# Adsorption of Pb(II) from aqueous solutions by wheat straw biochar

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**Abstract.** This work focuses on the preparation of biochar and the study of the adsorption properties of lead ions on it in water. CS (carbon wheat straw) was obtained by carbonizing 60 min at 300˚C. Batch experiments were conducted to study the effects of initial pH value, contact time, adsorbent dose, initial concentration and temperature on the adsorption properties. Pseudo first order and pseudo second order models were used to study the kinetics of the process, and results showed adsorption of $Pb^{2+}$ by CS followed pseudo second order kinetic model. The Langmuir isotherm model provided the best correlation for $Pb^{2+}$ adsorption, indicating that the adsorption was chemical monolayer adsorption. The adsorption capacity $q_m$ was increased with increasing temperature, reached 149.701mg/g for CS and 44.663 mg/g for NS (natural straw), at 35˚C, respectively, showing the adsorption was exothermic. It was concluded that the adsorption capacity of CS is 3.3 times of that of NS which means that the carbonization of wheat straw was of certain value in the treatment of lead ions in wastewater.

## 1. Introduction

Many researchers turned to study of biochar as the heavy metal adsorbent due to the characteristics of carbon-rich, fine-grained, and porous. The biochar usually produced by thermal decomposition under oxygen-limited conditions at temperature <900˚C [1]. Heavy metal ions are reported as priority pollutants [2], because of their enrichment and biological toxicity. The toxic effect against living organisms varies owing to the differences between heavy metals, lies on their nature, concentration, mode of action, valence state and bioavailability [3]. The application of biochar to the adsorption of heavy metals has many notable properties, such as low cost, eco-friendliness, and the wide range of available feedstock materials, as well as mechanical and thermal stability [4]. The properties of biochar are affected by the temperature of pyrolysis and the properties of raw materials. Biochar has a wide range of sources, such ashardwoodand corn straw [5], waste marine macro-algal [4], rape straw [6] and so on.

The aim of this study was to use wheat straw biochar as an adsorbent for the removal of Pb(II) in aqueous solutions. The effects of the initial lead concentration, pH, contact time, and temperature on the adsorption properties were studied. In addition, adsorption kinetic and isotherms models were applied in order to study the adsorption mechanism.

## 2. Materials and methods

*2.1. Preparation of the wheat straw biochar*

The wheat straw was lapping to a mean particle size of less than 0.2 mm, rinsing with deionized water for several times until the filtered water was colorless. Finally, the wheat straw was dried at 60˚C in an oven. The natural straw was made from this, called NS.

At room temperature (25±0.2˚C), NS was dipped into 200 mL of 20% zinc chloride solution for 12 h. In the process, they were agitated to make them mixed fully. Next, it was dried and burning at 300˚C for 60min in a muffle furnace and were then washed several times with distilled water until the pH values remain stable while washing after natural cooling. At last, they were dried at 60˚C in an oven continuously for 24h and stored in plastic airtight container for subsequent stand by application.

*2.2. Preparation of the metal solution*

The stock lead solutions (1000 mg/L) were prepared by dissolving lead nitrate ($Pb(NO_3)_2$)in distilled water. The initial pH of the solution was adjusted by 0.1 mol/L HCl or NaOH at designed values.

*2.3. Batch equilibrium studies*

The adsorption experiments were carried out in 250 mL erlenmeyer flasks containing 150 mL of $Pb^{2+}$ solution in batch at 25˚C. A given dose of adsorbent was mingled with the desired concentration. The mixture was shook for a certain time with a shaker oscillator, time much more than the time it took to achieve adsorption equilibrium. After resting for 5 min, they were filtered through 0.45 μm microporous filter membrane, and then the concentration of lead ions in the supernatant was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, optima 7000DV) until the adsorption equilibrium was reached. The percentage removal of $Pb^{2+}$ was calculated using the equation:

$$\text{Removal}(\%) = \left(C_0 - C_e\right) \times 100\% / C_0 \tag{1}$$

The adsorption capacity $q_e$(mg/g) was calculated according to the following equation:

$$q_e = \left(C_0 - C_e\right)V / m \tag{2}$$

Where $C_o$ and $C_e$ are the initial metal ions concentration and equilibrium metal ions concentration, mg/L, respectively; V is the volume of metal ions solution, L; m is the mass of adsorbent used, g.

