Effects of Pyrolysis Temperature on ZnCl$_2$ Impregnated Corn Straw-derived Biochar Properties and Vanadium (III, IV, V) Adsorption in Aqueous Solution

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Keywords: Corn straw, Adsorption capacity, Vanadium (III, IV, V), Pyrolysis temperature, Adsorption mechanism.

Abstract. In this study, corn straw derived biochars were prepared at different temperatures of 300, 500, 700°C, respectively, and the characteristics of corn straw biochars were investigated. Additionally, the adsorption behaviors of vanadium (III, IV, V) on biochars were systematically studied by batch experiments. The absorbents were characterized by ion-exchange capacity (IEC), X-ray Diffraction, N$_2$ adsorption-desorption, and FTIR. The yield of biochar decreases with the increase of pyrolysis temperature. The more ash content is retained, the more alkaline biochar is. The specific area of biochars increased with the rising pyrolysis temperature. With the increase of temperature, the structure became porous and the content of surface functional group elements remained low. Although the content of zinc in biochar is relatively high, the leaching toxicity of biochar does not exceed the Chinese standard. The adsorption capacity of biochars for vanadium (V) decreased under high temperature (700°C). In the contrast, The adsorption capacities of biochars for vanadium (IV) and vanadium (III) improved under high temperature. The adsorption mechanisms for vanadium (V), vanadium (IV) and vanadium (III) were surface complexation, which can be proved by FTIR analysis.

Introduction

Mining and smelting of vanadium have caused widespread pollution in many countries, such as Russia, South Africa and China. For instance, many studies have been reported about vanadium-contamination, especially in China, such as Sichuan province, Hubei province, Hunan province. Leaching from contaminated soil and vanadium tailings led to high accumulation of vanadium in groundwater recharging to waters. The concentration of vanadium in groundwater detected in the investigated area is between 1-30 mg/L, which is dozens of times or even hundreds times higher than the drinking water standard (0.05mg/L) according to California Department Public of Health’s emergency standard and China’s drinking water standard (GB 5749-2006). Therefore, it is crucial to remove concentrated vanadium from aqueous solutions.

Vanadium has various valence states of +3, +4 and +5, and vanadium (V) is most commonly present as a vanadate oxyanion (e.g., VO$_4^{3-}$, VO$_3^-$, H$_2$VO$_4^-$ and HVO$_4^{2-}$). Vanadium (V) is considered to be the most toxic and highly migratory, while vanadium (IV) is insoluble at a neutral pH and less toxic (Wang and Ren, 2014). Vanadium(II) is unstable in the environment. Vanadium(III) is more stable than Vanadium (II), but it is also easily oxidized in the air. Vanadium(V) is is the main form of water in the environment, whereas Vanadium(IV) may exists in the reduction environment (Wang and Sañudo Wilhelmy, 2009). The treatment of metal contaminated wastewater includes chemical precipitation, ion exchange, adsorption and coprecipitation. Among these, adsorption is one of the most promising water pollution control
technologies. Biochar is one of the main by-products of pyrolyzing biomass under anoxic conditions. It can be used to remove heavy metals from groundwater and wastewater. Biomass waste from agriculture, industry and forestry is used as raw materials (Glaser et al. 2001; Downie et al. 2009). In China, annual crop straw production is expected to be about 600 million tons, including 250 million tons of corn straw. The utilization of corn straw is beneficial to reduce the storage of straw and air pollution caused by burning (Sharratt et al., 2006). If biochar prepared from corn straw can effectively remove organic and inorganic pollutants, it will be used as a low-cost carbon-based adsorbent to effectively treat wastewater.

