The adsorption performance of hexavalent chromium Cr(IV) in aqueous with three biomass carbons materials

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Abstract: The paper reported the adsorption capacity of hexavalent chromium Cr(VI) in aqueous solutions with three agricultural waste by five awns (PE), corn stalks (CM), peanut shells (HS) and prepared the adsorbent by carbonization at 550℃. A series of adsorption experiments were performed to investigate the effect of Cr(VI) concentration, contact time. The results indicated that peanut shells (HS) have a higher removal rate than the other two materials. The Langmuir and Freundlich adsorption isotherm models are used to describe the adsorption process. The adsorption isotherm of Langmuir well explained the balance mechanism and the research showed that adsorption conformed to the pseudo-second kinetic model.

1. Introduction
It become a major problem to us that a lot of heavy metals release to wastewater because of human and industrial activities\textsuperscript{[1]}. Chromium is widely used in industry, such as in cooling towers, leather tanning, textile and wood preservation\textsuperscript{[2]}. However, it is harmful for our body. The existence forms of hexavalent chromium is both trivalent Cr(III) and hexavalent Cr(VI). It reported that high chromium concentration may cause kidney and liver of human, low concentration may cause shin irritation and ulceration\textsuperscript{[3]}. Some technologies are adopted to removal heavy chromium, such as ion exchange, membrane process, precipitation, adsorption\textsuperscript{[4]}. Adsorption becomes a preferred method to eliminate heavy ions dosage because it has high efficiency and low coast\textsuperscript{[5]}.

There are many investigations to relate the removal of heavy metals from local agricultural wastes\textsuperscript{[4]}. The present study is carried out to investigate the removal of chromium Cr(VI) from aqueous solution with five awns (PE), corn stalks (CM), peanut shells (HS) waste materials. The effect’s parameters with initial concentration, contact time were investigated. The reaction mechanism were analyzed by Langmuir and Freundlich isotherm models.

2. Materials and methods

2.1 Adsorbent preparation

The corn stalks (CM) were taken from the experimental field near the school, the peanut shells (HS) were from a farmer’s house, and the five-section awns (PE) were taken from the Qionghai Wetland Park. Firstly, washed the materials with tap water, then rinsed with deionized water, dried it, putted it in a dryer and bake it to constant weight at 105°C. Secondly, used a pulverizer to pulverize, screen out particles with a particle size (0.45-0.178mm) between 40-80 meshes, putted them into a prepared
150mL crucible with a lid, and finally calcinate in a muffle furnace at 550° for 2h, cooled to room temperature, and then putted the biomass carbons into the drying bottle.

2.2 Adsorption experiments
A series of solutions with different Cr(VI) concentrations were prepared by K₂Cr₂O₇. A certain dosage with three biomass carbon materials (CM, PE, HS) were added into a series of adsorption experiments. Such three biomass carbons are placed in 250mL erlenmeyer flasks with different initial concentration of Cr(VI) solution from 25mg/L to 200mg/L and different temperature from 20°C to 70°C.

The biomass carbons before and after adsorption were measured using the spectrophotometer at 554 nm[6].

The removal percentage (R%) of Cr(VI) solution is calculated as following equation:

\[ R(\%) = \frac{C_0 - C_e}{C_0} \]

R(%) is the removal percentage; \(C_0\) (mg/L) is the initial concentration of Cr(VI) solution; \(C_e\) (mg/L) is the concentration at equilibrium.

3. Results and discussion

3.1 Effect of contact time
The three biomass carbons of CM, HS, PE with the mount of 0.3g were added into 250mL erlenmeyer flasks, and then added 50mL of 300mg/L Cr(VI) solution, set the constant temperature for 30-180min, and set the temperature to 30°C, the stirred speed to 160r/min, to study the effect of reaction time on removal rate under the above conditions. The results was shown in Fig.1. The removal rate of Cr(VI) by CM, HS and PE increased with the increase of adsorption time, and the removal rate of three biomass carbons were HS>PE>CM, and the removal rate of HS rised from 93.43% to 99.3%.

Rai[7] reported that all the cative sites on the adsorbent are vacant and the removal rate of Cr(VI) increased and the removal rate decreased with the active sites were occupied.

3.2 Effect of initial concentration of Cr(VI)
The three biomass carbons of CM, HS, PE with the mount of 0.3g were added into 250mL erlenmeyer flasks, and added 50mL of Cr(VI) solution with a concentration of 25 mg/L to 500 mg/L. Set the temperature from 30°C to 120°C minutes in gas bath oscillator, and set the rotation speed to 160r/min to study the effect of the initial concentration of Cr(VI) on the removal rate under the above conditions. The results can be seen from Fig.2. It indicated that the removal rate of Cr(VI) increased with
increasing Cr(VI) concentration, however, the removal rate gradually reduced at higher concentrations and eventually became constant with increase the Cr(VI) concentration. The results with the removal rate obtained from the experimental were HS>PE>CM.

