Adsorption behaviors on trace Pb$^{2+}$ from water of biochar adsorbents from konjac starch

Yinhui Li
School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, China
China Engineering Research Center of Seawater Utilization Technology, Ministry of Education, Tianjin, China

Longfei Peng and Weixin Li
School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, China

Abstract
Biochar adsorbents used to treat different heavy metals in water are efficient and low-cost. Appropriate raw materials, excellent selectivity and detailed adsorption mechanism are of important for research on biochar adsorbents. In this work, konjac starch was dispersed in polyvinylpyrrolidone (PVP) solution to prepare different sizes hydrophilic carbon spheres (HCSs) by hydrothermal synthesis method. Adsorption kinetics of the HCSs towards Pb$^{2+}$ is described perfectly by the pseudo-second-order equation. With the temperature increasing, adsorption thermodynamics are more consistent with the Freundlich model. The calculated $\Delta G$, $\Delta H$ and $\Delta S$ shows the adsorption of the HCSs towards Pb$^{2+}$ is a spontaneous, endothermic and entropy increase process. In addition, HCSs have excellent selectivity for the adsorption of Pb$^{2+}$ and Cu$^{2+}$. HCSs prepared from konjac starch make full use of natural biomass resources, they can be used as a potential adsorbent material in treatment on heavy metal ion from water field.

Keywords
Carbon spheres, PVP, adsorption, kinetics, thermodynamics

Submission date: 26 May 2020; Acceptance date: 15 July 2020
Introduction

In recent years, with the increase of water pollution, biochar adsorbents have attracted more and more attentions due to their outstanding advantages in environmental protection (Wang and Wang, 2018). Biochar is effective for wastewater treatment and soil improvement (Lu et al., 2012). It is called “charred organic matter” which can be prepared by a variety of organic matter (Mohan et al., 2014). The main source of biochar raw materials is agricultural biomass (Tan et al., 2015). Banana peel (Anwar et al., 2010), chestnut shell (Hong et al., 2017), corn straw (Yang et al., 2018) and other agricultural wastes were used to prepare for biochar which has good adsorption effect on heavy metal ions. Many studies have shown that different biochar has a high adsorption capacity for Pb\(^{2+}\), and the adsorption performance of biochar is closely related to their structure and composition (Jia et al. 2019; Li et al., 2020; Niu et al., 2020). In addition, researchers have also contributed to some research on the mechanism of biochar adsorption (Liu et al., 2019; Zhang et al. 2020a, 2020b; Zhao et al., 2019). The main interaction mechanism between the functional groups of biochar and heavy metal ions includes complexation, surface precipitation and cation exchange (Li et al., 2017; Qian and Chen, 2013). Ding et al. (2014) reported that the proportion of the cation exchange accounted for 62% in the adsorption mechanism of bagasse biochar adsorbents on Pb\(^{2+}\). Lu et al. used sludge-derived to prepare biochar adsorbents for Pb\(^{2+}\) adsorption, the proportion of the complexation with carboxyl and hydroxyl groups accounts for 38–42% in adsorption mechanism (Lu et al., 2012). However, the biochar adsorption mechanism is also affected by the raw materials and preparation methods (Li et al., 2017). Hydroxyl, carboxyl and other oxygen-containing functional groups which are used to adsorb heavy metal ions are on the surface of biochar (Qiu et al., 2008). Through physical and chemical methods, the amount and type of functional groups on the surface of biochar can be improved for increasing adsorption capacity on heavy metal ions. The downside is that these raw materials are not the mainly agricultural crops and the yield is very limited.

Starch is a polysaccharide that can provide humans valuable energy (Zhang et al., 2017) and it is also one of the three major natural polymer (Espíndola-Gonzále et al., 2011). Starch has been widely used in various fields, such as papermaking (Tajik et al., 2018), drug synthesis (Chen et al., 2018), adsorbent preparation, etc. (Ma et al., 2018). Among them, the adsorbents prepared by starch have been widely concerned. A series of starch adsorbents are prepared by modifying (Liu et al., 2018), crosslinking (Prakash et al., 2016), and compounding (Yu et al., 2018) the starch. Starch has higher raw material yield and is relatively less affected by seasons and regions. It is a very good potential adsorbent raw material. However, there are few studies on starch biochar and its adsorption performance on heavy metal ions in water.