The pyrolysis process has a significant impact on the surface properties, carbonization degree and pyrolysis process of biochar, including temperature, pyrolysis time, raw materials and other factors (Li et al., 2014; Low et al., 2015). In particular, pyrolysis temperature is the most important factor, because the release of volatiles and low-boiling compounds from biomass is closely related to temperature. It has been reported that when the pyrolysis temperature increased from 300°C to 800°C, the carbon content of biochar increased from 56% to 93%, while the biochar yield decreased from 67% to 27% (Okimori et al.). Day et al. (Day et al., 2005) found that the biochar surface area increased from 120 at 400 to 460 m²/g at 900°C. These authors also observed that biochar created at low temperatures may be suitable for controlling the release of nutrients in soils, but have hydrophobic properties and may limit the capacity for soil water storage. Song and Guo (Song and Guo, 2012) studied the quality of poultry litter biochar generated at different pyrolysis temperatures and concluded that for agricultural use, a low pyrolysis temperature, between 300 and 500°C, was adequate. Ippolito et al. (Ippolito et al., 2012) observed that surface area, pH, ash content and total surface charge increases with pyrolysis of switchgrass from 250 to 500 °C. Kloss et al. (Kloss et al., 2012) observed that the H/C ratio and surface area increased and the cation exchange capacity CEC decreased in biochar prepared from straw and woodchips at 525 °C with respect to biochar prepared at 400 °C. Wang et al. concluded that increasing pyrolysis temperature from 500 to 700°C resulted in decrease in biochar yield, total acidic functional groups, cation exchange capacity, and N content and increase in BET surface area, ash content, pH, and total Ca and P contents (Wang et al., 2013).

Although some studies have explored the influence of temperature on the physical and chemical properties of biochar, the relationship between the physical and chemical properties of biochar and its adsorption capacity to remove pollutants in aqueous solutions needs to be further investigated (Kloss et al., 2012; Sun et al., 2014; Wang et al., 2015). In addition, previous studies focused on the influence of surface properties of biochar on their adsorption performance in terms of heavy metals, such as copper and nickel (Uchimiya et al., 2011a; Ding et al., 2014; Inyang et al., 2015). Therefore, it is necessary to study the effect of biochar's physicochemical properties on vanadium (III, IV, V) adsorption. In order to meet these needs, the physicochemical properties of corn straw biochar at different pyrolysis temperatures were systematically studied. The adsorption behavior of vanadium (III, IV, V) on biochar was investigated systematically to expand the previous studies on the relationship between adsorption capacity and physicochemical properties. In this study, biochar was prepared with ZnCl₂ impregnated with corn straw at different pyrolysis temperatures (300°C, 500°C and 700°C). The obtained biochars were characterized by Fourier-transform infrared spectroscopy (FT-IR), thermal analysis, and X-ray diffraction (XRD). The adsorption of vanadium (III, IV, V) on the obtained biochars were carried out by batch sorption experiments. The objectives of this study were (1) to reveal the effects of the pyrolysis temperature on the physicochemical properties of biochar, and (2) to elucidate the linkage between the physicochemical properties of biochars and their sorption abilities. The purpose of this study were (1) to reveal the influence of pyrolysis temperature on the physicochemical properties of biochar; (2) to illuminate the relationship between adsorption capacity of biochar and physicochemical properties

Material and Methods

Materials

All chemicals used in the present work were analytically pure. All the working solutions of different concentrations were obtained by diluting the stock solution with deionized water. NH₄VO₃,
VO\textsubscript{3}O\textsubscript{4}, VCl\textsubscript{3} were obtained from Tianjin Guangfu Fine Chemical Research Institute, China. Corn straw raw material was collected from the suburb of Xinle, Hebei, China.

**Preparation of Biochars**

Raw corn straw was dried in air for 48 h, and then heated at 80 °C to constant weight. The dried corn straw was powdered and seized by 0.45 mm mesh for further chemical modification. ZnCl\textsubscript{2} impregnated corn straw was prepared according to the following procedures (Namasivayam and Sangeetha, 2006). Corn straw was impregnated with zinc chloride solution with a weight ratio of 2:1. The filtered material was washed and dried and finally carbonized at 700°C, 500°C and 300°C, respectively. Biochar was prepared by fast pyrolysis according to the method reported by Chen et al., which was conducted in a tube furnace. Fast pyrolysis was conducted at different pyrolysis temperature with N\textsubscript{2} as internal shielding gas. Corn straw in heating area were kept for 0.5 h. The resulting biochars were sieved to obtain particles from 40 mesh (0.45 mm) Chen et al., 2014). The obtained biochars were denoted as CS-700, CS-500 and CS-300, respectively.

