Adsorption of cadmium by biochar produced from pyrolysis of corn stalk in aqueous solution
Fengfeng Ma, Baowei Zhao and Jingru Diao

ABSTRACT
The purpose of this work is to investigate adsorption characteristic of corn stalk (CS) biochar for removal of cadmium ions (Cd\(^{2+}\)) from aqueous solution. Batch adsorption experiments were carried out to evaluate the effects of pH value of solution, adsorbent particle size, adsorbent dosage, and ionic strength of solution on the adsorption of Cd\(^{2+}\) onto biochar that was pyrolytically produced from CS at 300 °C. The results showed that the initial pH value of solution played an important role in adsorption. The adsorptive amount of Cd\(^{2+}\) onto the biochar decreased with increasing the adsorbent dosage, adsorbent particle size, and ionic strength, while it increased with increasing the initial pH value of solution and temperature. Cd\(^{2+}\) was removed efficiently and quickly from aqueous solutions by the biochar with a maximum capacity of 33.94 mg/g. The adsorption process was well described by the pseudo-second-order kinetic model with the correlation coefficients greater than 0.986. The adsorption isotherm could be well fitted by the Langmuir model. The thermodynamic studies showed that the adsorption of Cd\(^{2+}\) onto the biochar was a spontaneous and exothermic process. The results indicate that CS biochar can be considered as an efficient adsorbent.

Key words | adsorption, biochar, cadmium, corn stalk

INTRODUCTION
Traditional techniques to removal cadmium from wastewater include ion exchange, reverse osmosis, precipitation, membrane separation, solvent extraction and adsorption. Among these techniques, adsorption is considered to be one of the simplest, most economical and effective ways to removal cadmium from aqueous solution (Kılıç et al. 2015). Especially for the treatment of a very large amount of wastewater with low concentration of cadmium, adsorption has been demonstrated to be the most cost-effective method. The key to the adsorption technique lies in the effectiveness of adsorbent. Due to their unique porous structure and surface chemistry, activated carbon, graphene and carbon nanotubes exhibit strong adsorptive affinity to heavy metals and are the most popular adsorbents for the application in wastewater treatment (Tan et al. 2015a). However, their application in wastewater treatment on a large scale is limited due to their expensive price. In addition, release of nano-adsorbents into air, water, and soil could cause potential toxicity to humans and organisms (Wang et al. 2011). Therefore, novel adsorbents with abundant availability, that are environmentally friendly, low-cost and have a high adsorption capacity are urgently needed for application to reduce heavy metal pollution of water.

Researchers have recently focused on biochar as a novel adsorbent for the treatment of heavy metal-polluted wastewater (Bogusz et al. 2015). Biochar is a carbon-rich and solid byproduct produced by pyrolysis of biomass under oxygen-limited conditions, such as sludge, agricultural waste and manure (Tan et al. 2015b). Biochar is a potential low-price adsorbent with stronger adsorption capacity and is frequently applied to remove various pollutants, such as heavy metals, pesticides and dyes from wastewater (Deveci & Kar 2015). The effectiveness of biochars in removing heavy metals from wastewater, however, varies greatly among different types of biochars and can be significantly influenced by several factors including feedstock type, processing conditions, and production methods. It is important that the choice of precursor materials will have an effect on the adsorption capacity of different biochars, especially for heavy metals.

In recent years, researchers are seeking the potential of using various high-efficiency biochars derived pyrolytically...
from agricultural wastes, industrial solid wastes and natural materials as the precursors (Tan et al. 2015b). According to the previous literature, the adsorption capacity of the biochars for Cd$^{2+}$ increased in the order of wood and bark < dairy manure < crop straw (Ahmad et al. 2013; Vladimir et al. 2014). Obviously, choice of feedstocks for preparing biochars is critical as the raw materials often determine the adsorption performance and capacity of resultant biochars. Corn is widely cultivated as a major food crop in China. Therefore, a large number of corn stalk (CS) as agriculture residuals is co-generated with the grain each year. It is estimated that approximately 47,097 million tons of CS are generated each year in China (Chen et al. 2014). However, most of the CS residuals are not adequately used. Burning of CS residuals in the farmland is a usual exercise of disposal of crop waste and land preparation in China, which releases a mass of pollutants into the environment and causes severe environmental problems (Zhang et al. 2013). As a result of abundant availability and high carbon content, CS residuals can be used as a precursor of biochar for the treatment of heavy metal-polluted wastewater.

