The Research on Adsorption of Cd (II) by Magnetic Biochar

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Abstract. In order to get a deeper understanding of the impact on environmental behavior of Cd (II) made by application of magnetic biochar, this article discusses possible adsorption mechanism of magnetic biochar to Cd (II). We made six magnetic biochars through coprecipitation method and pyrolysis under N2 at 200 ℃ -600 ℃ using pine and corn straw. The magnetic biochars (MB) were characterized by element analyzer, FTIR, zeta potential and SEM. The adsorption behavior was studied by batch experiments. The results are as follows: with pyrolysis temperature improving, indicators such as pH, aromaticity, surface area of magnetic biochars improves; the Freundlich model shows better fitting result of adsorption to Cd(II) by magnetic biochar and 400 ℃ magnetic biochars have highest capacity for Cd(II) with MB coming from corn straw higher performance.

1. Introduction
Heavy metals such as cadmium have caused enviromental and health concern in the world for its high toxicity and mobility [1] Report on the national soil contamination in China published in 2014 [2] showed 19.4% agricultural land was affected by chemical polluton to varying degrees which Cd pollution was principal in southwest and southeast region. Soil exposed to Cd pollution for a long term may induce its accumulation in ecological system [3] and even threats human health through food chain directly or indirectly such as lung cancer and hematuresis. So it’s necessary to make remediation for polluted water and soil. currently adsorption method has become a simple but efficient way to fix heavy metals and biochar as an efficient adsorption material is environment-friendly and have low cost. biochar can fix heavy metals effectively for its high carbon content, CEC and surface area, rich oxygen-containing functional groups[4],but it will be influenceed by environment and cause re-emission [5]. Compared with biochar, magnetic biochar can be removed from soil with farming machinery using magnetism and reduce total heavy metals in farmland as well as bioavailability,so magnetic biochar is a research focus as an remediation material for heavy metal polluted soil.

At present, magnetic biochar has plentiful raw material source such as corn straw, rice husk [6]-[7] and various synthetic method ,for example, chemical co-precipitation [8], impregnation, hydrothermal [9], oxidation reduction methods [10]. What’s the relationship between carbonization condition (such as ram material source and carbonization temperature) and characteristics of MB? How will they make a influence on adsorption to Cd (II) by MB? This question need us make study. This article choose residual in agriculture and forestry (corn straw and pine chip) as material to prepare MB and discuss adsorpton mechanism of MB at different pyrolysis temperature to Cd (II) which is helpful to its proper application in polluted soil remediation process.
2. Experiment method

2.1. Preparation of MB
Magnetic biochar was prepared by chemical co-precipitation method [11]. First, adjust mixed solution’s pH containing Fe(NO3)3·7H2O and FeSO4·9H2O to 12 controlling Fe3+:Fe2+ was 2:1; then add biomass (corn straw and pine chip) to the solution above making Fe/C 0.6 and stir uniformly; activate in N2 atmosphere at 60℃ for 2h with magnetic stirring. The residual was cold dried and pyrolysis at 200℃, 400℃, 600℃ in muffle furnace for 2h. The MBs obtained finally were sighed with PMB2, PMB4, PMB6, CMB2, CMB4, CMB6 which number (2, 4, 6) represents pyrolysis tempreture.

2.2. Characteristics of MB
C, H, O, S and N element in MB was measured by element analyzer (vario MICRO cube, Elementar, Germany). Specific surfac area of MB was finished by full automatic absorption apparatus (ASAP2020M, Micromeritics, America) under N2 atmosphere. MB’s FTIR characterization was finished by Varian640-IR with scanning area 4000~400 cm⁻¹ after fully grinding with KBr and tableting. MB’s pH was measured by pH meter (AB15, Fisher Scientific, America). Surface morphology of MB was scanned by SEM (VEGA3 SBH, Czech Republic) at 10-100um.

2.3. Isothermal adsorption test of Cd (II)
Cd (II) (1000 mg•L⁻¹) reserving solution: was prepared using Cd (NO3)2 and 0.01 mg•L⁻¹NaNO3 solution.