**Characterization of Biochars**

**General Nature.** The biochar was calcined at 650°C for 2h to constant weight in muff furnace, and the mass residual percentage of the sample was ash content. The element analysis of C/H/O/N in biochar was detected by elemental analyzer (EuroVector, EA3000, Italy). Biochar and deionized water were mixed to determine pH at a ratio of 1:10 (w/v). The measurement method of zero charge point refers to Mahmood et al. (2011). The ion exchange capacity (IEC) of biochar was tested using ion exchange method proposed by Hu et al. (2000). Due to the residual zinc in biochar, it is necessary to determine the leaching toxicity of heavy metals in biochar. The extraction methods of leaching toxicity was using nitric acid and sulfuric acid method according to the Chinese standard HJ/T 299-2007. The heavy metal concentration in the biochar and solution was deteted by ICP-OES (Prodigy7, Leeman Labs, USA). The thermogravimetric (TG) curves were obtained from a thermogravimetric system (STA 409C, NETZSCH, German).

**Surface Characters.** The pore characteristics and surface area of the biochar were measured by the N\textsubscript{2} adsorption-desorption isotherm with a gas sorption apparatus (Autosorb-1-C, Quantachrome, USA). The samples were outgassed at 200°C for 4 h. Crystalline structure was analysed through XRD with an X-ray diffractometer (D8 advance, Bruker, Germany), which was operated at 40 mA and 40 kV under Cu K\textalpha radiation. Characteristic functional groups in the adsorbents were analysed through FTIR (Spectrum GX, Perkin Elmer, USA), with wave number in the region of 4000-400 cm\textsuperscript{-1}.

**Adsorption Experiments.**

Adsorption of vanadium (III, IV, V) onto biochar was studied by batch experiments with the blank solution as control. The raw solutions of vanadium (III), vanadium (IV) and vanadium (V) were prepared by dissolving VCl\textsubscript{3}, VO\textsubscript{3}O\textsubscript{4} and NH\textsubscript{4}VO\textsubscript{3} in deionized water, respectively. Before adsorption, the pH levels of vanadium (III, IV, V) solutions were measured as initial pH.

Adsorption experiments were carried out by agitating 25 mg of adsorbent with 25 mL of vanadium (III, IV, V) solution of different initial concentration (0-250 mg/L) in a vortex maker for 72 h at 200 rpm, 25 °C. At the end of adsorption, the residual solutions were filtered with 0.45 μm polysulfone filter membrane. The concentrations of vanadium (III, IV, V) in the residual solutions were determined by ICP-OES. In the adsorption experiment, the adsorbent was added into vanadium solution with different initial concentration with an amount of 1g/L. The mixture was oscillated in the oscillator for 72 h at 200 rpm. After equilibrium, the supernatant was filtered with 0.45 μm, and the supernatant concentration was determined by ICP-OES (Prodigy7, Leeman Labs, USA).

The removal capacity of vanadium (III, IV, V) were calculated as follows:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]
where $q_e$ is the uptake of vanadium (III, IV, V) at equilibrium (mg/g); $C_e$ and $C_0$ are the equilibrium and initial concentrations of vanadium (III, IV, V) (mg/L); $m$ is the weight of biochar (g) and $V$ (L) is the volume of the solution (L).

**Sorption Isotherm Models**

In this work, Langmuir model and Freundlich model were used to fit isotherm data, as presented in Eq(2) and Eq(3), respectively:

\[
q_e = \frac{Q_{\text{max}} K L C_e}{1 + K L C_e} \tag{2}
\]

\[
q_e = K_F C_e^{1/n} \tag{3}
\]

where $Q_{\text{max}}$ (mg/g) is the theoretical maximum adsorption capacity of the biochar. $K_L$ (L/mg) is the Langmuir isotherm constant. $K_F$ ((mg/kg)/(mg/L)$^n$) and $1/n$ are the sorption affinity and the nonlinearity index, respectively.