In this study, the biochar is obtained from CS residuals through slow pyrolysis at 300 °C. This temperature was selected based on the previous research (Tan et al. 2015b), in which the prepared biochar had a greater adsorption capacity for heavy metals and superior balance between the energy costs and biochar yield. The specific objectives of this work are to: (1) prepare CS biochar and characterize its physicochemical properties; (2) determine the adsorptive characteristics of Cd$^{2+}$ onto the biochar; (3) examine Cd$^{2+}$ adsorptive kinetics and isotherms onto biochar.

**MATERIALS AND METHODS**

**Preparation of biochar**

CS was collected from farmland near Wuwei, Gansu Province, China. CS was air-dried for one week, then crushed into pieces and ground into particles with a diameter less than 0.18 mm. The powdered CS was tightly placed in a ceramic pot. The filled pot was covered with a lid for pyrolysis in a muffle furnace (KSW 12-11, Shanghai Laboratory Equipment Company Limited, China) under an O$_2$ limited atmosphere. The starting temperature was fixed to 100 °C for 1 h. Then the temperature was elevated to 300 °C at a rate of 20 C/min and maintained for 6 h. After cooling to room temperature, the biochar was gently ground and sieved through a 0.18 mm mesh. Then, the produced biochar was washed with 0.1 M HCl, which was followed by deionized water flushing until the liquid part reached a neutral pH. A 0.1 M HCl was selected to wash biochar in order to decrease pH values of biochar and also to remove dissolved organic matter, some nutrients and carbonates. The obtained biochar was referred to as CSBC.

**Characterization**

The yield (%) of CSBC was obtained by the following equation: yield (%) = (weight of CSBC)/(weight of CS) × 100. The ash content of CSBC was determined as follows: 1.00 g of CSBC was heated at 800 °C for 2 h in a muffle furnace and the ash (%) was obtained from the equation: ash (%) = (weight of ash)/(weight of CSBC) × 100. The pH value of CSBC was measured in deionized water at the ratio of 1:10 w/v CSBC/water with a pH meter (PHS-3C, Shanghai Analytical Instrumental Company, China). The C, H, and N contents in CS and CSBC were determined on a varioELcube elemental analyzer (Heraeus, Germany), and the O content was determined by a mass balance. The H/C and (O + N)/C ratios were calculated to evaluate the aromaticity and polarity of CS and CSBC, respectively. The pore structure parameters of CSBC were measured by N$_2$ sorption measurements using a surface area analyzer (Micromeritics ASAP 2010, USA), the specific surface area (SSA) was calculated with the multipoint Brunauer–Emmett–Teller method, and the pore volumes were measured using the Barrett–Joyner–Halenda equation. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) analysis of CSBC were obtained using a SEM (JSM-5600LV, Japan) operated at 20 kv. Fourier transform infrared (FTIR) spectra were carried out on Nexus870 FTIR spectrophotometer (USA). X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250 Xi system (Thermo Fisher Scientific, USA) with a Monochromated Al Kα X-ray radiation source and a hemispherical electron analyzer. Thermogravimetry-differential thermal analysis of CSBC was conducted using a thermoanalyzer (Netzsch STA 449F3, Germany) to determine weight changes during heating and heat release.

**Batch adsorption experiments**

The adsorptive kinetics experiments were carried out by adding 0.1 g of CSBC to 20 mL of Cd$^{2+}$ solution (50 and 100 mg/L) in a glass bottle at 25 °C on a reciprocating shaker (CHA-S Shaker, Jintan Danyang Instrumental Company, China). At appropriate intervals (0.17–24 h), aliquots
of solution were taken from the glass bottle and immediately filtered through 0.45 μm nylon membrane. The Cd$^{2+}$ concentrations were determined using an atomic absorption spectrophotometer (AA110/220, Varian Co. Ltd., USA). The adsorptive isotherm experiment was determined by mixing 0.1 g of CSBC with 20 mL of Cd$^{2+}$ solution with the concentrations in the range of 10–500 mg/L. The glass bottles were shaken in the reciprocating shaker for 24 h. Then, the mixtures were separated by filtration to determine the remaining Cd$^{2+}$ concentration in solution.