Seidu[8] reported that the removal rate increased with the temperature in the begging maybe the high concentration and many active sites on the surface of adsorbent, the removal increased slowly with the temperature increased because it limited mass transfer of the metal ion from the liquid phase to the surface of the adsorbent.

3.3 Adsorption mechanism

3.3.1 Adsorption isotherm study

The model of Langmuir and Freundlich are the most frequently used to describe the mechanism of adsorption experiments. The model of Langmuir is to describe the adsorption process in homogeneous solution, the model of Freundlich is to describe the multilayer adsorption model in heterogeneity solution[8].

The equation of Langmuir isotherm is given by the following:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{q_{max}}{K_L} C_e
\]

where 
\( C_e \) (mg/L) is the concentration of biomass carbon after adsorption reaction; 
\( q_e \) (mg/g) is the adsorbed amount after adsorption reaction; 
\( q_{max} \) (mg/g) is the most adsorption amount; 
\( K_L \) (L/mg) is constant with Langmuir.

The equation of Freundlich isotherm is given by the following:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where 
\( q_e \) (mg/g) is the adsorbed amount at after adsorption reaction; 
\( C_e \) (mg/L) is the concentration after adsorption reaction; 
\( K_F \) is the Freundlich constant.

The adsorption isotherm parameters for Cr(VI) removal was shown in table 1.

| Material | Langmuir Isotherm | Freundlich Isotherm |
|----------|------------------|---------------------|
|          | \( q_{max} \) (mg/g) | \( K_L \) | \( R^2 \) | \( K_F \) | \( 1/n \) | \( R^2 \) |
| CM       | 45.45            | -1.61              | 0.9985 | 53.06 | -0.0411 | 0.9972 |

Fig.2 Effect of temperature
It can be seen from table 1 that the adsorption of Cr(VI) by the three biomass adsorbents can be seen from the linear correlation coefficient $R^2$ fitted by the two models. The Langmuir model can better describe the adsorption isotherm behavior of the three types of biomass carbons, indicating that the adsorption of Cr(VI) by the biomass carbon. Mainly in the form of monolayer adsorption. The adsorption capacity of the three kinds of biochar for Cr(VI) is HS>PE>CM.

3.3.2 The study of biomass carbon's adsorption
Kinetic studies indicated that the reaction rate and the mechanism of adsorption can be determined by kinetic equation\cite{8}. The kinetics of Cr(VI) adsorption on the three biomass carbon with the CM, PE and HS were analyzed using two kinetic models. The pseudo-first-order kinetic model and the pseudo-second-order adsorption kinetics can be expressed as shown in table 2.

| Material | $K_1$ | $q_e$ | $R^2$ | $K_2$ | $R^2$ |
|----------|-------|-------|-------|-------|-------|
| CM       | 0.0371| 5.42  | 0.9718| 0.0018| 0.9813|
| HS       | 0.0491| 20.04 | 0.976 | 0.0024| 0.9933|
| PE       | 0.0415| 13.14 | 0.9517| 0.0011| 0.9608|

It can be seen from table 2 that the correlation coefficients of the pseudo-first-order and pseudo-second-order models were 0.9718, 0.976, 0.9517 and 0.9813, 0.9933, 0.9608, respectively, which proved that this experiment conforms to the two models. However, the correlation coefficient of the pseudo-second-order is higher than that of the pseudo-first-order kinetic equation, indicating that the pseudo-second-order is more suitable to describe the adsorption kinetic behavior of these three adsorbents on Cr(VI) solution, and the calculation results of $q_e$ with the pseudo-second-order is 51.28, 52.08, 54.05, which further shows that the pseudo-second-order kinetic equation can better describe the adsorption behavior of the three kinds of biomass carbons on Cr(VI).

4. Conclusions
In this study, three kinds of biomass carbons (CM, HS, PE) were prepared from the abundant agriculture waste and showed high removal rate of hexavalent chromium Cr(VI) from aqueous solution. The results indicated that Cr(VI) maximum removal could reach above 95% with three biomass adsorbents when the initial concentration was 300mg/L, the contact time was 120min, the react tempeture was 30°C. The isotherm data were analyzed by the Langmuir and Freundlich isotherms and the results of analysis indicated it fitting Langmuir isotherm model. The results of kinetic data were well fitted by the pseudo-second model.

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