 100 mL Cr(VI) solution with various initial concentrations were mixed at 25°C. The solution pH was also adjusted to 1.8. About 1 mL water sample was taken at desired time intervals. The uptake of Cr by per unit mass of biochar at time $t$, $q_t$ (mg/g), was calculated by the following equation:

$$q_t = V \cdot \frac{([\text{Cr(VI)}]_0 - [\text{Cr}]_t)}{m}$$

where $[\text{Cr}]_t$ is the aqueous concentration of total Cr (mg/L) at time $t$.

In pH studies, various dosages of NaOH or HCl solution (1 mol/L) were added to adjust solution pH. The ultimate pH values at equilibrium were measured. In temperature studies, 15, 25, 35, and 45°C were chosen to study the effects.

These experiments were conducted in triplicate and the standard errors were within 5%.

Analysis of Chromium

The aqueous concentrations of Cr species were measured by a colorimetric method (19). Cr(VI) reacts with 1,5-diphenylcarbazide in acidic solution to form a pink complex, which was analyzed using a spectrophotometer at 540 nm. After the conversion of Cr(III) into Cr(VI) under acidic condition using KMnO$_4$ as the oxidant, Cr(VI) was analyzed as described before, which was taken as the total Cr. Cr(III) concentration was calculated as the difference between total Cr and Cr(VI).

The amount of Cr(VI) present on biochar surface was analyzed after chemical extraction. After the filtration of supernatant, 50 mL 0.28 mol/L Na$_2$CO$_3$/0.5 mol/L NaOH solution was added to extract Cr(VI). The mixture was stirred strongly for 2 h. The amount of extracted Cr(VI) was used to calculate the surface conversion rate (SCR) of Cr(VI) on biochar (the ratio of extracted Cr(VI) to the uptake).

RESULTS AND DISCUSSION

Surface Characteristics of Biochars

The specific surface areas of BC-0, BC-1, BC-2, BC-3, and BC-4 were measured as 4.28, 218.8, 206.1, 247.1, and 272.2 m$^2$/g. The total pore volumes were 0.001, 0.0974, 0.0912, 0.107, and 0.116 cm$^3$/g for BC-0, BC-1, BC-2, BC-3, and BC-4, respectively. Obviously the pretreatment of wheat straw with H$_2$PO$_4$ largely promoted the development of biochar porosity. The pore size distributions were illustrated in Fig. 1. The pores of these biochars were mainly consisted of micropores, but considerable mesopores were also available. In the micropore range (below 2 nm), two peaks were distinct which could be classified as ultra-micropores (around 0.5 nm) and super-micropores.
(around 1.2 nm). The ultra-micropores of BC-1 were more developed which comprised a larger portion of total pores.

The pH$_{pzc}$ values were measured as 7.25, 2.55, 2.50, 2.42, and 2.38 for BC-0, BC-1, BC-2, BC-3, and BC-4, respectively. The results reflected an ever increased surface acidity of the SMBs with the increase of H$_3$PO$_4$.

The FTIR spectra of various biochars are quite similar, so only one is presented in Fig. 2. The band at 3390 cm$^{-1}$ was assigned to the O–H stretching vibration. The band at 2918 cm$^{-1}$ was attributed to the C–H stretching vibration. The band at 1707 cm$^{-1}$ corresponded to the C=O stretching. The bands at 1580 and 1400 cm$^{-1}$ were derived from –COO$^-$ anti-symmetric and symmetric stretching (20). The band at 1182 cm$^{-1}$ was related with the C–O stretching vibration of carboxylic groups.

Based on XPS, the relative contents of various elements on biochar surface are tabulated in Table 1. The O contents of various SMBs increased with the increase in surface acidity. The O content of BC-0 was also high. Except for BC-4, the O contents became higher after contact with Cr(VI), indicating the formation of new surface groups due to Cr(VI) oxidation, as observed by previous studies (21, 22). However, the surface contents of P and Cr showed unexpected trends. The total contents of P, measured colorimetrically after digestion, were 2.44, 9.55, 9.97, 11.36, and 16.46 mg/g for BC-0, BC-1, BC-2, BC-3, and BC-4, respectively, whereas the surface contents of P, measured by XPS method, showed a different trend. The surface content of Cr was also unusual. As XPS probed a depth of several nanometers (23), the results suggested that the vertical distribution of P and Cr was not uniform.

**Equilibrium Studies of Cr(VI) Removal**

The sorption isotherms of total Cr onto various biochars were obtained at 25 °C, as shown in Fig. 3. As can be seen, the sorption of Cr was related to the equilibrium concentration ($C_e$). At low range ($C_e < 5$ mg/L), BC-1 showed the highest affinity; at intermediate range ($5 < C_e < 15$ mg/L), BC-2 exhibited the strongest sorption; at high range ($C_e > 15$ mg/L), BC-3 gave the largest uptake. BC-0 showed weak affinity for Cr at low range, but the uptake increased steadily at high range. Although BC-1 had strong affinity for Cr at low range, the isotherm reached a plateau at $C_e > 10$ mg/L, which was the lowest at that range. A sorption amount up to 188.1 mg/g was obtained for BC-3. Although a favorable sorption was achieved at high range for BC-4, its performance was unexpectedly poor at low range. The sorption capacities of various biochars followed the order of BC-1 < BC-0 < BC-2 < BC-3 = BC-4.