The impact of pH value of solution on the Cd$^{2+}$ adsorption onto CSBC was investigated with 100 mg/L of the initial Cd$^{2+}$ concentration and the pH values that were adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0, using 0.1 M NaOH and 0.1M HNO$_3$. To test the effect of adsorbent dosage, the dosage was varied between 5 and 25 g/L. The adsorptive isotherm experiment was determined by mixing 0.1 g of CSBC with 20 mL of Cd$^{2+}$ aqueous solution (mg/L), and the concentrations in the range of 10–500 mg/L. The glass bottles were shaken in the reciprocating shaker for 24 h. Then, the mixtures were separated by filtration to determine the remaining Cd$^{2+}$ concentration in solution.

Adsortion models

In order to examine the processes governing the adsorption of Cd$^{2+}$ onto CSBC and its adsorption capacity, kinetic studies were performed and a number of well-known adsorption models were applied. The pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models were used to fit the kinetic data, and the equations are listed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \text{pseudo-first-order}$$

(3)

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \text{pseudo-second-order}$$

(4)

$$\frac{dq_t}{dt} = \alpha \exp (-\beta q_t) \quad \text{Elovich}$$

(5)

$$q_t = h d^{1/2} + C_i \quad \text{intra-particle diffusion}$$

(6)

where $q_t$ (mg/g) and $q_e$ (mg/g) are the amount of Cd$^{2+}$ adsorbed at time $t$ (h) and at equilibrium, respectively; $h_1$ (h$^{-1}$), $h_2$ (g/mg/h), and $h_3$ (mg/g/h$^{-1/2}$) are the pseudo-first-order, pseudo-second-order, and intra-particle diffusion sorption rate constants, respectively; $\alpha$ (mg/g/h) is the initial adsorption rate, $\beta$ (g/mg) is the desorption constant, and $C_i$ is the intercept reflecting the boundary layer thickness.

Langmuir, Freundlich, Langmuir-Freundlich, and Temkin were used to fit the isotherm experimental data, and the equations are:

Langmuir equation: $q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$

(7)

Freundlich equation: $q_e = K_F c_e^{1/n}$

(8)

Langmuir-Freundlich equation: $q_e = \frac{q_m K_L F c_e^2}{1 + K_L F c_e^2}$

(9)

Temkin equation: $q_e = A \ln K_t c_e$

(10)

where $q_e$ is the equilibrium adsorption amount of Cd$^{2+}$ on CSBC (mg/g), $c_e$ is the equilibrium concentration of Cd$^{2+}$ in the aqueous solution (mg/L), $V$ is the batch volume (L) and $m$ is the mass of CSBC (g). The percent of removal efficiency of Cd$^{2+}$ ($R$) from the solution was determined using:

$$R(\%) = \left(\frac{c_0 - c_e}{c_0}\right) \times 100\%$$

(2)

$K_L$ denotes the
Langmuir constant. The value of $R_L$ indicates the shape of isotherm to either the unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

**RESULTS AND DISCUSSION**

**Characterization of biochar**

The physicochemical properties of CS and CSBC are presented in Table 1. The ash content of CSBC was relatively higher than that of CS because CS lost large part of its volatile compound during pyrolysis. The yield of CSBC was 40.66%. The SSA of CSBC was found to be 3.52 m$^2$/g with a total pore volume (TPV) of 0.0162 cm$^3$/g. The SSA obtained here was comparable to those of biochars obtained in other studies (Zhang et al. 2013), indicating that the SSA of CSBC was extremely low. The low SSA and TPV of CSBC are possibly related to pore blockage because of the presence of organic matter (Leng et al. 2015). The relative element contents showed the loss of oxygen and the enrichment of carbon, which was obtained from the pyrolysis of CS. The mole ratios of H/C and O/C of CSBC decreased obviously, compared to those of CS, indicating the involvement of demethylation (loss of CH$_3$) and decarboxylation (loss of CO$_2$) during pyrolysis, respectively (Huang et al. 2013).