## 3. Results and discussion

*3.1. Effect of initial pH*

The scope of the initial pH value in the solution was studied from 2 to 6.5 due to the existence of $Pb(OH)_2$ at pH＞6.5 [7], and $Pb^{2+}$ dominates at pH≤6.5. The significant influence of pH in the adsorption was reflected on the surface charge state of adsorbents and adsorbates and the degree of dissociation of functional groups [8]. The effect of initial pH value on the removal percentage of $Pb^{2+}$ is shown in figure 1. There was an obvious increase of the adsorption rate in the range of pH value between 2.0-4.0, meanwhile, the removal rate of CS was higher than the NS in that range. They were reached 97.24% and 76.46% at pH of 4, respectively, which indicated that the method of making wheat straw into biochar was successful. Whereas a gradual increase in removal percentage was observed with increase of pH from 4 to 6.5, >76% and >97% removal was observed above pH of 4, respectively. The removal percentage reached a plateau and there was no significant increase at pH>5 for CS. At pH of 6, the removal rate of NS has a little drop, but it was above 75%. This phenomenon can be explained as follows: The high concentration of active $H^+$ in the solution made the adsorbent surface protonated and positively charged, and the lead ion was a positive ion, which was far away from the surface of the adsorbent under the action of the electrostatic repulsion at low pH, so the adsorption rate was low. With the increase of pH value, the adsorption sites became negatively charged and the presence of a large number of ligands reacting with Pb(II) ions in solution would promote adsorption and gradually reach the optimum state. They were pH=5 for all adsorbents.

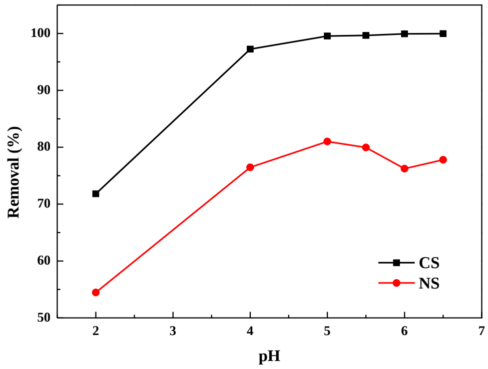


**Figure 1.** Effects of initial pH on $Pb^{2+}$ removal by CS and NS.
notes: m=1 g for NS and 0.5 g for CS,V=150 ml, T=25˚C, $C_0$=100 mg/L, d≤0.2 mm, shaking speed = 150 rpm, t=2 h

### *3.2. Effect of the dosage of CS*
The influence of different adsorbent dosage on the removal of Pb(II) by CS and NS was shown in figure 2. It is obvious that the removal rate reached 98.27% at 0.3g for CS and 79.86% at 1g for NS. And the removal rate was not increasing when adding more adsorbents, tending to reach the adsorption equilibrium. This could be explained that there were more available adsorption sites as the adsorbent dosage was increased. Under the same adsorption state, the adsorption capacity of CS was higher than that of NS, and they are 49.13, 11.99 mg/g, respectively.

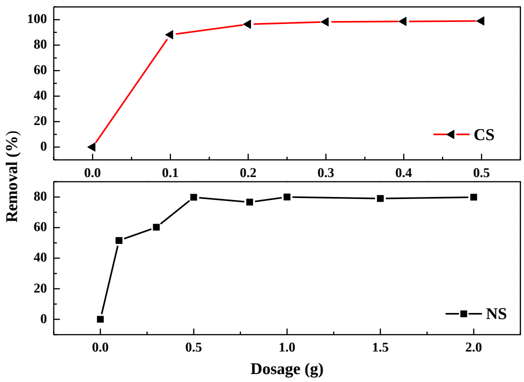


**Figure 2.** Effect of the adsorbent dosage on $Pb^{2+}$ removal by CS and NS.
notes: V=150 ml, T=25˚C, $C_0$=100 mg/L, d≤0.2 mm, shaking speed = 150 rpm, t=2 h, pH 5.

### *3.3. Adsorptionkinetic analysis*
The adsorption kinetic is used to analyze the variation tendency of adsorption capacity with the increase of contact time. Figure 3(a) shows that with the increase of time from 0 to 60 min, the adsorption capacity of the two adsorbents gradually increased and reached the adsorption equilibrium at 60 min, and the time was no longer changed. After this equilibrium period, there was a very small change in adsorption. It's notable that the adsorption capacity of CS was nearly three times that of NS from the comparison of two kinds of adsorbents under the same adsorption state which was 29.58 mg/g and 11.99 mg/g. The research of adsorption kinetics can provide valuable reference for the mechanism of adsorption [9], at the same time it was useful for the design and modeling of the

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adsorption system [8].

