Study on adsorption of phenol from aqueous media using biochar of Chinese herb residue

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Abstract. The biochar adsorbent was prepared at 400, 500 and 600 °C using the discarded Chinese herb residue as raw material to remove the phenol in the waste water. The results of adsorption experiments show that the initial concentration of phenol in wastewater, the preparation temperature of biochar, the temperature and time of adsorption can affect the adsorption effect of biochar on phenol. The adsorption capacity with three kinds of biochar to phenol was BC600> BC500> BC400. When the initial concentration of phenol was 50 mg/L and the temperature was 45 °C, the removal rate of phenol was up to 97% after BC600 adsorption. The isothermal adsorption line for phenol conforms to the Langmuir mode and the Freundlich mode.

1. Introduction

China is a big consumer of traditional Chinese herb resources. With the development of traditional Chinese herb, the amount of waste residue is increasing. According to records, 30 million tons of plant residues were produced annually. Due to the high water content and residual active ingredients, the improper disposal of the herb residue will lead to the occurrence of environmental pollution. Therefore, how to deal with the traditional Chinese herb residue efficiently and environmentally-friendly is the key for the utilization of waste biomass [1]. In recent years, biochar technology has provided good resource utilization for low value or abandoned biomass. On the other hand, biochar can be used as a new environmental protection material for the treatment and restoration of contaminated water and soil [2-3].

Phenol and its derivatives are very important raw materials, widely used in chemical, pharmaceutical, paper making and many other industrial processes, the use of pesticides and some aromatic organic pollutants such as polycyclic aromatic hydrocarbons, incomplete degradation of PCBs can be introduced into the environment of phenolic pollutants [4-5]. Phenolic compounds and their derivatives are toxic, carcinogenic, teratogenic and mutagenic, and can exist in the environment for a long time, potentially affecting human health [6-7]. Adsorption method has been widely used.
because of its simple method, low cost and fast speed. It has become one of the effective methods to control phenol pollution [8-9].

Biochar is mainly produced by heating pyrolysis, the preparation process is a process of organic biomass by pyrolysis into stable carbon. The research shows that the pyrolysis temperature of biomass material is the most important factor for the properties of biochar. At present, the relationship between the pyrolysis temperature and the corresponding biochar characteristics and the adsorption behavior of biochar to hydrophobic organic compounds has not been clearly studied. Therefore, systematic research on the pyrolysis temperature is how to influence the physical and chemical properties of biochar, and thus affect the biochar adsorption of hydrophobic organic compounds is the key to research and develop new environmentally-friendly biochar adsorbent, repair agent widely used in pollution control of water and soil. In this study, the adsorption characteristics of phenol in aqueous solution prepared by Chinese herb residue at different pyrolysis temperatures were studied.

2. Materials and Methods

2.1. Biochar preparation

Chinese herb residue was used as raw material to prepare biochar from the hospital of Shaanxi University of Chinese Medicine. Take a certain amount of dry residue in the small porcelain crucible covered with lid, placed in a muffle furnace, with 2 ℃/min heating rate to the target temperature (400, 500 and 600 ℃), then keep the temperature for 2 h. After cooling, grinding over 60 mesh sieve, sealing in reagent bottles and stored in a desiccator standby. The markings are BC400, BC500, BC600.

2.2. Removal rate of phenol from different initial concentrations by biochar

The concentration of phenol after adsorption was measured by UV spectrophotometry (λ =270 nm). 3 parallel experiments were carried out in each group, and the average value was obtained. Phenol adsorption capacity of \( q_e \) reached the adsorption equilibrium and the removal rate is calculated by the following formula:

\[
q_e = \frac{(C_0 - C_e)}{W} \times V
\]

\[
\eta = \frac{C_0 - C_e}{C_0} \times 100\%
\]

Formula: \( q_e \) is the adsorption capacity of equilibrium, mg/g, \( C_0 \) and \( C_e \) are content of phenol before adsorption and after adsorption, mg/L, \( V \) is volume of solution, L, \( W \) is adsorbent dosage, g, respectively.