Figure 1 is a SEM micrograph with the corresponding EDS spectra of CSBC. As can be seen, the surface of CSBC is not highly porous, which is consistent with its less SSA. The CSBC structure is not homogeneous and the irregular pores with different sizes and shapes are observed. From the micrograph of CSBC and the result of its SSA, it can be seen that CSBC has the fine macropore structure with less micropores. A chemical analysis of CSBC obtained by SEM-EDS reveals the presence of 74.36 wt.% of C and 22.43 wt.% of O as the basic elements in CSBC. The results demonstrate that C, O, Ca, and Si elements dominate the surface of CSBC, with Mg, S, K, and N elements presenting at different proportions.

Figure 2(a) presents the FTIR spectra of CSBC, where a very large number of functional groups can be observed. This may be beneficial for heavy metal adsorption. The broad band at about 3,423 cm$^{-1}$ is attributed to the stretching vibration of hydroxyl groups (Keiluweit et al. 2010). The C–H stretching bands at 2,925 cm$^{-1}$ (asymmetric) and 2,856 cm$^{-1}$ (symmetric) are assigned to the –CH$_2$ and –CH$_3$ groups, respectively (Keiluweit et al. 2010). The aromatic C=C stretching and C=O stretching of conjugated ketones and quinones (C=C and C=N functional groups) are identified as the bands at 1,614 cm$^{-1}$ and 1,702 cm$^{-1}$ (Keiluweit et al. 2010). The peak observed at 1,614 cm$^{-1}$ can be attributed to secondary aromatic amines, such as C=N stretching of pyridine rings. The peak at 1,438 cm$^{-1}$ indicates the presence of aromatic C=C stretching (Keiluweit et al. 2010). The peak at 1,106 cm$^{-1}$ is related to symmetric C–O stretching and aromatic C–H groups, respectively (Keiluweit et al. 2010). The peak at 802 cm$^{-1}$ is assigned to the aromatic C–H out-of-plane bending vibrations.

The thermogravimetry-differential scanning calorimetry (TG-DSC) analysis of CSBC is shown in Figure 2(b). CSBC was thermally stable up to a temperature about 190 °C and lost about 90% weight in the range 190–510 °C due to decomposition of carbon. Generally, thermal degradation of a biochar can be divided into three stages (Ming et al. 2012). The first stage is the loss of surface water at the

Table 1  | Physicochemical properties of CS and CSBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>CS</th>
<th>CSBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>42.61</td>
<td>64.25</td>
</tr>
<tr>
<td>C (%)</td>
<td>6.37</td>
<td>4.57</td>
</tr>
<tr>
<td>H (%)</td>
<td>1.23</td>
<td>1.97</td>
</tr>
<tr>
<td>N (%)</td>
<td>42.74</td>
<td>21.73</td>
</tr>
<tr>
<td>O (%)</td>
<td>1.79</td>
<td>0.85</td>
</tr>
<tr>
<td>H/C</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>O/C</td>
<td>0.78</td>
<td>0.28</td>
</tr>
<tr>
<td>(O + N)/C</td>
<td>7.05</td>
<td>7.48</td>
</tr>
<tr>
<td>pH</td>
<td>4.39</td>
<td></td>
</tr>
<tr>
<td>SSA (m$^2$/g)</td>
<td>–</td>
<td>3.52</td>
</tr>
<tr>
<td>TPV (cm$^3$/g)</td>
<td>–</td>
<td>0.0162</td>
</tr>
</tbody>
</table>
temperature ranging from 50 to 100 °C. The second one is during the temperature ranging from 100 to 350 °C, where the degradation of surface functional groups occurred. At the last stage (>350 °C), the carbon skeletons started to disappear. As the temperature increased from 350 to 500 °C, there is a steady and steep weight loss of CSBC. Once the temperature was beyond 500 °C, the mass decreased little with the recombination of structure and formation of fundamental carbon skeleton. The DSC curve of the combustion process in Figure 2(b) represents differentiations of the combustion heat release rate with the increasing temperature, suggesting the different exothermic properties for CSBC.

To further clarify the components and surface group of CSBC, XPS analysis was carried out. As is demonstrated in the overall XPS spectra in Figure 2(c), CSBC is mainly composed of carbon and oxygen elements, locating at the binding energies about 285 (C 1s) and 533 (O 1s) electron volts. After deconvolution in Figure 2(d), a detailed XPS scan of the C 1s of CSBC showed four peaks, which are corresponding to the C–C/C–H (284.39 eV), graphite C (284.96 eV), C–O (285.87 eV), and C=O (288.82 eV) groups, respectively (Wang et al. 2015). The main peaks of graphite C and amorphous C were the dominant speciation of C in CSBC. In general, the XPS and FTIR results identify the presence of oxygen-containing functional groups on the surface of CSBC.