PVP is a polymer that is often used as a nonionic surfactant due to its non-toxic, biocompatible and good hydrophilicity (Huang et al., 2017a). Gouthaman et al. (2018) used PVP to fully disperse polyaniline and ZnO to prepare an adsorbent that can remove dyes in water. The PVP additive not only allows adsorbent to have a rich pore structure, but also enhances its hydrophilicity. In addition, PVP also contains a large number of amide group, which have a strong interaction with some heavy mental ions (Huang et al., 2017b). Hence, dispersing the konjac starch into the PVP solution can better adjust the size of the adsorbent and improve its adsorption performance during the process of the preparation for starch biochar.
In this work, using PVP as dispersant and stabilizer and konjac starch as carbon source, hydrophilic carbon spheres were prepared by a simple hydrothermal synthesis and the size of the HCSs was suitable. After preparing HCSs, we carried out a series of experiments and made a discussion and explanation on the Pb\(^{2+}\) absorption mechanism.

**Experimental sections**

**Materials**

Konjac starch was purchased from supermarket. Polyvinylpyrrolidone (PVP, AR, K30), lead nitrate (Pb(NO\(_3\))\(_2\), >99.0%), copper chloride dehydrate (CuCl\(_2\)2H\(_2\)O, >99.0%), magnesium sulfate (MgSO\(_4\), >99.0%), calcium chloride (CaCl\(_2\), >96.0%) and cadmium chloride (CdCl\(_2\)2.5H\(_2\)O, >99.0%) were of analytical grade without further purification. Water was repeatedly distilled with purification system.

**Methods**

**Preparation of HCSs.** In a typical experiment, firstly, 0.043 g of PVP was stirred and completely dissolved in 80.0 mL of distilled water at room temperature for 0.5 h, and then a transparent solution was obtained. Nextly, 2.160 g of konjac starch was added into the transparent solution for dissolving and obtained a transparent konjac starch gel (The weight percentage of PVP and konjac starch is 2 wt.%). Then, the as-prepared gel was transferred into a small Teflon-sealed autoclave and kept at 453\(^\circ\)C for 10 h to yield brown precipitates. The brown precipitates were washed with distilled water for several times, repeatedly. Finally, the brown precipitates were placed in an oven and dried at 373 K for 10 h and the HCSs were obtained. (According to the mass percentage of PVP and konjac starch, the resulting products were labeled as HCSs-0, HCSs-0.05, HCSs-2 and HCSs-10.)

**Adsorption experiments.** 0.050 g of the HCSs was added into 50.0 mL, 10 mg/L of Pb\(^{2+}\) solution. The suspension was sucked by the syringe and filtered by a filter which was equipped with a 0.45-\(\mu\)m membrane (Polytetrafluoroethylene, Shanghai xinya purification equipment factory, China.) at set intervals. Atomic Absorption Spectrometry (TAS-990F, Beijing Pui General Instrument Co. Ltd., China) was used to detect Pb\(^{2+}\) solution concentration at different moment. Adsorption kinetics experiments were performed at room temperature (292 K). Adsorption isotherms were obtained by varying initial Pb\(^{2+}\) concentration from 5 mg/L to 25 mg/L. Among them, a case study of the adsorption of 10 mg/L of Pb\(^{2+}\) solution, different adsorption isotherms were obtained by changing adsorption temperature (such as 292 K, 313 K, 323 K and 333 K). In addition, the adsorption thermodynamic parameters were calculated.

The amounts of Pb\(^{2+}\) adsorbed onto the surface of HCSs at equilibrium time and at any time are calculated by the following formula:

\[
Q_{e,t} = \frac{(C_0 - C_{e,t})V}{m}
\]

Where \(Q_{e,t}\) (mg/g) is the adsorption amount of HCSs towards Pb\(^{2+}\) at equilibrium \((Q_e)\) and at a certain time \((Q_t)\), \(V\)(L) is the volume of Pb\(^{2+}\) solution, \(C_0\) (mg/L) is Pb\(^{2+}\) starting
solution concentration, \( C_{e,r} \) (mg/L) is the Pb\(^{2+}\) concentrations at equilibrium (\( C_e \)) and at some point (\( C_t \)) and \( m \) (g) is the mass of the HCSs.