Adsorption isotherm of Cd (II) by MB: according to pre-experiment we set equilibrium time as 48h. Firstly, dilute the Cd (II) reserving solution to 1~10 mg•L⁻¹ by 0.01 mg•L⁻¹NaNO3 solution and every adsorption isotherm conclude 8 concentration points which contains 2 parallel samples. Then add 8±0.05 mg MB to 8 mL sample vials as well as 8±1 mL 1~10 mg•L⁻¹ Cd (II) (pH3.0±0.05) with solid-liquid ratio 1 g•L⁻¹ and the sample vials were transferred to shaking table reacting at 25±0.5 ℃ and 150 rpm for 48h. After reaction, the samples were centrifuged at 2500 rpm for 15 minutes and filtered by 0.45 µm microporous membrane. And filtrate were measured for Cd (II) equilibrium concentration with FAAS (Z-2000, Hitachi, Japan). Adsorption capacity under different initial concentration C0 was cauculated by equation (1) as follow:

\[
Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}
\]

where \(Q_e\) represents capacity of MB to Cd (II) after equilibrium, mg•g⁻¹; \(C_0\) and \(C_e\) is respectively Cd (II) concentration in initial stage or equilibrium time, mg•L⁻¹; \(V\) is solution volume, mL; \(m\) is MBs’ weight, mg.

Adsorption isotherm is fitted with Langmuir (2) and Freundlich (3) model, fitting formula as bellow:

Langmuir Model (LM):

\[
Q_e = \frac{Q_mK_LC_e}{(1 + K_LC_e)} \tag{2}
\]

Freundlich Model (FM):

\[
\log Q_e = \log K_f + n\log C_e \tag{3}
\]
where $Q_e$ and $Q_a$ represents adsorption capacity of solid after equilibrium or on extremum condition, mg·g$^{-1}$; $C_e$ is Cd concentration in solution after equilibrium, mg·L$^{-1}$; $K_L$ is adsorption coefficient of Langmuir model, L·mg$^{-1}$; $K_F$ is adsorption coefficient of Freundlich Model, (mg·g$^{-1}$)$^n$; $n$ is Freundlich constant. It’s different between the number of coefficients in model and data points that common determination coefficient $r^2$ can’t be compared directly [12]. Formula (4) turn $r^2$ into $r_{adj}^2$ for comparison:

$$r_{adj}^2 = 1 - \frac{(1 - r^2)(m - 1)}{m - b - 1}$$  (4)

where $m$ is the number of data points used for fitting; $b$ is the number of coefficient in formula.

3. Result and Discussion

3.1. Characteristics of Magnetic biochar

Table 1 shows two kinds of MB’s (corn straw and pine chip) physicochemical properties. With pyrolysis temperature improving, the two kind MBs’ surface area and pore volume increases gradually while pore size decrease indicating that the amount of micropore become larger. O and C content in MBs become lower by degrees with increasing temperature may because (1) the exist of iron element induces cracking and volatile process of carbon-containing compounds; (2) oxygen-containing macromolecules complex with Fe(OH)$_3$ in hydrothermal basic media and reduction reaction happened during carbonization process resulting in iron oxides preserving oxygen in a way [13]. Besides, O/C increases while H/C reduces in MBs with higher temperature showing the higher pyrolysis temp preture the more aromatic the MBs is [14]. 400℃ MBs’ zeta potential is highest which may be intimately relative to abundant carboxyl and hydroxy groups on them which adsorb large amount of protons and thus a lower electronegativity with less eletrons on the surface [15]. Comparing with corn straw magnetic biochar (CMB), pine chip magnetic biochars (PMB) have higher surface area. This may be relative ti its higher amount of lignin of which structure is stable and will form graphene sheet during pyrolysis process inserting into amorphous carbon matrix at high temperature. When temperature get to 400℃ or above, the aromaticity of PMB is better than CMB which may because pine chip contain larger amount of lignin [16]. PMB and CMBs’s pH is almost same for modification process weaken this difference.