Adsorption kinetics

Figure 3(a) presents the time profile of Cd²⁺ adsorption by CSBC under batch process, with two initial Cd²⁺ concentrations (50 and 100 mg/L). The kinetic experimental data were characterized with initial rapid reaction during the first 2 h and then smoothly reached equilibrium after 6 h. The kinetic model parameters are listed in Table 2. Among the three models tested, the pseudo-second-order one fits the experimental data better with 0.9907 and 0.9863 of $R^2$, indicating that Cd²⁺ adsorption onto CSBC could be
controlled by a chemical adsorption. Moreover, the \( q_e \) value predicted from the pseudo-second-order model is very close to the experimental \( q_e \) value.

To gain insight into the rate-controlling steps and adsorption mechanism, the intra-particle diffusion model was further examined to fit the data. The plots of \( q_t \) versus \( t^{1/2} \) for the intra-particle diffusion of Cd\(^{2+}\) onto CSBC are shown in Figure 3(b). The dots represent the experimental data, and the lines are the fitted ones for the data. According to the intra-particle diffusion model, the experimental data points are related to two straight lines for Cd\(^{2+}\) during the adsorption process. The first sharper portion was attributed to the diffusion of Cd\(^{2+}\) through the solution to the external surface of CSBC (external diffusion). The second portion was described as the gradual adsorption stage, corresponding to the diffusion of Cd\(^{2+}\) inside CSBC (intra-particle diffusion). Table 2 gives the intra-particle diffusion parameters of the two portions according to Equation (6). For both initial concentrations, the value of \( k_{d1} \) is larger than that of \( k_{d2} \), while the value of \( C_1 \) is less than that of \( C_2 \), which indicates that the rate of Cd\(^{2+}\) adsorption was higher in the beginning of adsorption due to large available surface area of CSBC. After Cd\(^{2+}\) formed a thick layer (caused by the molecular association and inter-ionic attraction), the capacity of CSBC was exhausted and the adsorption rate was controlled by the rate at which Cd\(^{2+}\) was transported from the exterior to the interior sites of CSBC. Moreover, none of the plots passes through the origin (Figure 3(b)), which indicates that the intra-particle diffusion was part of the adsorption but was not the only rate-controlling step. Some other

![Figure 3](https://iwaponline.com/wst/article-pdf/74/6/1335/458566/wst074061335.pdf)

Figure 3 | (a) Fitting of Elovich, pseudo-first- and pseudo-second-order models for adsorption of Cd\(^{2+}\) onto CSBC, (b) intra-particle diffusion plots for adsorption of Cd\(^{2+}\) onto CSBC.

| Table 2 | Kinetic parameters of adsorption of Cd\(^{2+}\) onto CSBC |
|---------|---------------------|---------------------|---------------------|
|         | Pseudo-first-order  | Pseudo-second-order | Elovich             |
| \( c_0 \) (mg/L) | \( q_m \) (mg/g) | \( k_1 \) (h\(^{-1}\)) | \( R^2 \) | \( q_m \) (mg/g) | \( k_2 \) (g/mg/h) | \( R^2 \) | \( \alpha \) (mg/g/h) | \( \beta \) (g/mg) | \( R^2 \) |
| 50      | 3.0872 | 3.3325 | 0.8674 | 3.2222 | 1.6885 | 0.9907 | 1245.76 | 3.3567 | 0.8778 |
| 100     | 4.3916 | 3.8781 | 0.8875 | 4.5729 | 1.4081 | 0.9863 | 4585.04 | 2.5926 | 0.8458 |
| Intra-particle diffusion |
| \( c_0 \) (mg/L) | \( K_{d1} \) | \( C_1 \) | \( R^2 \) | \( K_{d2} \) | \( C_2 \) | \( R^2 \) |
| 50      | 1.8004 | 0.9511 | 0.9111 | 0.1323 | 4.0348 | 0.8285 |
| 100     | 2.6201 | 1.4665 | 0.8307 | 0.0877 | 2.8549 | 0.6552 |
mechanisms such as ion-exchange or complexes may also control the rate of adsorption (Cheung et al. 2007).