Weigh 0.1 g biochar (BC400, BC500, BC600), 20 mL phenol solution were added to the pre-configured 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L 50 mL stoppered Erlenmeyer flask, in the constant temperature water bath box oscillation with 150 r/min 6 h oscillation at 25 ℃ in order to reach the equilibrium state, the residual phenol concentration was calculated according to the standard curve.

2.3. Effect of reaction time on adsorption

Under the room temperature, samples of phenol concentration of 50 mg/L were placed in 50 mL Erlenmeyer flask, adding 0.1 g BC400, BC500, BC600, respectively. Determine the residual phenol concentration at 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420, 480 min, then calculate the removal rate of phenol.
2.4. Discussion on the mechanism of adsorption

The adsorption isotherms of BC400, BC500 and BC600 on phenol were fitted by Langmuir and Freundlich models. The Langmuir model is an ideal single molecular layer adsorption model, and the single molecule adsorption formula is:

\[ q_e = \frac{abC_e}{1 + aC_e} \]  \hspace{1cm} (3)

In the formula, \( q_e \) is the adsorption capacity, \( C_e \) is the adsorption equilibrium concentration, and \( a \) and \( b \) are constant, and the reciprocal formula is:

\[ q_e^{-1} = \frac{1}{ab} C_e^{-1} + \frac{1}{b} \]  \hspace{1cm} (4)

In form (4), we can see that \( q_e^{-1} \) has a linear relationship with \( C_e^{-1} \). According to the Freundlich experiential formula:

\[ q_e = KC_e^{1/n} \]  \hspace{1cm} (5)

In the formula, \( K \) is a constant, the linear form of its equation:

\[ \lg q_e = \lg K + \frac{1}{n} \lg C_e \]  \hspace{1cm} (6)

3. Results and Discuss

3.1. Removal rate of phenol with different initial concentrations by biochar

The removal rate of phenol after adsorption of 8 h by BC400, BC500 and BC600 is shown in Figure 1. From Figure 1, when the initial concentration of phenol was 20 mg/L, the maximum removal rate of phenol by BC600 was 92.69%. When the initial concentration of phenol is 20 mg/L, the removal rate of BC400 to phenol is 48.54%, the removal rate of BC500 to phenol is 71.59%, and the removal rate of BC600 to phenol is 92.69%. With the initial concentration of phenol increasing, the removal rate of phenol decreased by BC400 and BC500. The removal rate of phenol to BC600 was almost 92% when the initial concentration of phenol was no more than 70 mg/L.

Therefore, the adsorption of phenol on the different pyrolysis temperature of herb residues biochar has great difference, during the temperature range selected in this experiment, with increasing pyrolysis temperature, the removal rate increased significantly, the average removal rate was around 40% when the pyrolysis temperature was 400°C, when the pyrolysis temperature rise to 500°C the average removal rate increased to about 60%, the average removal rate was as high as 90% when the pyrolysis temperature was 600°C.
3.2. Effect of reaction time on adsorption

From Figure 2, we can see that in the first hour of the reaction, the removal rate increases rapidly. With the reaction going on, the removal rate increases. The removal rate is almost unchanged after the reaction exceeds 360 min. The removal rate of phenol from high temperature biochar was significantly higher than that of low temperature biochar. At the beginning of the reaction, the removal rate increased fast, the reaction was over 360 min, and the reaction time was prolonged. The removal rate was basically unchanged. Therefore, the biochar adsorption reaction time is suitable for 360 min, the adsorption reaction can basically reach the equilibrium state, with the increase of time continue to maintain a high removal rate, almost no desorption phenomenon, indicating strong chemical bond formation in the adsorption sites.
3.3. Discussion on the mechanism of adsorption
The 2 fitting models have a good linear relationship, and the values of each parameter are shown in Table 1. From the Langmuir adsorption isotherm \( R^2=0.8903 \) of BC400 at 25°C, it can be seen that the adsorption of BC400 on phenol is also basically in accordance with the Langmuir model.

