Adsorption Characteristics of Sea buckthorn Residue Biochar on Ethyl paraben

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Abstract. The biochar adsorbent was prepared at 300, 400 and 500°C using the Seabuckthorn seed as raw material to remove the ethyl paraben in waste water. The results of adsorption experiments show that the initial concentration of ethyl paraben in wastewater, the preparation temperature of biochar, the temperature of adsorption can affect the adsorption effect of biochar on ethyl paraben. The adsorption capacity of three kinds of biochar to ethyl paraben was BC400> BC500> BC300. The isothermal adsorption line for ethyl paraben conforms to the Langmuir mode and the Freundlich mode.

1. Introduction
Ethyl paraben is a kind of common medicines and personal care products, mainly used as food, cosmetics, and medical antiseptics. It is reported that ethyl paraben (EP) is a new kind of environmental estrogen pollutant with endocrine disruption and widely exists in various water bodies. Therefore, it is of great significance to effectively control the concentration of EP in water for the remediation of environmental pollution [1-2].

In this study, the biochar adsorbent prepared from sea buckthorn residues was used to adsorb EP in wastewater [3-4]. The purpose was to provide a reference for the transformation and comprehensive utilization of waste Chinese medicine resources.

2. Materials and Methods

2.1. Preparation and acidification of biochar
Seabuckthorn residue were taken from a pharmaceutical factory in Xixian New Area of Shaanxi Province. After cleaning and drying, the residue were crushed with a crusher and burned in a muffle furnace. After pyrolysis at 300, 400 and 500°C, it was cooled to room temperature and grinded through a 100-mesh sieve.

To remove the ash from the biochar, the grinded and sifted biochar was treated for 6 hours with 1M HCl, washed to neutral with distilled water, baked in an oven at 105°C until constant weight, sealed in a brown reagent bottle and stored in a desiccator, marked BC300, BC400 and BC500 (BC stands for biochar, digital represents biochar Carbonization temperature).
2.2. Removal rate of EP from different initial concentrations

The concentration of EP after adsorption was measured by UV spectrophotometry ($\lambda_\text{max} = 247$ nm). 3 parallel experiments were carried out in each group, and the average value was obtained. EPI adsorption capacity of $q_e$ reached the adsorption equilibrium and the removal rate is calculated by the following formula:

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

(1)

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

(2)

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

Weigh 0.1 g biochar (BC300, BC400, BC500), 20 mL EP solution were added to the pre-configured 20, 30, 40, 50, 60, 70 and 80 mg/L 50 mL stoppered Erlenmeyer flask, in the constant temperature water bath box oscillation with 150 r/min 3 h oscillation at 25°C in order to reach the equilibrium state, the residual EP concentration was calculated according to the standard curve.

2.3. Effect of reaction time on adsorption

Under the room temperature, samples of EP concentration of 50 mg/L were placed in 50 mL Erlenmeyer flask, adding 0.1 g BC400, BC500, BC600, respectively. Determine the residual EP concentration at 5, 10, 30, 60, 90, 120, 150, 180 min, then calculate the removal rate of EP.

2.4. Discussion on the mechanism of adsorption

The adsorption isotherms of BC300, BC400 and BC500 on EP 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:

$$q_e = \frac{abC_e}{1+aC_e}$$

(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:

$$q_e^{-1} = \frac{1}{ab} C_e^{-1} + \frac{1}{b}$$

(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:

$$q_e = KC_e^{1/n}$$

(5)

In the formula, $K$ is a constant, the linear form of its equation:

$$\lg q_e = \lg K + (1/n) \lg C_e$$

(6)
3. Results and Discuss

3.1. Removal rate of EP with different initial concentrations
The removal rate of EP after adsorption of 3 h by BC300, BC400 and BC500 is shown in Figure 1. From Figure 1, when the initial concentration of EP was 20 mg/L, the maximum removal rate of EP by BC400 was up to 95.5%. The adsorption capacity of three kinds of biochar to ethyl paraben was BC400 > BC500 > BC300.

Figure 1. The removal rate of EP with different initial concentrations of EP.

3.2. Effect of reaction time on adsorption
From Figure 2, we can see that in the 30 min of the reaction, the removal rate increases rapidly. With the reaction going on, the removal rate increased gradually. The removal rate was almost unchanged after the reaction exceeds 150 min.

Figure 2. Effect of Reaction Time on Adsorption
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.

| Adsorption mode | Linear regression equation | $R^2$ | Adsorption isotherm constant | $p$ |
|-----------------|---------------------------|-------|-----------------------------|-----|
| Langmuir        | 45°C $y = 0.5393x + 0.0526$ $0.917$ | $a=0.10$, $b=19.01$ | $<0.05$ |
|                 | BC300 35°C $y = 0.3193x + 0.0072$ $0.9995$ | $a=0.02$, $b=138.89$ | $<0.05$ |
|                 | 25°C $y = 0.313x + 0.0055$ $0.9991$ | $a=0.02$, $b=181.82$ | $<0.05$ |
|                 | 45°C $y = 0.3877x + 0.016$ $0.9983$ | $a=0.04$, $b=62.50$ | $<0.05$ |
|                 | BC400 35°C $y = 0.2446x + 0.009$ $0.9977$ | $a=0.04$, $b=111.11$ | $<0.05$ |
|                 | 25°C $y = 0.1849x + 0.0061$ $0.9962$ | $a=0.03$, $b=163.93$ | $<0.05$ |
|                 | 45°C $y = 0.0436x + 0.0405$ $0.9941$ | $a=0.03$, $b=24.69$ | $<0.05$ |
|                 | BC500 35°C $y = 0.0501x + 0.0361$ $0.9862$ | $a=0.02$, $b=27.7$ | $<0.05$ |
|                 | 25°C $y = 0.1683x + 0.0263$ $0.9837$ | $a=0.16$, $b=38.02$ | $<0.05$ |
|                 | 45°C $y = 1.3753x + 0.2608$ $0.9564$ | $K=1.82$, $1/n=1.3753$ | $<0.05$ |
|                 | BC300 35°C $y = 1.0573x + 0.5017$ $0.9996$ | $K=3.17$, $1/n=1.0573$ | $<0.05$ |
|                 | 25°C $y = 1.0441x + 0.5092$ $0.9987$ | $K=2.33$, $1/n=1.0441$ | $<0.05$ |
|                 | 45°C $y = 0.8746x + 0.4132$ $0.9974$ | $K=2.59$, $1/n=0.8746$ | $<0.05$ |
| Freundlish      | BC400 35°C $y = 1.071x + 0.6274$ $0.9979$ | $K=4.24$, $1/n=1.071$ | $<0.05$ |
|                 | 25°C $y = 0.9207x + 0.7258$ $0.9942$ | $K=5.32$, $1/n=0.9207$ | $<0.05$ |
|                 | 45°C $y = 0.6941x + 0.7357$ $0.9964$ | $K=5.44$, $1/n=0.6941$ | $<0.05$ |
|                 | BC500 35°C $y = 0.6377x + 1.0416$ $0.9989$ | $K=11.01$, $1/n=0.6377$ | $<0.05$ |
|                 | 25°C $y = 0.6223x + 1.0541$ $0.9651$ | $K=11.33$, $1/n=0.6223$ | $<0.05$ |

4. Conclusion

1) The biochar of sea buckthorn residue has strong adsorption for EP.
2) The adsorption capacity of three kinds of biochar to ethyl paraben was BC400> BC500> BC300.
3) The adsorption isotherms of EP from the biochar of sea buckthorn residue conformed to the two modes of Langmuir and Freundlich.

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