**Adsorption isotherms**

The isotherm results shown in Figure 4 indicate that CSBC has a great Cd\(^{2+}\) adsorption ability over 100 mg/L. The experimental results and fitting curves from the four adsorption isotherms of Cd\(^{2+}\) onto CSBC are shown in Figure 4, and the estimated model parameters along with the correlation coefficient \(R^2\) for the four equations are summarized in Table 3. It can be observed that the data of Cd\(^{2+}\) adsorption isotherm of CSBC are well fitted by both Langmuir and Langmuir-Freundlich models with \(R^2\) exceeding 0.982, indicating that the adsorption of Cd\(^{2+}\) onto CSBC surface was maybe energetically homogeneous. The Langmuir maximum capacity of Cd\(^{2+}\) on CSBC was around 33.94 mg/g. The higher adsorption capacity of Cd\(^{2+}\) can be mainly attributed to (1) the abundant oxygen-containing functional groups on CSBC surface (FTIR analysis) that can easily bind Cd\(^{2+}\); (2) the delocalized \(\pi\) electron systems of CSBC as the Lewis base and Cd\(^{2+}\) act as the Lewis acid. The delocalized \(\pi\) electron systems can form electron donor acceptor complexes with Cd\(^{2+}\) through the Lewis acid base interaction (Ping et al. 2015).

In this study, the values of \(R_L\) and \(K_L\) are listed in Table 3. The value of \(R_L\) is calculated between 0.4651 and 0.9775 for the adsorption of Cd\(^{2+}\) on CSBC, which indicates that the adsorption is a favorable process.

**Thermodynamics study**

The influence of the solution’s temperature on the adsorption of Cd\(^{2+}\) onto CSBC was studied at 298 K, 308 K, and 318 K. The results are presented in Figure 5(a), which indicates that an increase in the solution temperature resulted in an increase in the amount of Cd\(^{2+}\) adsorption by CSBC. This result shows the process was endothermic and high temperature favored the adsorption. The Gibbs free energy change \(\Delta G^0\) of the process is related to the standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\) by the following equation:

\[
\Delta G^0 = -RT\ln K_L
\]

where \(K_L\) is the Langmuir constant when the concentration term is expressed in L/mol, \(T\) (K) is the absolute temperature and \(R\) (8.314 J/mol/K) is the universal gas constant.

According to van’t Hoff’s thermodynamics equation, the \(\Delta G^0\) is related to the standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\) by:

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

\(\Delta G^0\) is related to the standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\) by:

\[
\Delta G^0 = -RT\ln K_L
\]

where \(K_L\) is the Langmuir constant when the concentration term is expressed in L/mol, \(T\) (K) is the absolute temperature and \(R\) (8.314 J/mol/K) is the universal gas constant.

According to van’t Hoff’s thermodynamics equation, the \(\Delta G^0\) is related to the standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\) by:

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

Table 3: Isotherm and thermodynamic parameters for Cd\(^{2+}\) adsorption onto CSBC

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(K_L) 0.0023</td>
<td>(q_m) 33.9369</td>
<td>(R_L) 0.4651–0.9775</td>
<td>0.9845</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(K_F) 0.2468</td>
<td>(n) 1.4268</td>
<td>--</td>
<td>0.9817</td>
</tr>
<tr>
<td>Langmuir-Freundlich</td>
<td>(K_{LF}) 0.0026</td>
<td>(q_m) 40.3544</td>
<td>(n) 1.0749</td>
<td>0.9822</td>
</tr>
<tr>
<td>Temkin</td>
<td>(A) 3.4478</td>
<td>(K_T) 0.1154</td>
<td>--</td>
<td>0.7709</td>
</tr>
</tbody>
</table>

Thermodynamic parameters

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(K_L) (L/mol)</th>
<th>(\Delta G^0) (kJ/mol)</th>
<th>(\Delta H^0) (kJ/mol)</th>
<th>(\Delta S^0) (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>253.44</td>
<td>-13.73</td>
<td>-6.92</td>
<td>22.99</td>
</tr>
<tr>
<td>308</td>
<td>245.73</td>
<td>-14.09</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>318</td>
<td>214.03</td>
<td>-14.19</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
and standard entropy change ($\Delta S^0$) at constant temperature by the following equation:

$$\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$  \hspace{1cm} (13)$$

Therefore, from the linear plots of $\ln K_L$ versus $1/T$, $\Delta H^0$ and $\Delta S^0$ were obtained from the slope and intercept, respectively. The plots of $\ln K_L$ versus $1/T$ are show in Figure 5(b) and the thermodynamic parameters are listed in Table 3.