**Results and Discussion**

**Characteristics of Biochars**

| Parameter       | CS-700          | CS-500          | CS-300          |
|-----------------|-----------------|-----------------|-----------------|
| Yield percentage/wt.% | 30.79±0.56 | 40.95±0.29 | 50.16±0.28 |
| Ash content percentage/wt.% | 20.55±0.33 | 9.44±0.15 | 3.64±0.16 |
| Elemental analysis/wt.% |          |          |            |
| C               | 76.17±0.76      | 52.43±0.51     | 33.26±0.34     |
| H               | 1.88±0.13       | 2.76±0.03      | 3.55±0.01      |
| O               | 5.58±0.15       | 10.06±0.31     | 20.3±0.02      |
| N               | 0.96±0.03       | 0.98±0.01      | 1.14±0.04      |
| Atomic ratio    | C+H+O+N         | 84.60          | 66.23          | 58.25          |
|                 | H/C             | 0.025          | 0.053          | 0.107          |
|                 | O/C             | 0.073          | 0.192          | 0.610          |
|                 | (O+N)/C         | 0.086          | 0.211          | 0.644          |
| pH(S/L=1:10)    | 6.64            | 7.05           | 6.94           |
| pH_{PZC}        | 6.98            | 7.21           | 7.06           |
| CEC (cmol/kg)   | 47.68           | 57.72          | 82.97          |
| Zinc leached (%)| 0.02            |                |                |

The properties of the biochars, including ash content, yield rate, elemental composition, pH, CEC and pH_{PZC} are shown in Table 1. The percentage of CS-300, CS-500 and CS-700 yield rate is 50.16%, 40.95%, 30.79% respectively. As the pyrolysis temperature rises from 300 to 700°C, the percentage of ash content in the biochars reduces by ten percents from 50.16% to 30.79%. The elemental content of biochars showed relative increase in C and decrease in H, O, and N with rising pyrolysis temperature (Table 1). For example, CS-700 was the most carbonized biochar, and its carbon mass percentage was 76.17%. Atomic ratios of O/C (0.610 - 0.073), H/C (0.107 - 0.025), and (O + N)/C (0.644 -0.086) decreased with rising pyrolysis temperature. Keiluweit et al. reported that H/C and O/C atomic ratios of the biochars with a range of pyrolysis temperature increasing from 100°C to 700°C (Uchimiya et al., 2011). The lower O/C ratio (0.073) in CS-700 indicated that the hydrophilicity of biochar surface was poor at high pyrolysis temperature. The polarity index decreased, suggesting that the content of polar groups decreased as the pyrolysis temperature increased.

Surface charges of biochar were characterized by ion exchange capacity (IEC) and pH_{PZC}. The
pH<sub>PZC</sub> indicates the acid or basic character of the adsorbent surface. At pH < pH<sub>PZC</sub> (point of zero charge), the biochar surface is positively charged, which is beneficial to anion adsorption. While at pH > pH<sub>PZC</sub>, the surface charge of biochar is negative, which is favorable for adsorbing cations. The pH<sub>PZC</sub> value of the biochars is neutral, because of Acid washing during prepared progresses. This result indicates that when the solution is acid or neutral, their surface is positive charged and will attract the metal anions. The CEC biochars values in our work differed obviously with rising pyrolysis temperature from 300°C to 700°C (Table 1).

Surface Property of Biochar

The specific surface areas of biochars enhanced from 23.288 m²/g for CS-300 to 139.708 m²/g for CS-700 (Table 2). In a literature review, Ahmad et al. reported that specific surface area of the biochars increased from 0 to 490.8 m²/g with pyrolysis temperature ranging from 100°C to 900°C (Ahmad et al., 2014). The increase of pyrolysis temperature led to a significant increase in the surface area of biochar (Ahmad et al., 2014). Our results were consistent with those reports.

The pore diameter distribution of biochar is similar to the peak level (about 1.4 nm), as shown in Figure 1b. According to the classification of IUPAC (Sing et al., 1985), the pores of the biochars are mainly mesopores (pores of widths under 2 nm). The N<sub>2</sub> adsorption–desorption isotherms of all the adsorbents correspond to a similar Type IV isotherm and Type H4 hysteresis loop behavior.

