Adsorption of Cd (II) From Aqueous Solutions by Raw and Modified Tea Residue Biochars

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Abstract. In this study, tea residue was used as raw material for biochar to investigate the adsorption performance. Brunauer–Emmett–Teller (BET) analysis and Fourier transform infrared spectroscopy (FTIR) were used to determine the characteristics of adsorbents and to investigate the adsorption mechanism. The results showed that: (1) After modified with different concentration of KOH, the oxygen-containing functional groups and organic functional groups on the surface increased, specific surface area and pore structure amplified. Base modification provided ways for Cd (II) adsorption, such as ion exchange or cooperate with heavy metal, and provided more adsorption sites. (2) In the isothermal adsorption experiment, the Langmuir model could better match the adsorption behavior of biochars on Cd (II). 3 mol/L KOH modified biochar had the optimal adsorption effect. Under the condition of temperature was 45°C and pH was 6, the maximum saturated adsorption capacity can reach 120.028 mg/g, significantly higher than the unmodified biochar (G0 = 80.418 mg/g).

1. Introduction
Nowadays due to the rapid industrial development, such as application of phosphate fertilizers, mining activity, battery plants, zinc-smelting factories, heavy metals have been released to aquatic and soil environments [1]. Cadmium (Cd) has been recognized as one of the strongest environmental heavy metal pollutants. It has been classified as a human carcinogen and causes organ failure [2, 3]. Therefore, Cd removal from water sources has given rise to serious public concern.

Biochar is a form of carbon-rich materials derived from various biomass residues such as wood materials, crops straw, animal manure, sewage sludge, or other agricultural byproducts [4]. Biochar has been recognized as a highly efficient and cost-effective adsorbent for organic and inorganic pollutants, contributing to its porous structure, hydrophobicity, high pH and cation exchange capacity.

Tea tree cultivation and tea production are highly significant agricultural activities in China, with approximately 2.87×10⁴ km² planting area [5]. Tea is a kind of porous bio-adsorbent that has reticulate structure and high surface areas [6]. In addition, tea has abundant chemical component, which is identified that tea contains almost 600 kinds of organic and inorganic compounds. The presence of hydroxyl and phenolic groups in tea leaves can react with metal ions through adsorption and complexation [7]. Conversion of this natural wastes to value-added product such as porous carbon materials for water decontamination could help remediate the pollution problem [8].
For now, there are many modification methods for improving the adsorptive capacity of biochars, such as magnetic treatment, base treatment and acid modification [9]. Base modification of biochars may enlarge surface areas, improve pore structure and increase hydroxyl groups [10]. Thus, the objectives of this study were to investigate the effectiveness of tea residue biochar as adsorbent in removing Cd (II) from aqueous solution by comparing the differences in adsorption capacity between modified and unmodified biochars.

2. Material and methods

2.1. Biochar and reagents
Green tea residue sample was collected from the tea market in Chengdu, China. After removing impurities, the green tea residues was steeped in deionized water for 24 hours. Then the sample was dried and then was loaded into porcelain crucible and placed in the middle of the muffle furnace (M110 Thermo Scientific, America). Then, the temperature of the furnace was increased at a heating rate 15 °C/min and maintained at 550°C temperature for 2 h. After biochar was cooled to room temperature, then was crushed using blender to pass a 0.25 mm sieve for analyses. The unmodified biochar was labeled as TB0.

2.2. Preparation of modified biochars
The modified biochar was produced as follow: green tea residue was mixed with different concentrations (1M, 2M, 3M and 4M) of KOH solution, then was stirred vigorously at 25°C for 1h. The materials were washed several times with distilled water. After the sample was dried at 55°C, the carbonization process was the same as the untreated biochar. The modified biochar was labeled as TB1, TB2, TB3 and TB4.

2.3. Characteristic of biochars
Surface area, pore volume and pore size were determined by Brunauer–Emmett–Teller (BET) analysis, using a NOVA 1200 surface area pore analyzer (Quantachrome Instruments, USA). Functional groups were identified by FTIR spectroscopy (Thermo Fisher Scientific, USA).

2.4. Adsorption studies

2.4.1. Preparation of solution. The Cd solution was prepared by dissolving cadmium chloride (CdCl2·2.5H2O) in deionized water. Hydrochloric acid and sodium hydroxide (0.01 M HCl and NaOH) were prepared to adjust pH of solutions.

2.4.2. Sorption methods. Approximately 0.08 g biochar was added to 50 ml artificially contaminated cadmium solution with a range of concentrations (5–200 mg/L) in glass tube over a 1h contact period at 40°C. The initial pH of each Cd (II) solution was adjusted to around 6.0. After sorption, the suspension was centrifuged and filtered through 0.45 μm pore polypropylene membrane filters. The final concentration of Cd in the obtained supernatants was determined by atomic absorption spectrometry (GTAAS-M6). All batch experiments were run in triplicate.

2.5. Statistic analysis
All data were statistically analyzed using software of IBM SPSS Statistics 20.0 (SPSS Inc, Chicago, IL, USA). Origin 2018 software was used for drawing.
3. Results and discussion

3.1. BET analysis

The biochar after modification of KOH, specific surface area, pore volume and pore diameter were all increased. The possible reason was that KOH solution had strong corrosive effect, through the process of chemical modification, the obstruction in the pores was cleaned up and the pore structure space was enlarged, which provided more sites for heavy metal adsorption [11].

| Biochars | SSA (m² g⁻¹) | PV (cm³ g⁻¹) | PZ (nm) |
|----------|--------------|--------------|---------|
| TB0      | 18.393       | 0.840        | 1.638   |
| TB1      | 26.135       | 0.948        | 2.938   |
| TB2      | 28.788       | 0.960        | 3.467   |
| TB3      | 48.183       | 0.971        | 5.201   |
| TB4      | 38.398       | 0.938        | 3.495   |

SSA, specific surface area; PV, pore volume; PZ: pore size.