**Other metal ion adsorption experiment.** 0.050 g of HCSs-2 was added to 50.0 mL, 15 mg/L of divalent metal ions (Cu\(^{2+}\)/Mg\(^{2+}\)/Ca\(^{2+}\)/Cd\(^{2+}\)) solution under stirring condition. The suspension is sucked by the syringe and filtered by a filter that was equipped with a 0.45 μm membrane (PTFE, Shanghai xinya purification equipment factory, China.) at fixed intervals. Atomic Absorption Spectrometry (TAS-990F, Beijin Pui General Instrument Co. Ltd., China) was used to determine the Cu\(^{2+}\)/Mg\(^{2+}\)/Ca\(^{2+}\)/Cd\(^{2+}\) concentration at different time.

**Characterization.** The structures and morphology of the HCSs were observed with scanning electron microscope (SEM, FEI, NanoSEM450, 15 kV, America). The crystal structure of the HCSs was studied using X-ray diffraction (XRD, Bruker, D8-Advance X-Ray diffractometer, CuK\(_{\alpha}\), \( \lambda = 1.5406 \) Å, Germany). The contact angle of HCSs film was measured by a contact angle meter (CAM, Krüss, DSA100, Germany). Chemical bonds of the HCSs were measured by Fourier transform infrared spectroscopy (FT-IR spectrum, Bruker, TENSOR 27, Germany).

**Results and discussion**

**Characterization of HCSs**

Figure 1 shows XRD pattern of HCSs-2, FT-IR spectrum of HCSs-2, SEM image of HCSs-2 film and contact angle image of HCSs-2 film. The XRD pattern of HCSs-2 can clearly show a broad peak with low peak intensity in Figure 1(a). The result proves that the as-prepared HCSs-2 is a typical disordered glassy polymers of carbon (Yang et al., 2018). The FT-IR spectrum is shown in Figure 1(b), the existence of hydroxyl group was confirmed by the broad and strong absorption peak of the O-H stretching vibration at 3420 cm\(^{-1}\) (Tran et al., 2017). Hydroxyl groups can increase the hydrophilicity of carbon spheres which are beneficial to Pb\(^{2+}\) adsorption. The peaks at 1650 cm\(^{-1}\), 1460 cm\(^{-1}\), 1420 cm\(^{-1}\) and 1290 cm\(^{-1}\) are the C=O stretching vibration, the -CH\(_2\)- torsion out of plane, the -CH\(_2\)- bending vibration and the -C-N- stretching vibration, respectively (Kaur et al., 2018). The three groups belong to the PVP on the surface of HCSs-2. Figure 1(c) and (d) display that HCSs-2 is evenly dispersed on the coverslip, its contact angle is 32° (<90°), which means that HCSs-2 exhibits good hydrophilicity.

The SEM images of HCSs including different PVP amount are shown in Figure 2. The average particle sizes of these HCSs are analyzed by Image pro plus (IPP, version 6.0). The average diameters of HCSs-0, HCSs-0.05, HCSs-2 and HCS-10 were calculated as 3.22 ± 0.03 μm, 3.32 ± 1.87 μm, 3.37 ± 1.67 μm and 5.35 ± 1.27 μm, respectively. These data indicate that PVP affects the size distribution of HCSs. The diameters of the HCSs increase with the increasing addition of PVP. It is possible that konjac starch gel is uniformly dispersed in water by PVP, in the process of hydrothermal synthesis, PVP acts as dispersant and stabilizer, which can effectively prevent the aggregation of carbon spheres during carbonization, after PVP was added, the diameters of HCSs are affected by the size of the PVP micelles due to the konjac starch gel encapsulated by PVP micelles.
Figure 1. Characterization of HCSs-2 and HCSs-2 film (a) XRD pattern of HCSs-2 (b) FT-IR spectrum of HCSs-2 (c) SEM image of HCSs-2 film (d) contact angle image of HCSs-2 film.