XRD Analysis and Thermal Stability of Biochars

XRD technique is a powerful tool to analyze crystalline nature of materials. The XRD result of biochar is displayed in Figure 2(a). There was a significant difference observed in biochars with different pyrolysis temperatures. Cs-300 has broad peaks and no obvious amorphous structure peak, which is a favorable property for well-defined adsorbents. In the CS-300, a broad peak appearing at 20 = 21.8° was referred to the characteristic crystalline structure of cellulose. The crystal structure of the cellulose did not change significantly after the reaction of the carbonization process. Additionally, this obtained amorphous structure could provide a rapid pathway for ion exchange between the heavy metal solution and the fibers. The peak strength significantly decreased after carbonization with high pyrolysis temperature, due to the decomposition of the cellulose. The diffraction peak intensity of CS-500 and CS-700 is high, which indicated that the zinc chloride on
CS might cause bulk phase transition. In addition, the XRD pattern of CS-700 sharply peaked at $2\theta = 11.4^\circ$ (003), which was due to the existence of zinc carbides and zinc oxide on the washed CS-700 surface. The peak sharpness suggested that zinc was still in the micro range (Danish et al., 2013).

The weight loss of the biochar was continuous in the range of 38-1000 °C, as shown in Figure 2b. In general, the thermal degradation of carbon-based materials went through three stages. (Zhang et al., 2012). In the first stage, surface water loss occurred in the temperature range of 50 to 100 °C. The second stage, the surface functional group loss occurs in the temperature range of 100-350 °C. In the final stage, when the temperature exceeded 350 °C, the carbon skeletons began to decompose. As the temperature rose from 350 to 700 °C, the weight of CS-700 dropped steadily(Figure 2b). The decomposition curves of CS-300, CS-500 and CS-700 are almost different at 700-1000°C, and the thermal stability of CS-700 is better than that of CS-500 and CS-300.

**Adsorption Isotherm**

The vanadium (III, IV, V) adsorption isotherms were studied at different initial vanadium (III, IV, V) concentrations, as summerized in Figure 3. The adsorption capacity of CS-300 and CS500 prepared in lower pyrolysis temperature were higher than that of CS-700 prepared in high pyrolysis temperature. Whereas, for vanadium (III) and vanadium (IV), in lower states, the opposite trends were observed. These results indicated that the adsorption mechanisms of vanadium in different valence states differed.

Experimental data were further fitted with Langmuir (Eq. (2)) and Freundlich (Eq. (3)) adsorption isotherm models. The adsorption correlation coefficients and constants of Freundlich and Langmuir isotherms for vanadium (III, IV, V) onto the biochars were shown in Table 3. Correlation coefficients indicated that the both Freundlich model and Langmuir model can fit the data well ($R^2 = 0.8735-0.9959$ for Langmuir model and 0.8708-0.9988 for Freundlich model). Parameters such as $Q_{max}$ are important for optimizing the design of the adsorption system. The $Q_{max}$ (maximum adsorption capacities) obtained from the Langmuir equation were given in the table 3.

![Figure 2. Characterization of different adsorbents. (a) XRD pattern of CS-300, CS-500 and CS-700; (b) TGA profiles of CS-300, CS-500 and CS-700.](image)

![Figure 3. Adsorption performance of vanadium (III, IV, V) onto different adsorbents. Equilibrium conditions: adsorbent dosage 1g/L, 25.0 ± 1.0°C. (a) Adsorption isotherms of vanadium (III) by CS-300, CS-500 and CS-700. (b) Adsorption isotherms of vanadium (IV) by CS-300, CS-500 and CS-700. (c) Adsorption isotherms of vanadium (V) by CS-300, CS-500 and CS-700.](image)
Table 3. Langmuir and Freundlich parameters for vanadium (III, IV, V) adsorption on the biochars.