The equilibrium concentration of aqueous Cr(VI) versus initial concentration was depicted in Fig. 4. Obviously, the critical initial concentration at which aqueous Cr(VI) could be detected varied greatly within these samples. For BC-1, Cr(VI)
was detectable at $C_0 = 80 \text{ mg/L}$, while this value was 350 mg/L for BC-4. In these cases, the reduction of Cr(VI) was limited by the electron donor groups rather than by proton, as the ultimate pH was below 3.0 for each test.

The SCR of Cr(VI) as a function of Cr uptake was illustrated in Fig. 5. For these samples, this parameter was above 90% at a wide range of uptake, meaning that the sorbed Cr existed mainly in the form of Cr(III). Moreover, an optimal uptake range was observed for SCR in most cases. The presence of Cr(III) on biochar surface caused electrostatic attraction for Cr(VI), thus favoring its contact with electron donor groups. This effect was promoted with the increase of Cr uptake. Meanwhile, an increase of uptake implied the exhaustion of electron donor groups. The two contradictory factors might explain the change in SCR. Combined with the equilibrium concentration of aqueous Cr(VI) (Fig. 4), the reducing capacities of biochars were well correlated to their sorption capacities, implying that similar groups were involved in the reduction and complexation reactions.

Electrostatic force was presumed to be dominant for Cr(VI) sorption (24), while surface precipitation, ion-exchange and surface complexation were commonly employed for Cr(III) sorption (25-27). In this study, surface precipitation should be excluded as the solution was strongly acidic. The importance of ion-exchange was evaluated by the measurement of dissolved ions (Table 2). Only slight changes in Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ were detected after the addition of Cr(VI), noting that the increase in K$^+$ was caused by the addition of $K_2Cr_2O_7$. Hence, surface complexation should be dominant for Cr(III) sorption.

Based on the characterization results, the sorption of Cr(III) was closely related to the oxygen-containing groups. Groups such as carboxylic, hydroxyl, carbonyl, and ether were possibly involved (6,8,11). Some newly formed groups due to Cr(VI) oxidation also served as ligands. For the SMBs, their sorption capacities were in general consistent with the O contents. Although the O content of BC-0 was comparable to SMBs, its sorption performance was poor especially at low range. This phenomenon suggested that the original surface groups on BC-0 was not so effective in the reduction and sorption of Cr(VI). But they were converted to effective forms after contact with high concentration of Cr(VI). The P-containing groups probably participated in the complexation. In view of the low content of P, their contribution represented a small fraction of the sorption. Physical force also played a role in the sorption, especially at low range. The high affinity of BC-1 for Cr at low range was related to its microporous nature, as it had higher ultra-micropore portion. In narrow micropores, physical forces such as Van der Waals force were enhanced,
which helped to entrap Cr species. The competitive sorption of redundant proton also influenced the isotherm shapes of BC-3 and BC-4, which will be discussed in the pH section.

More insight into Cr sorption was gained through the sequential sorption of Cr species using BC-3. In the first stage, Cr(III) or Cr(VI) was added alone to reach equilibrium; in the second stage, the same amount of the other anion/ion was added to reach a new equilibrium. The uptakes of Cr in the two stages were recorded in Fig. 6. When Cr(III) was first added, the sorption was unfavorable. The following addition of Cr(VI) strongly promoted the overall sorption. In contrast, the sorption was favorable when Cr (VI) was first added. In the second stage, little increase in the uptake was observed at low range, but the increase was noticeable at high range, resulted from the participation of newly formed surface groups. The results proved that the initial presence of Cr in a form of Cr(VI) favored the following sorption. One reason was that the deprotonation of surface groups alleviated the competitive effect of proton for sorption (28). Also, the reduction of Cr(VI) introduced new surface groups to supply additional sorption sites. Furthermore, the conversion of Cr(VI) influenced the electrostatic force. When the converted Cr(III) was bounded, the positivity of biochar surface was enhanced, which created electrostatic attraction to facilitate the diffusion and sorption processes. In contrast, when Cr was present initially as Cr (III), there was electrostatic repulsion which hindered the contact between Cr(III) and biochar to form inner sphere complex.