As the temperature is elevated from 298 K to 318 K, the values of $\Delta G^0$ decreased from $-13.73$ to $-14.19$ kJ/mol, indicating that the process of Cd$^{2+}$ adsorption onto CSBC was spontaneous and turns favored at the highest temperature. The values of negative $\Delta G^0$ were in the range of 0 to $-20$ kJ/mol, suggesting that the process of Cd$^{2+}$ adsorption onto CSBC was mainly physical adsorption (Zhu et al. 2014). The negative value of $\Delta H^0$ implies that the adsorption was exothermic. The positive value of $\Delta S^0$ indicated that randomness at the solution state and solid/solution interface increased during the adsorption process. Although the isotherm and kinetic results suggest that chemical adsorption could be the major mechanisms of Cd$^{2+}$ adsorption onto CSBC, the thermodynamic parameters point out occurrence of physical adsorption. The conclusion can be drawn that both chemical adsorption and physical adsorption occur.

### Effect of pH value of solution

The adsorption behaviors of heavy metal ions by an adsorbent are highly dependent upon the initial pH value of solution. Indeed, pH value of solution affects the speciation of adsorbate and changes the charge distribution on the adsorbent during the adsorption process (Bogusz et al. 2015). The effect of pH value of solution on the adsorption capacity of Cd$^{2+}$ was studied at different pH values of solution ranging from 2.0 to 8.0. These studies were not extended to higher pH values of solution (>8) because of the hydroxides precipitation of Cd$^{2+}$. Figure 6(a) shows the effect of pH value of solution on Cd$^{2+}$ adsorption onto CSBC. The adsorption amount shows a rapid rise with initial solution pH values (2.0–5.0) increasing. Then, when the solution pH increases up to 6.0, the increasing tendency begins to level off.

The influence of pH value of solution on adsorption capacity could be explained by the functional groups involved in metal chemistry and metal uptake. The FTIR spectroscopic analysis indicates that CSBC has a variety of functional groups such as carboxyl and hydroxyl groups which are responsible for almost all the potential binding mechanisms. Additionally, depending on the pH value of the solution, the functional groups participate in metal ion binding. At low pH value of solution, H$^+$ ions occupy most of the adsorption sites on CSBC surface and less Cd$^{2+}$ could be adsorbed because of electric repulsion with H$^+$ ions on CSBC surface.
The effect of pH value of solution on Cd\(^{2+}\) adsorption could also be explained by zero point charge (pH\(_{zpc}\)) of CSBC. Additionally, at solution pH < pH\(_{zpc}\) (3.95), the predominant metal species will be positively charged \([\text{M}^{n+} \text{and M(OH)}^{(n-1)+}]\). Hence, the adsorption of Cd\(^{2+}\) in the pH range below pH\(_{zpc}\) is a H\(^+\)-M\(^{n+}\) or M(OH)\(^{(n-1)+}\) exchange process. The increase in solution pH above pH\(_{zpc}\) will show a slower increase in adsorption as long as the metal species are still neutral or positively charged even though CSBC surface is negatively charged. In higher pH systems, the slight increase in adsorption was due to the formation of soluble hydroxyl complexes.

**Effect of adsorbent particle size**

The effect of particle size on Cd\(^{2+}\) adsorption was examined, and the results are presented in Figure 6(b). As illustrated, the adsorption capacity for CSBC increased with the particle size decreasing. The adsorption amounts increased from 2.67 to 4.82 mg/g as the CSBC particle size decreased from 40 to 80 mesh. This phenomenon could be related to the rate of diffusion of Cd\(^{2+}\) and surface area of CSBC. In general, surface area of adsorbent increases with smaller particle sizes and assuming that the rate of adsorption is solely dependent on the surface area, then smaller adsorbent particles would have shortened diffusion paths because they present a better opportunity for Cd\(^{2+}\) to penetrate all internal pore structures (Kizito et al. 2015). And this could be explained by that adsorption capacity for Cd\(^{2+}\) increased as the particle size of CSBC decreased.

