Study on the Adsorption Properties of Different Insect Feces on Cu$^{2+}$ and Cd$^{2+}$

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Abstract. In order to understand the adsorption properties of insect feces on heavy metals, White grubs feces and Black soldier fly larvae (BSFL) feces were selected as the adsorption materials to study the adsorption properties of insect feces on Cu$^{2+}$ and Cd$^{2+}$. The results showed that the adsorption effect increased significantly with the increasing of the amount of insect feces, and the best adsorption effect were 2g White grubs feces and 4g BSFL feces in 100ml (10mg/L) Cu$^{2+}$ and Cd$^{2+}$. With increasing of concentration Cu$^{2+}$ and Cd$^{2+}$ (0-20 mg/L), the adsorption quantity of Cu$^{2+}$ and Cd$^{2+}$ increased. Adsorption quantity of BSFL feces for Cu$^{2+}$ was more than White grubs feces, while for Cd$^{2+}$ was less than White grubs feces when concentration of Cd$^{2+}$ was over 10mg/g. With the increase of pH, the adsorption rate of White grubs feces and BSFL feces on Cu$^{2+}$ and Cd$^{2+}$ decreased significantly.

Keywords: White grubs feces; BSFL feces; Adsorption properties; Cu$^{2+}$; Cd$^{2+}$

1. Introduction
With the development of agricultural planting industry in China, heavy metal pollution in farmland soil has attracted more and more attention [1]. The accumulation of heavy metals has seriously affected the micro-ecological environment of the soil [2], resulting in a series of harms such as longer growth cycle and slower growth and development of crops [3]. Therefore, the treatment of heavy metals is also extremely necessary. At present, many types of adsorbents are used to treat heavy metals at home and abroad. Rastogi Shivani et al. [4] used the newly prepared silk fibroin protein composites to adsorb heavy metal ions such as Cd$^{2+}$ and Cu$^{2+}$, and the results showed high adsorption efficiency and large adsorption capacity. Dai Bing et al. [5] showed that the YM organic fertilizer selected in the experiment had a significant adsorption effect on Cd$^{2+}$.

Insect feces are natural new biological organic fertilizer. However, the adsorption of insect feces on heavy metals has not been reported. In this experiment, White grubs feces and BSFL feces in different amount were added. Different concentrations of Cu$^{2+}$ and Cd$^{2+}$ were added; The effects of different pH and other environmental conditions on the adsorption properties of insect feces on Cu$^{2+}$ and Cd$^{2+}$ were studied to provide theoretical basis for the application of insect feces in contaminated soil.
2. Materials and Methods

2.1. Experimental Materials
White grubs feces: The White grubs feces come from transforming mushroom residue by grubs.
BSFL feces: The BSFL feces come from transforming chicken manure by BSFL.

2.2. Experimental Setup and Measurement

2.2.1. Effects of Amount of Insect Feces on Adsorption Properties of Insect Feces on Cu$^{2+}$ and Cd$^{2+}$.
White grubs feces and BSFL feces were accurately measured in turn, 0.05g, 0.10g, 0.50g, 1.00g, 2.00g, 4.00g and 6.00g, and then added into 100mL Cu$^{2+}$ standard solution and Cd$^{2+}$ standard solution (10mg/L), the experiment was conducted in triplicate. After being shaken for 3h at room temperature and stand still for 30 min, a syringe was used to absorb the supernatant solution and make it pass through the 0.45m microporous filter membrane. Flame atomic absorption meter was used for measurement, data recording and adsorption rate calculation.

2.2.2. Effects of concentrations of Cu$^{2+}$ and Cd$^{2+}$ on adsorption properties of Insect feces on Cu$^{2+}$ and Cd$^{2+}$.
The results showed that 0.50g of White grubs feces and 0.50g of BSFL feces were collected and added into 100mL Cu$^{2+}$ standard solution and Cd$^{2+}$ standard solution with concentrations of 0, 5, 10, 15 and 20mg/L, respectively. The sample processing process was the same as above.