### Table 2

<table>
<thead>
<tr>
<th>Ions</th>
<th>BC-0</th>
<th>BC-1</th>
<th>BC-2</th>
<th>BC-3</th>
<th>BC-4</th>
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<td>135.0</td>
<td>0.92</td>
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</tr>
<tr>
<td>Na⁺</td>
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<td>8.98</td>
<td>2.28</td>
<td>4.98</td>
<td>2.86</td>
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<tr>
<td>Ca²⁺</td>
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<td>16.64</td>
<td>9.68</td>
<td>11.84</td>
<td>10.94</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4.82</td>
<td>3.68</td>
<td>0.98</td>
<td>1.52</td>
<td>1.54</td>
</tr>
</tbody>
</table>

![FIG. 6. Sequential sorption of Cr species onto BC-3: (a) Cr(III) was firstly added; (b) Cr(VI) was firstly added.](image1.jpg)

![FIG. 7. Cr sorption isotherms of SMBs at pH = 2.4.](image2.jpg)
Effects of pH

First, the isotherms of SMBs were obtained at pH = 2.4 (the added H\(^+\) was 25% of that in equilibrium studies), as given in Fig. 7. Comparing the isotherms with those in Fig. 3, it was found that different SMBs showed varied performance. BC-1 gave markedly inferior sorption except at quite low \(C_e\) range. BC-2 exhibited slightly increased sorption at low \(C_e\) range. For BC-3 and BC-4, the sorption was notably improved at low \(C_e\) range. All of these isotherms reached a plateau at high \(C_e\) range caused by the exhaustion of proton. Obviously, the presence of redundant proton, which competed with Cr for active sorption sites, had a negative effect on the sorption at low \(C_e\) range. This effect was more evident for the over protonated SMBs. Hence, the observed poor sorption of BC-3 and BC-4 at low \(C_e\) range (Fig. 3) was partially resulted from this effect.

Then, tests were carried out at a wide pH range from 1.8 to 7.8, using BC-3 at \(C_0 = 180\) mg/L (Fig. 8). As can be seen, Cr (VI) removal was favorable under strongly acidic conditions. The sorption amount of total Cr was high at pH 1.8~3.1, which dropped gradually at elevated pHs. The aqueous Cr(VI) showed a sharp rise with the increase of pH, even at pH 3.1 when the sorption was still strong. The aqueous Cr(III) dropped sharply at pH above 3.1. The SCR values were measured as 95.3, 88.4, 93.4, 94.9, 94.1, and 91.7% at pH 2.2, 3.1, 5.5, 6.3, 6.8, and 7.8, respectively. Accordingly, the sorbed Cr was mainly constituted of Cr(III) even under basic condition. Hence, the decrease in Cr sorption with pH increase was ascribed mainly to the abatement in Cr(VI) reduction.

Effects of Temperature

The sorption performance of SMBs was studied at various temperatures, as demonstrated in Fig. 9. An increase in temperature caused complex effects upon the sorption, which were related to the equilibrium concentration. At low range, it was interesting to see that the sorption was slightly decreased with an increase in temperature. At high range, the sorption was prominently enhanced for all SMBs. Taking BC-3 as an example, the evolution of aqueous Cr species with temperature at various initial concentrations (\(C_0\)) is plotted in Fig. 10. In general, there were minor

![Fig. 8. Effects of pH on Cr sorption and aqueous Cr species.](image)

![Fig. 9. Effects of temperature on the sorption of Cr: (a) BC-1; (b) BC-2; (c) BC-3; (d) BC-4.](image)
variations in aqueous Cr(III) at the same $C_0$, except for a noticeable decrease at high $C_0$ at 45°C. In contrast, a remarkable drop in aqueous Cr(VI) took place.

The slight decrease at low range with temperature increase should be ascribed to the higher kinetic energy of Cr species. The opposite trend at high range was closely associated with an increase in the oxidation potential of Cr(VI). As proved by the change of aqueous Cr species, Cr(VI) was reduced more heavily at high temperature, which favored the formation of new surface groups and the deprotonation of biochar surface. The promotion of diffusion process with temperature increase also made its contribution.

Removal Kinetics of Cr(VI)

The sorption kinetics of total Cr onto BC-3 at various initial concentrations is displayed in Fig. 11. As can be seen, the sorption amount rose rapidly at the start, caused by the fast sorption of Cr(VI) through electrostatic attraction. Afterwards, it increased at a lower rate, corresponding to the diffusion, reduction, and complexation of Cr species.

The evolution of SCR and aqueous Cr species with time at $C_0 = 180$ mg/L is shown in Fig. 12. The aqueous Cr(VI) dropped sharply at the start. Meanwhile, the SCR increased gradually from 74.4% at 0.5 h to 92.5% at 32 h. Accordingly, the reduction of Cr(VI) on biochar surface proceeded at a high rate. The aqueous Cr(III) reached 8.9 mg/L at 0.5 h and showed limited increase afterwards, although an ever increasing amount of Cr(III) was present on biochar surface.

CONCLUSIONS

The pretreatment of wheat straw using $\text{H}_3\text{PO}_4$ promoted the development of biochar porosity, and introduced abundant oxygen-containing groups. The removal of Cr(VI) from aqueous solutions was largely enhanced using SMBs, with a maximum sorption amount of 188.1 mg/g. Various SMBs gave the best sorption in varied $C_e$ range. The surface physical and chemical characteristics influenced the sorption behavior of Cr. The electrostatic force also played an important role in the sorption. The removal of Cr(VI) was favorable at low pHs, but redundant proton affected Cr(III) sorption at low $C_e$, especially for over protonated SMBs. The abatement in Cr(VI) reduction with pH rise was responsible for a decrease in Cr sorption. With temperature rise, the reduction of Cr(VI) was enhanced, which made contribution to an increase in Cr sorption at high concentration.
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