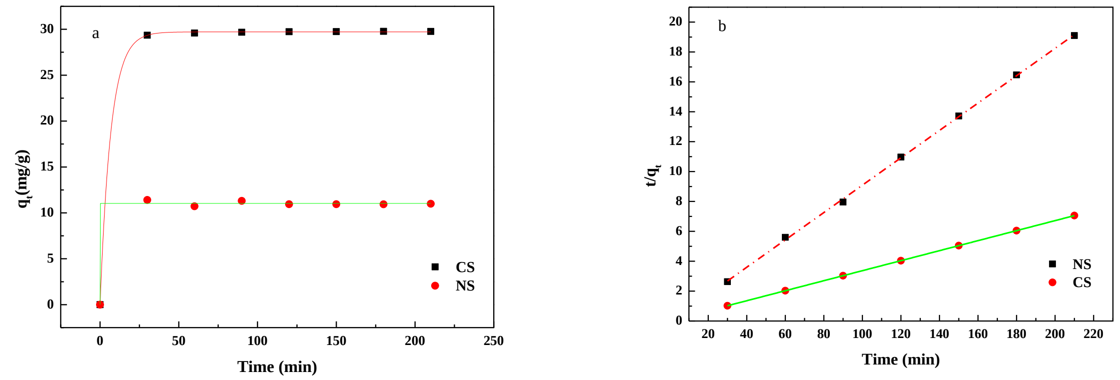


**Figure 3.** Pseudo-first-order (a) and Pseudo-second-order (b) for $Pb^{2+}$ adsorption. notes: m=1 g for NS and 0.5 g for CS, V=150 ml, T=25˚C, $C_0$=100 mg/L, d≤0.2 mm, shaking speed = 150 rpm, pH 5.

The experimental data were fitted to the kinetic model called Pseudo-first-order and Pseudo-second-orderto to make a more intuitive analysis of the kinetic characteristics of the adsorption process. Table 1 tabulates the calculated kinetics parameters for adsorption of lead ions onto the wheat straw biochar and natural straw. It is very clearly that the correlation coefficients of these two models were higher than 0.99 ($R^2 \geq 0.98$) and the pseudo-secondorder equation appeared to be a best-fitting model than pseudo-first-order. The specific fitting results were shown in the figure 3. The pseudo-second-order is an equation based on the sorption capacity on the solid phase, indicated that theadsorption of the lead ion onto the CS and NS controlled by chemisorption [10].

**Table 1.** Parameters of Pseudo-first-order and Pseudo-second-order for $Pb^{2+}$ adsorption.

| $Pb^{2+}$ | | | | | | |
|---|---|---|---|---|---|---|
| | Pseudo-first-order | | | Pseudo-second-order | | |
| | $q_e$(mg/ g) | $R^2$ | $k_1$ | $q_e$(mg/ g) | $R^2$ | $k_2$ |
| NS | 11.034 | 0.996 | 2.399 | 10.922 | 0.999 | -0.128 |
| CS | 29.716 | 0.999 | 0.146 | 29.842 | 1.000 | 0.068 |

### *3.4. Adsorption isotherms analysis*

The isothermal model was analyzedto account for the adsorptionbehavior of lead ion on the wheat straw biochar, and the most commonly used adsorption models are Langmuir and Freundlich, which can provide information about the nature of the material's adsorption and adsorption capacity [11]. The Pb(II) adsorption isotherms were studied at different initial heavy metal concentrations ranging from 20 to 700 mg/L and were shown in figure 4. The adsorption constants and correlation coefficients obtained from Langmuir and Freundlich isotherms were given in table 2. We can see that the adsorption process of lead on CS and NS can be better fitted to Langmuir model compared to Freundlich equation, means the surface was completely homogeneous and it was mainly chemical monolayer adsorption [12]. Based on the Langmuir equation, the value of $q_m$ increased with increasing temperature, and reached 149.701 mg/g for CS and 44.663 mg/g for NS at 35˚C, which confirms that the adsorption process for Pb were endothermic reaction.