Figure 2. SEM images of HCSs (a) HCSs-0 (b) HCSs-0.05 (c) HCSs-2 (d) HCSs-10.
Adsorption of Pb$^{2+}$

Effect of PVP. The adsorption capacities of HCSs including different PVP amount towards Pb$^{2+}$ are shown in Figure 3. Among the HCSs with different PVP amount, the adsorption capacity of HCSs-2 is the highest up to 10.826 mg/L. It is probably that the adsorption capacity is inversely proportional to the size of the average diameter of HCSs with different PVP amount while HCSs-2 has a smaller average diameter, meaning it has a larger surface area and can provide more active sites.

Adsorption kinetics. Pseudo-first-order equation (Ragren, 1898) and pseudo-second-order equation (Ho and Mckay, 1999; Li et al., 2019) are the most commonly used linear equations to describe adsorption kinetics (Javed et al., 2018). In this work, the two equations will be used to describe the adsorption kinetics of Pb$^{2+}$ absorbed on the surface of HCSs. The pseudo-first-order equation (equation (2)) and the pseudo-second-order equation (equation (3)) are calculated using the following formula:

$$
\ln\left(\frac{Q_e}{Q_t} - Q_1\right) = \ln\frac{Q_e}{C_0} - K_1 t
$$

(2)

$$
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2}
$$

(3)

Where $K_1$ (min$^{-1}$) and $K_2$ are the equilibrium constant of the pseudo-first-order equation and the pseudo-second-order equation, and $t$ (min) is the adsorption time. Kinetic parameters of HCSs-2 are listed in Table 1.

Where $Q_{e,exp}$ is the actual saturated adsorption capacity, $Q_{e,cal1}$ is the saturation adsorption capacity of the pseudo-first-order equation, $Q_{e,cal2}$ is the saturation adsorption capacity of the pseudo-second-order equation, $R^2$ is correlation coefficients.

As shown in Table 1, the calculated value of $R^2$ (>0.99) is more close to 1. The results demonstrate that the adsorption kinetics of HCSs-2 can be described well by the pseudo-second-order equation. In addition, all the value of $Q_{e,cal2}$ are closer to $Q_{e,exp}$ than that of...

**Figure 3.** Adsorption capacity of HCSs including different PVP amount towards Pb$^{2+}$. 

![Image of Figure 3](image-url)
which fully demonstrates that the pseudo-second-order equation is more consistent with adsorption kinetics. The pseudo-first-order equation holds that the physical adsorption is the control step of reaction rate and can accurately describe the adsorption process for the initial 20–30 min stage. The equation only describes part of the adsorption process instead of the entire process (Ajmal and Piergiovanni, 2018). The pseudo-second-order equation is very suitable to describing the entire adsorption process. At $C_0 = 10$ mg/L, $Q_{e,exp}$ reached a maximum of 10.826 mg/g. This phenomenon may explained that when $C_0$ ($< 10$ mg/L) is little, the adsorption driving force is insufficient and $Q_e$ is less, while in an opposite picture ($C_0 > 10$ mg/L), $Q_e$ decreased due to competitive adsorption.

The surface of HCSs-2 is rich in hydroxyl groups and the hydroxyl group has two pairs of lone pair electrons. Pb$^{2+}$ is positively charged and can be adsorbed by these pairs of electrons. In addition, -O/C0 can be formed by ionization of hydroxyl groups and has stronger electronegativity to adsorb more Pb$^{2+}$. Therefore, Pb$^{2+}$ adsorbed onto HCSs-2 should be chemical adsorption, which is consistent with the fitting results in Table 1.

### Equilibrium isotherms
Adsorption isotherms are fitted by fourth-order polynomial fitting lines. Adsorption isotherms of HCSs-2 at different temperatures are shown in Figure 4. With the temperature increases, the adsorption isotherms change gradually type IV into type II. This may be single layer chemisorption at first stage during the adsorption process. After single layer adsorption of Pb$^{2+}$ on the surface of HCSs-2, $Q_e$ decreased slightly due to competitive adsorption. With the temperature increases, hydroxyl ionization forms a large amount of -O$. Since -O$ has strong electronegative, it still has the ability to attract Pb$^{2+}$ after single layer adsorption of Pb$^{2+}$ on the surface of HCSs-2, which forms multilayer adsorption. The adsorption process is shown in Figure 5. In theory, the value of $Q_e$ at certain temperature should go up again significantly. The conjecture is well confirmed in the 323 K and 333 K adsorption isotherms. Since the temperature is not high enough, the hydroxyl group dissociates less -O$ and the effect of competitive adsorption. Therefore, $Q_e$ does not continue to rise in the high $C_e/C_0$ region at 292 K. The adsorption isotherm at 313 K is in the transitional stage. $Q_e$ increases in the higher $C_e/C_0$ interval, but the fitted line shows a decreasing trend.