![Table 1. Physical and chemical properties of magnetic biochars](image)

Surface functional groups of MBs are characterized by FTIR and results are showed at Figure 1. Peak of Fe-O at 534 cm$^{-1}$ is obvious for both PMB and CMB showing magnetic particles impregnating successfully. Types of functional groups in MBs with different raw material source has no distinct difference but adsorbance of functional groups among each material is slightly different indicating the amount of functional groups in identical kind is controlled by biomass resource. During pyrolysis process cellulose started to dehydrate and decarboxylate and the hydroxy (3800~3200 cm$^{-1}$) in MBs
decreases gradually [17]. When temperature improves carbohydrates, aliphatic and alicyclic compounds in biomass crack weakened antisymmetric vibrated peaks of -CH$_2$ and C-H (2942 and 2904 cm$^{-1}$). Vibrated peaks of aromatic –CH (640 cm$^{-1}$) become sharp with temperature improving resulting in higher aromaticity [18]. Also peaks of C=O in carboxyl and ketones or C=C (1640 cm$^{-1}$) in aromatic ring decrease.

![Figure 1. FTIR.](image1)

Surface morphology of MBs is measured by SEM and showed at Figure 2. MBs pyrolysis at 200°C and 600°C present features of nonuniform distribution. 200°C MBs have poor pore structure while 600°C MBs have a better pore structure as well as uniform surface morphology. At the same time, inorganic compound in biochar have been preserved in the form of ash during carbonization.

![Figure 2. SEM.](image2)

3.2. Research on adsorption isotherm of Cd (II)
The adsorption isotherms of Cd (II) by PMB and CMB are fitted by Langmuir Model (LM) and Freundlich Model (FM) and relevant fitting parameters are listed on Table 2. As for PMB and CMB, Freundlich model’s corrective correlation coefficient ($r_{adj}^2$) (0.87~0.98) fitting adsorption isotherm is larger than Langmuir model’s (0.81~0.97) showing that Freundlich model (FM) fits adsorption of Cd (II) by MBs better. Nonlinear exponent(n) of FM is located in 0.34~0.62(<1.0) and becomes smaller with temperature improving indicating a strong heterogeneity effect happened between this two kind of
MBs coming from corn straw and pine chip during adsorption process of Cd (II). The capacity of Cd (II) gets to highest with 400℃ MBs which is the same as Zhang’s research [19]. Medium temperature biochar behaves better adsorption result for its abundant functional groups and π electron structure that holds a better influence in physico-chemical adsorption effect. Compares with pine chip MB, corn straw MB shows better performance on adsorption of Cd (II) which have more oxygen-containing functional groups and higher N, S element.

![Figure 3. Adsorption isotherm of Cd (II).](image)

| MB     | LM |   |   |   |   |   |
|--------|----|---|---|---|---|---|
| a      | b  | K_L| Q_m| R^2| a  | b  | K_F| n  | R^2 |
| PMB2   | 0.23| 0.16| 1.42| 0.94| 0.23| 0.62| 0.23| 0.62| 0.95 |
| PMB4   | 68.71| 6.22| 6.22| 11.05| 0.97| 9.73| 0.37| 9.73| 0.37| 0.94 |
| PMB6   | 6.31| 1.92| 1.92| 3.28| 0.81| 1.96| 0.34| 1.96| 0.34| 0.97 |
| CMB2   | 51.03| 3.96| 3.96| 12.89| 0.95| 11.30| 0.48| 11.30| 0.48| 0.96 |
| CMB4   | 253.96| 14.77| 14.77| 17.20| 0.94| 42.85| 0.61| 42.85| 0.61| 0.98 |
| CMB2   | 640.94| 56.94| 56.94| 11.26| 0.83| 26.98| 0.41| 26.98| 0.41| 0.87 |

4. Conclusion
(1) As pyrolysis temperature increases, characteristics of MBs such as surface area, pore volume, amount of negative charge and O/C shows improvement while pore size and C, O content become lower;
(2) Through fitting the adsorption isotherms of Cd (II) by Langmuir Model (LM) and Freundlich Model (FM), it’s been found that two models both get a good fitting result with Freundlich model being better; the adsorption capacity of Cd (II) by CMB is higher than PMB at each temperature.

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