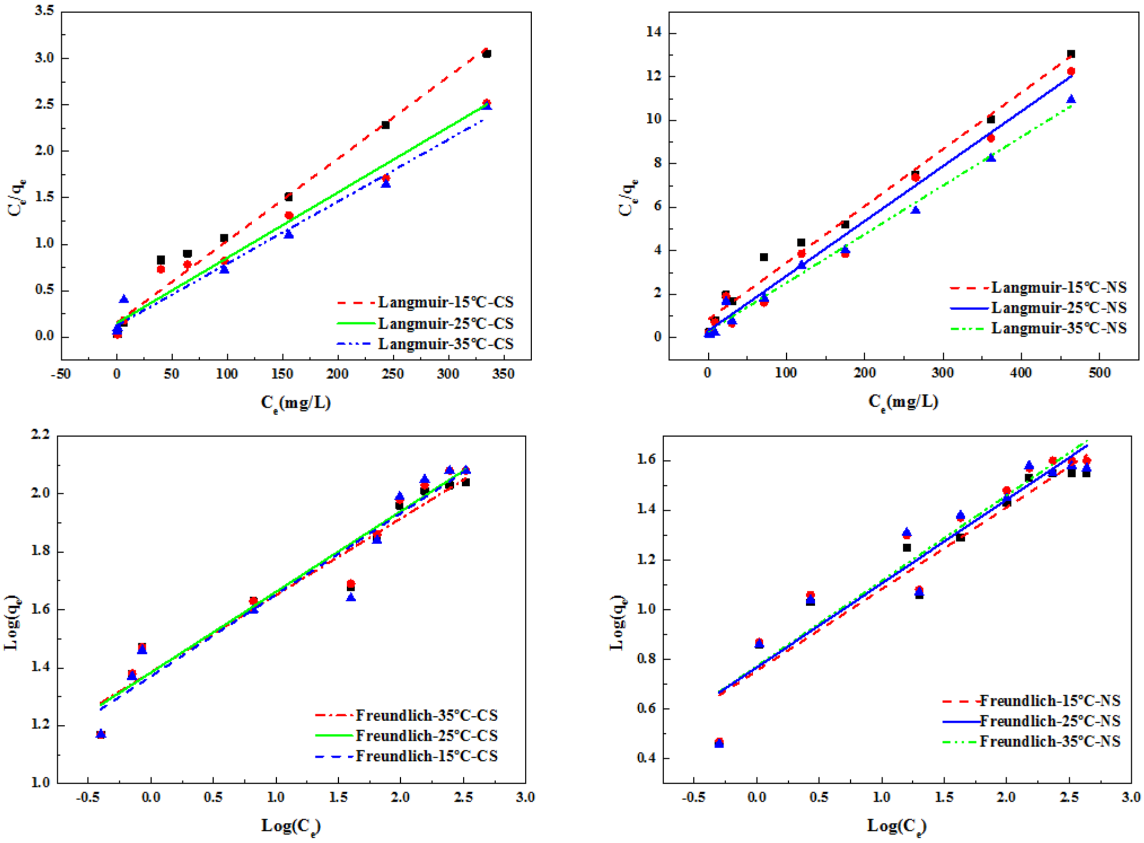


**Figure 4.**The linearized Langmuir and Freundlich adsorption isotherm of CS and NS.

**Table 2.** Parameters of Langmuir and Freundlich adsorption isotherm for CS and NS.

| Pb | NS | | | CS | | |
|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 15°C | 25°C | 35°C |
| Langmuir | | | | | | |
| $q_m$ (mg/g) | 38.241 | 39.557 | 44.663 | 113.250 | 142.248 | 149.701 |
| B (L/mg) | 0.031 | 0.081 | 0.077 | 0.057 | 0.047 | 0.054 |
| $r^2$ | 0.985 | 0.981 | 0.989 | 0.977 | 0.964 | 0.979 |
| Freundlich | | | | | | |
| $K_F$[mg/(g(mg/L)$^{1/n}$)] | 5.679 | 5.936 | 5.861 | 24.270 | 24.189 | 23.454 |
| n | 3.038 | 2.912 | 2.960 | 3.769 | 3.594 | 3.550 |
| $r^2$ | 0.909 | 0.908 | 0.897 | 0.939 | 0.942 | 0.925 |

## 4. Conclusion

The adsorption properties of lead ions on the natural wheat straw and wheat straw biochar were compared in this paper. The removal rate of CS was higher than that of NS, remarkably, they were 99% and 79%, respectively. The solution pH plays a very important role in the adsorption and it was observed that the best pH value for these two adsorbents was at pH 5. The equilibrium time of the two adsorbents is close, but when the dosage of CS reached 0.3 g, the adsorption equilibrium was achieved, while the dosage for NS was 1 g, which proves the strong adsorption ability of biochar to lead ions. It can be applied to the heavy metal wastewater treatment with the advantage of solving the problem of heavy metal pollution and the problem of straw disposal.

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