The Langmuir model and Freundlich model are used to describe adsorption isotherms. Their expressions are as follows:

$$
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_l Q_m}
$$
\[ \text{In} Q_e = \text{In} K_F + \frac{1}{n} \text{In} C_e \]

(5)

Where \( Q_m \) represents the maximum adsorption capacity, \( K_L \) and \( n \) are empirical coefficient in adsorption process, \( K_F \) is a constant indicating the adsorption capacity of the adsorbent.

The fitting results are shown in Table 2. As the temperature increases, the \( R^2 \) of the Langmuir model decreases, while the \( R^2 \) of the Freundlich model increases. At 292 K, the \( R^2 \)
of the Freundlich model is only 0.2066 and that of Langmuir model is 0.9802. Adsorption isotherms can be better described by the Langmuir model. The Langmuir model assumes that the adsorption process is monolayer and uniformly adsorbed (Sahnoun and Boutahala, 2018), which is consistent with the adsorption kinetic results. However, when the temperature rises to 333 K, the $R^2$ of the Freundlich model increases to 0.8600 and the $R^2$ of the Langmuir model drops to 0.8362. The adsorption form is mainly monolayer adsorption at a lower temperature of 292 K and is mostly multilayer adsorbed at a higher temperature of 333 K, which is proved by the fitting data. The adsorption isotherms change gradually type IV into type II and $Q_e$ also improves more than double because of the existence of multilayer adsorption.

In addition, the value of $n$ in the Freundlich model can be used as an important reference for the degree of adsorption difficulty (Bazargan-Lari et al., 2014; Wang et al., 2018). At 292 K, the value of $n$ is 13.0208, which is much greater than 2. As the temperature rises to 333 K, the value of $n$ gradually decreases to 2.5742. The value of $n$ is smaller, the adsorption is easier. The value of $n$ decreases with the increase of the temperature, indicating that the adsorption is favorable at higher temperature.

**Adsorption thermodynamic.** Gibbs free energy ($\Delta G$) reflects the direction of adsorption, enthalpy change ($\Delta H$) is determined to exothermic or endothermic of adsorption process and entropy change ($\Delta S$) reflects degree of confusion on adsorption system. The thermodynamic parameters are calculated using the following equation:

$$\Delta G = -RT\ln K_L$$

The van’t hoff equation is used to calculate the adsorption thermodynamic parameters. The values of $\Delta H$ and $\Delta S$ can be calculated from the intercept and the slope of the linear plot of $\ln K_L$ versus $1/T$. The linear expression is as follows:

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Where $R$ is a universal gas constant (8.314 J/mol/K) and $T$ is adsorption temperature ($K = 273 + ^\circ C$)

As shown in Table 3, the value of $\Delta G$ is negative ($< 0$) at different adsorption temperatures and decreases with the increase of adsorption temperature. The result prove that the

**Table 2. Equilibrium parameters for Pb$^{2+}$ adsorbed onto the HCSs-2.**

| $T$ (K) | $Q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $n$ | $K_F$ ((mg/g) (L/mg)${^{1/n}}$) | $R^2$ |
|-------|-------------|-------------|-------|----|-----------------|-------|
| 292   | 8.8921      | 58.2694     | 0.9802|     | 13.0208         | 7.4484 | 0.2066 |
| 313   | 19.4326     | 0.2966      | 0.8744|     | 2.9817          | 6.4825 | 0.8062 |
| 323   | 17.1674     | 0.3447      | 0.9254|     | 3.9779          | 7.2825 | 0.6878 |
| 333   | 22.9516     | 0.2501      | 0.8362|     | 2.5742          | 6.4941 | 0.8600 |
adsorption of HCSs-2 towards Pb\(^{2+}\) is a spontaneous process. As the adsorption temperature increases, the spontaneous process becomes easier and easier. The calculation result shows \(\Delta H > 0\), meaning that the adsorption process of HCSs-2 needs to absorb heat (Munagapati and Kim, 2017). Increasing the adsorption temperature is favorable to the adsorption process, which is consistent with the decrease of \(n\) and \(\Delta G\).