| Absorbents | Adsorbate      | Freundlich       | Langmuir       |
|------------|----------------|------------------|----------------|
|            |                | $k_F$  | $1/n$ | $R^2$ | $Q_{max}$ | $k_L$ | $R^2$ |
| CS-700     | vanadium (V)   | 9.7554 | 0.1487 | 0.8708 | 20.3042 | 0.2288 | 0.8735 |
|            | vanadium (IV)  | 2.9475 | 0.4143 | 0.9331 | 20.7516 | 0.0604 | 0.9602 |
|            | vanadium (III) | 3.1047 | 0.4943 | 0.9864 | 34.5070 | 0.0403 | 0.9954 |
| CS-500     | vanadium (V)   | 3.4937 | 0.4722 | 0.9842 | 41.5809 | 0.0265 | 0.9699 |
|            | vanadium (IV)  | 1.0659 | 0.6790 | 0.9864 | 36.7338 | 0.0148 | 0.9904 |
|            | vanadium (III) | 1.7043 | 0.5682 | 0.9636 | 33.2635 | 0.0212 | 0.9825 |
| CS-300     | vanadium (V)   | 2.3140 | 0.5754 | 0.9674 | 47.0828 | 0.0205 | 0.9857 |
|            | vanadium (IV)  | 0.8921 | 0.7163 | 0.9960 | 37.6906 | 0.0134 | 0.9959 |
|            | vanadium (III) | 1.1987 | 0.6637 | 0.9988 | 43.2247 | 0.0131 | 0.9956 |

FTIR Analysis

FTIR analysis technique was used to characterize main functional groups on the surface of biochar. The FTIR spectra of absorbents and absorbents +V (after adsorption of vanadium on biochars) were summerized in Figure 4. Comparison of the FTIR spectra showed that the CS after carbonization have fewer absorption bands. The FTIR spectrum of CS-300, CS-500 and CS-700 also exhibits a broad absorption band at 3431 and 3458 cm$^{-1}$, which is referred to the overlap of different vibrations of O-H, C-H, and N-H groups. At wave number 1617 cm$^{-1}$ in CS-300 and CS-500 is referred to the carbonyl group C=O group and C=C group present in aldehyde, ester, ketone and acetyl derivatives. The C=O, -OH, and -CH groups might be responsible for the adsorption of vanadium (III, IV, V).

Changes in the function groups of adsorbents were obvious after vanadium (III, IV, V) sorption (Figure 4). After vanadium (III, IV and V) sorption, the peaks at 800-1000 cm$^{-1}$ appeared in CS-700, CS-500 and CS-300, which were assigned to vanadium oxide (Fan et al., 2013). These changes showed that carboxylate and hydroxyl groups may be involved in vanadium (III, IV and V) removal, which are consistent with other studies (Komy et al., 2006; Wang et al., 2010).

Figure 4. FTIR spectra of the biochars before and after treatment with vanadium (III, IV, V).
Adsorption Mechanism

In general, the possible adsorption mechanisms of heavy metals included various interactions, such as pore filling, ion-exchange, surface precipitation and/or complexation for metal anions and electrostatic attraction (Tan et al., 2015).

After vanadium (III, IV and V) sorption, the peaks at 800-1000 cm\(^{-1}\) appeared in CS-700, CS-500 and CS-300, which were assigned to vanadium oxide (Fan et al., 2013). According to FTIR analysis, it was concluded that surface complexation between zinc on the surface of the biochars and H\(_2\)V\(_2\)O\(_7\)\(^{2-}\) is the main adsorption mechanism of vanadium (V) on the obtained biochar in this work.

Conclusion

In the present study, CS were converted into the biochars with different pyrolysis temperatures (300°C, 500°C, and 700°C). The obtained biochar were characterized for their BET surface area, porosity, element analysis, and pH\(_{ZPC}\), element analysis, XRD and FTIR spectroscopy.

As the temperature increased, the content of functional group elements on the surface of biochar remained low, and the structure becomes porous. Although the content of zinc in biochar is relatively high, the leaching toxicity of biochar did not exceed the Chinese standard.

The adsorption capacity of biochars for vanadium (V) decreased at high temperature (700°C). While the adsorption capacities of biochars for vanadium (IV) and vanadium (III) improved. The adsorption mechanisms for vanadium (V), vanadium (IV) and vanadium (III) were surface complexation, which can be confirmed by FTIR analysis.

Aknowledgements

The authors gratefully acknowledge the financial support of the National Key Research and Development Program of China (2018YFE0196000) and the Critical Patented Projects in the Control and Management of the National Polluted Water Bodies (No. 2015ZX07205-003).

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