**Effect of adsorbent dosage**

Dosage of adsorbent is considered to be an important factor in the entire adsorption process because it determines the
adsorbent-adsorbate equilibrium of the system (Azouaou et al. 2010). The number of available binding sites and exchanging ions for adsorption is dependent on the amount of adsorbent in adsorption process. The effect of increasing the adsorbent dosage of CSBC on the removal of Cd\(^{2+}\) is shown in Figure 6(c). The results show that when the CS300 dosage increased from 5.0 to 25.0 g/L, the adsorption capacity of Cd\(^{2+}\) adsorbed from the aqueous solution decreased from 4.78 to 1.95 mg/g before equilibrium was attained. The removal percentage of Cd\(^{2+}\) increased from 23.89\% to 48.68\%. Increasing the dosage of CSBC gives more available exchangeable sites and adsorption sites to the Cd\(^{2+}\) to get attached to the CSBC. Hence, increasing the amount of the CSBC eventually increases the CSBC area giving rise to an increased removal efficiency of Cd\(^{2+}\) from aqueous solutions.

**Effect of ionic strength**

The presence of dissolved cations such as Na\(^+\), NH\(_4\)^+, and Ca\(^{2+}\) in wastewater can effect Cd\(^{2+}\) adsorption by competing with the active absorbent sites. Thus, the effects of ionic strength on the adsorption of Cd\(^{2+}\) by CSBC were investigated with the ionic strength range between 0 and 0.2 mol/L. The results are shown in Figure 6(d). It is observed that the adsorption capacity for Cd\(^{2+}\) remains almost at the same level with increasing concentration range of 0.01 to 0.2 mol/L of Na\(^+\). The results could be due to the relative weaker ionic strength. The presence of Ca\(^{2+}\) led to the slightly decrease of adsorption capacity for Cd\(^{2+}\). Moreover, the effects of the ionic strength on Cd\(^{2+}\) follow this order: Ca\(^{2+}\) > NH\(_4\)^+ > Na\(^+\). The binding attraction of Na\(^+\) for CSBC was found to be weaker than that of NH\(_4\)^+ and Ca\(^{2+}\). This may be due to the fact that Cd\(^{2+}\) and Ca\(^{2+}\) have similar ionic structures and compete for the same adsorption sites (Sharma & Lee 2014). As the increasing external salts would impose negative effects on adsorption capacity if the driving force of adsorption was electrostatic interaction, it could be extrapolated that the electrostatic interaction between CSBC and Cd\(^{2+}\) played a significant role in adsorption (Anirudhan & Ramachandran 2006).

**CONCLUSIONS**

The results indicate that the conversion of CS to biochar offers a solution for producing potentially valuable adsorbent. The adsorption process was well described by the pseudo-second-order model, and the intra-particle diffusion model showed that the adsorption process may be a complex naturally consisting of both external diffusion and intra-particle diffusion. The equilibrium data were analyzed using the Langmuir, Freundlich, Langmuir-Freundlich, and Temkin isotherm models. The Langmuir and Langmuir-Freundlich model yields a much better fit than that of Freundlich and Temkin model in describing Cd\(^{2+}\) adsorption. The calculated maximum adsorption capacities of Cd\(^{2+}\) by Langmuir model was 33.94 mg/g. The adsorption of Cd\(^{2+}\) on CSBC is strongly dependent on pH value of solution, adsorbent dosage, adsorbent particle size and ionic strength. The adsorption of Cd\(^{2+}\) is a spontaneous and exothermic of physical adsorption and chemical adsorption process. The results indicate that CS derived biochar could be a cost-effective, potential and efficient adsorbent for removal heavy metals from real wastewater.

**ACKNOWLEDGEMENTS**

This work supported by the National Natural Science Foundation of China (21167007, 21467013), Young Scholars Science Foundation of Lanzhou Jiaotong University (2013015) and Specialized Research Fund for the Doctoral Program of Higher Education of China (20136204110003).

**REFERENCES**


First received 27 March 2016; accepted in revised form 10 June 2016. Available online 24 June 2016.