The fitting result in Table 3 shows that \(\Delta S\) is positive (>0), which proves that the adsorption of HCSs-2 is a process in which the confusion degree of the surface of HCSs-2 increases, if the surface sedimentation or complexation occurs alone, the confusion degree should be reduced, in other words, \(\Delta S\) is negative (<0). Meanwhile, if surface precipitation and complexation occurs on the surface of HCSs-2, the surface will be covered by precipitates or complexes. Adsorption sites will be separated from Pb\(^{2+}\) by the cover layer. When the temperature rises, \(Q_e\) should fall or be invariant rather than rise. However, as shown in Figure 5, \(Q_e\) increases with enhancement of adsorption temperature. This fully shows that the main adsorption mechanism of HCSs-2 towards Pb\(^{2+}\) should be cation exchange. The proportion of surface precipitation and complexation is small or absent. This is consistent with the hypothesis that hydroxyl or -\(\text{O}^\cdot\) adsorbs Pb\(^{2+}\).

**Other metal ion adsorption experiment**

As shown Figure 6, HCSs-2 does not absorb Mg\(^{2+}\), Ca\(^{2+}\) and Cd\(^{2+}\), at the same time, HCSs-2 has higher adsorption capacity to Pb\(^{2+}\) than Cu\(^{2+}\). The results demonstrate that

| \(T\) (K) | \(\Delta G\) (kJ/mol) | \(\Delta H\) (J/mol) | \(\Delta S\) (J/mol/K) |
|----------|----------------------|---------------------|----------------------|
| 292      | -1.5206              | 9.8994              | 39.5510              |
| 313      | -2.7285              |                     |                     |
| 323      | -2.9933              |                     |                     |
| 333      | -3.0325              |                     |                     |

**Figure 6.** Adsorption capacity of HCSs-2 to different divalent metal ions.
the HCSs-2 has selectivity to Pb\(^{2+}\) and Cu\(^{2+}\). Deng et al. (2017) consider that C\(=\)O (N-C\(=\)O and -COOH) is a key functional group for adsorbing Cu\(^{2+}\). The surface of HCSs-2 contains -CONH- (from PVP), so Cu\(^{2+}\) can be adsorbed by the HCPs-2. But on the surface of HCSs-2, no functional group has adsorption effect on Mg\(^{2+}\), Ca\(^{2+}\) and Cd\(^{2+}\). In addition, the order of the electronegativity of these elements is Pb\(>\)Cu\(>\)Cd\(>\)Mg\(>\)Ca in turn (2.33 for Pb, 1.90 for Cu, 1.69 for Cd, 1.31 for Mg and 1.00 for Ca) (Kinraide and Yermiyahu, 2007). Park et al. (2016) think that Pb\(^{2+}\) is a stronger Lewis acid while Cd\(^{2+}\) is a weaker Lewis acid. The ability of HCSs-2 providing electrons is not extremely strong and only corresponds to a weak base. Therefore, the more acidic Pb\(^{2+}\) and Cu\(^{2+}\) can be adsorbed by HCSs-2, but the weaker Mg\(^{2+}\), Ca\(^{2+}\) and Cd\(^{2+}\) cannot.

Conclusions

HCSs were successfully prepared by hydrothermal synthesis method. The presence of numerous hydroxyl groups on the surface of HCSs might play a vital role in the adsorption process. These hydroxyl groups could be ionized to form O\(^-\) with increasing adsorption temperature, which forms a multi-layered adsorption to improve the adsorption capacity. The adsorption isotherm gradually shifts type IV to the type II. HCSs exhibits a certain adsorption capacity for Pb\(^{2+}\) and Cu\(^{2+}\), but no adsorption ability for Mg\(^{2+}\), Ca\(^{2+}\) and Cd\(^{2+}\). HCSs can be used as an exclusive biochar adsorbent for the treatment on heavy metal ions from waste.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the National Natural Science Foundation of China (No. 51309074), the Natural Science Foundation of Hebei Province (No. B2016202271) and the “Thirteen Five” national key R & D project (No. 2016ZX05025-004–006).