3.2. FTIR analysis

Biochar with more oxygen-containing functional groups has strong cation exchange capacity and strong adsorption capacity for Cd (II) [12, 13]. Fig.1 showed that, biochar exhibited various surface groups containing oxygen groups (C=O, -COO⁻, -OH) and other groups (olefins, CH₂-CH₃, aromatic rings). The spectras of different concentrations KOH modified biochars were similar because they all contained the same chemical composition. The 3414 cm⁻¹ band was the -OH stretch peak, increased in the spectra for the biochar after the base modification, indicating that the oxygen-containing functional groups on the surface of biochar increased [14]. Absorption at 700 cm⁻¹ - 900 cm⁻¹ corresponded to the bending vibration peak of the C-H benzene derivatives, increased in the spectra for the biochar with the base modification. TB2, TB3 and TB4 exhibited asymmetric and symmetric stretching vibration of C=O in the ionic carboxyl group (COO⁻) at 1400 cm⁻¹ and 1700 cm⁻¹. The results showed that after the base modification, surface oxygen containing functional group and organic functional groups were increased, providing ways to adsorb heavy metals in solution through ion exchange or coordination process.

Figure 1. FTIR infrared spectra of tea residue biochar (TB0) and biochars modified in different concentrations of KOH (TB1-TB4).
3.3. Equilibrium data and isotherm modelling

Adsorption isotherm can be used to describe the relationship between the balance of the adsorbent and the adsorbate, and can pass the relevant formula get maximum saturated adsorption amount. The Langmuir model is an ideal monomolecular adsorption model with the same affinity for all adsorption sites [15], and Freundlich model is suitable for adsorption under non-uniform surface conditions [16].

\[
\text{Langmuir: } Q_e = \frac{G_0 C_e}{A + C_e}
\]  

Where \( Q_e \) is the amount of Cd(II) adsorbed on per weight adsorbents after adsorption equilibrium (mg/g), \( C_e \) represents the metal equilibrium concentration in solution (mg/L), \( G_0 \) is the saturation value, which represents the maximum metal sorption capacity, \( A \) is a constant related to binding strength.

\[
\text{Freundlich (1906): } Q_e = K \cdot (C_e)^{1/n}
\]  

Where \( K \) and \( n \) are the isotherm constants. \( K \) is the Freundlich affinity coefficient, \( n \) is the indicator of adsorption intensity, respectively. The value of \( 1/n \) is less, the adsorptive property is better.

| Adsorbents | Langmuir | Freundlich |
|------------|----------|------------|
|            | \( G_0 \) | \( A \)    |
|            | \( R^2 \) |            |
|            | \( K \)  | \( 1/n \)  |
|            | \( R^2 \) |            |
| TB0        | 80.418   | 5          |
|            | 0.967    | 17.787     |
|            | 0.359    | 0.902      |
| TB1        | 95.974   | 4.651      |
|            | 0.962    | 23.138     |
|            | 0.336    | 0.847      |
| TB2        | 102.817  | 3.006      |
|            | 0.979    | 27.805     |
|            | 0.348    | 0.896      |
| TB3        | 120.028  | 2.782      |
|            | 0.978    | 33.867     |
|            | 0.339    | 0.822      |
| TB4        | 107.901  | 2.795      |
|            | 0.990    | 29.789     |
|            | 0.336    | 0.854      |

From Table 2, the isothermal adsorption of the unmodified and modified biochar on Cd\(^{2+}\) was more consistent with the Langmuir model. \( G_0 \) represented the maximum metal sorption capacity attained equilibrium time, the modified biochar was obviously higher than the raw biochar (\( G_0 = 80.418 \) mg/g), which illustrated the adsorption capacity of biochar after the modification process improved significantly. The constant \( K \) in Freundlich model reflected the strength of adsorption capacity, the biochar modified was higher than the unmodified. The 3 mol/L KOH modified biochar presented the best adsorption performance, \( K = 33.867, G_0 = 120.028 \) mg/g.

**Figure 2.** Adsorption isotherms using raw (TB0) and modified biochars (TB1-TB4) for the removal of cadmium, under optimized operating conditions.
The equilibrium sorption capacity of biochars for cadmium elevated with the increasing initial concentration and then plateaued at equilibrium concentrations (Fig 2.). This was probably due to the high driving force of mass transfer. When the equilibrium concentration of Cd (II) was low, the adsorbent had the sufficient adsorption site and active group, and as the initial concentration of solution increased, the adsorption site saturated, and the active group decreased, so the adsorbent reached the adsorption saturation [17]. From the Fig 2, it can be seen that the adsorption isotherms of all biochars were more consistent with the Langmuir isothermal equation, and the adsorption performance of the modified biochar improved.

4. Conclusion
The sorption capacities of tea residue biochars for Cd (II) was greatly enhanced after base treatment. Comparing with the unmodified biochar, the 3mol/L KOH modified biochar showed the highest adsorption capacity for Cd (120.028 mg/g), due to the improved pore structure and the enhance specific surface areas, and the increasing number of oxygen-containing functional groups. Hence, the tea residue biochar modified by KOH can provide an effective way to enhance Cd (II) removal from aqueous solutions under the optimum condition.

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