Table 1. Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of phenol

| Adsorption mode | Linear regression equation | \( R^2 \) | Adsorption isotherm constant | \( p \) |
|----------------|--------------------------|---------|----------------------------|-------|
| Langmuir       |                          |         |                            |       |
| BC400          | 45°C \( y = 1.9891x + 0.1166 \) | 0.8903 | \( a=0.06,b=8.58 \)        | <0.05 |
|                | 35°C \( y = 2.6309x + 0.105 \) | 0.9443 | \( a=0.04,b=9.52 \)        | <0.05 |
|                | 25°C \( y = 4.3817x + 0.123 \) | 0.9531 | \( a=0.03,b=8.13 \)        | <0.05 |
|                | 45°C \( y = 0.8748x + 0.0609 \) | 0.9841 | \( a=0.07,b=16.42 \)       | <0.05 |
| BC500          | 35°C \( y = 0.9349x + 0.0676 \) | 0.975  | \( a=0.07,b=14.79 \)       | <0.05 |
|                | 25°C \( y = 1.5109x + 0.0846 \) | 0.9662 | \( a=0.06,b=11.82 \)       | <0.05 |
|                | 45°C \( y = 0.1364x + 0.0327 \) | 0.998  | \( a=0.24,b=30.58 \)       | <0.05 |
| BC600          | 35°C \( y = 0.1704x + 0.0407 \) | 0.9848 | \( a=0.24,b=24.57 \)       | <0.05 |
|                | 25°C \( y = 0.3419x + 0.0287 \) | 0.9911 | \( a=0.08,b=34.84 \)       | <0.05 |
|                | 45°C \( y = 0.5497x + 0.0817 \) | 0.9719 | \( K=1.21,1/n=0.5497 \)    | <0.05 |
| Freundlich     | BC400                    |         |                            |       |
|                | 35°C \( y = 0.5981x + 0.1804 \) | 0.9851 | \( K=1.51,1/n=0.5981 \)    | <0.05 |
|                | 25°C \( y = 0.6159x + 0.3584 \) | 0.9881 | \( K=2.28,1/n=0.6159 \)    | <0.05 |
|                | 45°C \( y = 0.4959x + 0.3061 \) | 0.9432 | \( K=2.02,1/n=0.4959 \)    | <0.05 |
|                | BC500                    |         |                            |       |
|                | 35°C \( y = 0.4555x + 0.3153 \) | 0.9195 | \( K=2.07,1/n=0.4555 \)    | <0.05 |
|                | 25°C \( y = 0.4993x + 0.1176 \) | 0.9781 | \( K=1.31,1/n=0.4993 \)    | <0.05 |
|                | 45°C \( y = 0.6311x + 0.778 \) | 0.9748 | \( K=6.00,1/n=0.6311 \)    | <0.05 |
|                | BC600                    |         |                            |       |
|                | 35°C \( y = 0.6325x + 0.6824 \) | 0.9838 | \( K=4.81,1/n=0.6325 \)    | <0.05 |
|                | 25°C \( y = 0.6456x + 0.5338 \) | 0.9545 | \( K=3.42,1/n=0.6456 \)    | <0.05 |

4. Conclusion
1) The biochar of Chinese herb residue has strong adsorption for low concentration phenol. As a new adsorbent, biochar has achieved the goal of "using waste", and its manufacturing method is simple and has high development and application value.

2) The removal rate increases with the increasing of pyrolysis temperature. At 45°C, the adsorption rate of the initial concentration of 50 mg/L phenol at 600°C can reach 97%. Biological carbon from the pyrolysis of Chinese herb residue is a good adsorbent, and has a broad application prospect in the field of sewage treatment.

3) The adsorption isotherms of phenol from the biochar of Chinese herb residue conformed to the two modes of Langmuir and Freundlich.

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