ORCID iD

Yinhui Li https://orcid.org/0000-0002-5013-6307

References

Ajmal A and Piergiovanni PR (2018) Effect of mordanting on the adsorption thermodynamics and kinetics of cochineal for wool. Industrial & Engineering Chemistry Research 57(12): 4462–4469.

Anwar J, Shafique U, Salman M, et al. (2010) Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana. Bioresource Technology 101(6): 1752–1755.

Bazargan-Lari R, Zafarani HR, Bahrololoom ME, et al. (2014) Removal of Cu(II) ions from aqueous solutions by low-cost natural hydroxyapatite/chitosan composite: Equilibrium, kinetic and thermodynamic studies. Journal of the Taiwan Institute of Chemical Engineers 45(4): 1642–1648.

Chen J, Li X, Chen L, et al. (2018) Starch film-coated microparticles for oral colon-specific drug delivery. Carbohydrate Polymers 191: 242–254.
Deng J, Liu Y, Liu S, et al. (2017) Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. *Journal of Colloid and Interface Science* 506: 355–364.

Ding W, Dong X, Ime IM, et al. (2014) Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere* 105: 68–74.

Espindola-González A, Martínez-Hernández AL, Fernández-Escobar F, et al. (2011) Natural-synthetic hybrid polymers developed via electrospinning: The effect of PET in chitosan/starch system. *International Journal of Molecular Sciences* 12(3): 1908–1920.

Gouthaman A, Azarudeen RS, Gnanaprakasam A, et al. (2018) Polymeric nanocomposites for the removal of acid red 52 dye from aqueous solutions: Synthesis, characterization, kinetic and isotherm studies. *Ecotoxicology and Environmental Safety* 160: 42–51.

Ho YS and McKay G (1999) Pseudo-second order model for sorption processes. *Process Biochemistry* 34(5): 451–465.

Hong X, Fang C, Hui K, et al. (2017) Influence of interfering anions on Cu^{2+} and Zn^{2+} ions removal on chestnut outer shell-derived hydrochars in aqueous solution. *RSC Advances* 7(1): 51199–51205.

Huang J, Yang H, Chen M, et al. (2017) An infrared spectroscopy study of PES PVP blend and PES-g-PVP copolymer. *Polymer Testing* 59: 212–219.

Huang M, Mishra SB and Liu S (2017) Waste glass fiber fabric as a support for facile synthesis of microporous carbon to adsorb Cr(VI) from wastewater. *ACS Sustainable Chemistry & Engineering* 5(9): 8127–8136.

Javed SH, Zahir A, Khan A, et al. (2018) Adsorption of mordant red 73 dye on acid activated bentonite: Kinetics and thermodynamic study. *Journal of Molecular Liquids* 254: 398–405.

Jia Y, Zhang Y, Fu J, et al. (2019) A novel magnetic biochar/MgFe-layered double hydroxides composite removing Pb^{2+} from aqueous solution: Isotherms, kinetics and thermodynamics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2019) 567: 278–287.

Kaur A, Goyal D and Kumar R (2018) Surfactant mediated interaction of vancomycin with silver nanoparticles. *Applied Surface Science* 449: 23–30.

Kinaide T and Yermiyahu U (2007) A scale of metal ion binding strengths correlating with ionic charge, pauling electronegativity, toxicity, and other physiological effects. *Journal of Inorganic Biochemistry* 101(9): 1201–1213.

Li H, Dong X, Silva EBD, et al. (2017) Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere* 178: 466–478.

Li J, Li H, Yuan Z, et al. (2019). Role of sulfonation in lignin-based material for adsorption removal of cationic dyes. *International journal of biological macromolecules* 135: 1171–1181.

Li Y, Zhang X, Zhang P, et al. (2020) Facile fabrication of magnetic bio-derived chars by co-mixing with Fe_{3}O_{4} nanoparticles for effective Pb^{2+} adsorption: Properties and mechanism. *Journal of Cleaner Production* 262: 121350.

Liu L, Huang Y, Zhang S, et al. (2019) Adsorption characteristics and mechanism of Pb(II) by agricultural waste-derived biosolids produced from a pilot-scale pyrolysis system. *Waste Management (New York, N.Y.)* 100: 287–295.

Liu Q, Li F, Lu H, et al. (2018) Enhanced dispersion stability and heavy metal ion adsorption capability of oxidized starch nanoparticles. *Food Chemistry* 242: 256–263.

Lu H, Zhang W, Yang Y, et al. (2012) Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar. *Water Research* 46(3): 854–862.

Ma K, Zhao L, Jiang Z, et al. (2018) Adsorption characteristics of Cr(III) onto starch-graft-poly(acrylic acid)/organo-modified zeolite 4A composite: A novel path to the adsorption mechanisms. *Polymer Composites* 39(4): 1223–1233.

Mohan D, Sarswat A, Yong SO, et al. (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresource Technology* 160(5): 191–202.
Munagapati VS and Kim DS (2017) Equilibrium isotherms, kinetics, and thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano-goethite. *Ecotoxicology and Environmental Safety* 141: 226–234.

Niu Z, Feng W, Huang H, et al. (2020) Green synthesis of a novel Mn-Zn ferrite/biochar composite from waste batteries and pine sawdust for Pb²⁺ removal. *Chemosphere* 252: 126529.

Park JH, Ok YS, Kim SH, et al. (2016) Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere* 142: 77–83.

Prakash N, Vandan SA, Sudha P, et al. (2016) Biodegradable polymer-based ternary blends for adsorption of heavy metal from simulated industrial wastewater. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* 46(11): 1664–1674.

Qian L and Chen B (2013) Dual role of biochars as adsorbents for aluminum: The effects of oxygen-containing organic components and the scattering of silicate particles. *Environmental Science & Technology* 47(15): 8759–8768.

Qiu Y, Cheng H, Xu C, et al. (2008) Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. *Water Research* 42(3): 567–574.

Sahnoun S and Boutahala M (2018) Adsorption removal of tartrazine by chitosan/polyaniline composite: Kinetics and equilibrium studies. *International Journal of Biological Macromolecules* 114: 1345–1353.

Tajik M, Torshizi HJ, Resalati H, et al. (2018) Effects of cationic starch in the presence of cellulose nanofibers on structural, optical and strength properties of paper from soda bagasse pulp. *Carbohydrate Polymers* 194: 1–8.

Tan X, Liu Y, Zeng G, et al. (2015) Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125: 70–85.

Tran HN, Lee CK, Vu MT, et al. (2017) Removal of copper, lead, methylene green 5, and acid red 1 by saccharide-derived spherical biochar prepared at low calcination temperatures: Adsorption kinetics, isotherms, and thermodynamics. *Water, Air, & Soil Pollution* 228(10): 401.

Wang C and Wang H (2018) Pb (II) sorption from aqueous solution by novel biochar loaded with nano-particles. *Chemosphere* 192: 1–4.

Wang G, Zhang S, Yao P, et al. (2018) Removal of Pb(II) from aqueous solutions by *Phytolacca americana* L. biomass as a low cost biosorbent. *Arabian Journal of Chemistry* 11(1): 99–110.

Yang F, Zhang S, Li H, et al. (2018) Corn straw-derived biochar impregnated with α-FeOOH nanorods for highly effective copper removal. *Chemical Engineering Journal* 348: 191–201.

Yu C, Tang X, Liu S, et al. (2018) Laponite crosslinked starch/polyvinyl alcohol hydrogels by freezing/thawing process and studying their cadmium ion absorption. *International Journal of Biological Macromolecules* 117: 1–6.

Zhang S, Du Q, Sun Y, et al. (2020a) Fabrication of L-cysteine stabilized α-FeOOH nanocomposite on porous hydrophilic biochar as an effective adsorbent for Pb²⁺ removal. *The Science of the Total Environment* 720: 137415.

Zhang W, Du W, Wang F, et al. (2020b) Comparative study on Pb²⁺ removal from aqueous solutions using biochars derived from cow manure and its vermicompost. *The Science of the Total Environment* 716: 137108.

Zhang XT, Liu GJ, Ning ZW, et al. (2017) Boronic acid-based chemical sensors for saccharides. *Carbohydrate Research* 452: 129–148.

Zhao HT, Ma S, Zheng SY, et al. (2019) β-Cyclodextrin functionalized biochars as novel sorbents for high-performance of Pb²⁺ removal. *Journal of Hazardous Materials* 362: 206–213.