2.2.3. Effects of pH on Adsorption Properties of Insect Feces on Cu$^{2+}$ and Cd$^{2+}$.
The feces of grub and BSF were respectively 0.50g and added into 100mL Cu$^{2+}$ standard solution and Cd$^{2+}$ standard solution with a concentration of 10mg/L, and then 0.5mol/L HCL and NaOH were used to adjust the pH of the solution to 4, 5.5, 7, 8.5 and 10, respectively. The samples were shaken for 3h at room temperature and stand still for 30 min, and the treatment process was the same as above.

2.3. Statistical analyses
Through experiments, the concentration of Cu$^{2+}$ and Cd$^{2+}$ ions in the solution after reaction equilibrium was determined by flame atomic absorption spectrometer, and the adsorption rate of heavy metals by White grubs feces and BSFL feces was calculated by formula (1).

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\text{Adsorption Rate E} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)
\]

\[
\text{Adsorption Capacity Qe} = \frac{V(C_0 - C_e)}{W} \quad (2)
\]

In the formula:
Co: Initial concentrations of Cu$^{2+}$ and Cd$^{2+}$ (mg/L)
Ce: Concentration of Cu$^{2+}$ and Cd$^{2+}$ solution when adsorption reaches equilibrium (mg/L)
V: The volume of the Solution (mL)
W: The weight of the adsorbent material weighed, insect feces’ quality(g)
3. Results and analysis

3.1. Effects of Amount of Insect Feces on Adsorption Properties of Insect Feces on Cu$^{2+}$ and Cd$^{2+}$

According to the analysis in figure 1, the adsorption of White grubs feces on Cu$^{2+}$ shows a significant upward trend when the amount of insect feces is less than 1g. Compared with 0.05g White grubs feces, the adsorption rate of insect feces on Cu$^{2+}$ was increased 16.92% when the addition amount of White grubs feces was 1g, and the adsorption rate was close to saturation after the amount of White grubs feces exceeded 1g, with no significant difference. However, after more than 2g, the adsorption of BSFL feces was close to saturation, and the difference was not significant. As can be seen from figure 2, the adsorption rate of White grubs feces on Cd$^{2+}$ was significantly different between 0.05-2g, and the adsorption rate increased with the increase of the addition amount, but no significant difference was found after the addition amount exceeded 2g. When the addition amount was less than 0.5g, there was no significant difference in the adsorption rate of BSFL feces on Cd$^{2+}$, but there was a significant difference in 1-4g and an upward trend. Overall, the adsorption effects of BSFL feces on Cu$^{2+}$ was stronger than that in White grubs feces, while the adsorption ability of White grubs feces on Cd$^{2+}$ was stronger than that in BSFL feces.

3.2. Effects of concentrations of Cu$^{2+}$ and Cd$^{2+}$ on adsorption properties of Insect feces on Cu$^{2+}$ and Cd$^{2+}$

Figure 3 and figure 4 above show the relationship between Cu$^{2+}$ and Cd$^{2+}$ solutions at different concentrations and the adsorption volume Qe at the adsorption equilibrium of White grubs feces and...
BSFL feces. It can be seen that with the increase of ion concentration, the adsorption volume of insect feces on Cu$^{2+}$ and Cd$^{2+}$ also increases.

3.3. Effects of pH on Adsorption Properties of Insect Feces on Cu$^{2+}$ and Cd$^{2+}$

As can be seen from figure 5, the adsorption of White grubs feces on Cu$^{2+}$ by showed no significant difference at a pH of 4-5.5, and the adsorption rate between 5.5 and 8.5 decreased significantly with the increase of pH. When the pH was greater than 8.5, there was no significant difference in the adsorption, but the overall trend was downward. The adsorption rate at pH=10 decreased by 6.71% compared with that at pH=4. When pH=4, the maximums of adsorption of Insect Feces on Cu$^{2+}$ was 40.83%. the adsorption rate gradually decreased with the increase of pH. The adsorption rate at pH=10 decreased by 13.47% compared with that at pH=4. As can be seen from figure 6, the adsorption rate of grub’s feces on Cd$^{2+}$ by significantly decreased with the increase of pH, reaching the maximum value of 81.52% at pH=4 and decreasing by 14.34% at pH=10. The trend of adsorption of BSFL feces on Cd$^{2+}$ by was consistent with that of White grubs feces, and the adsorption rate at pH=10 decreased by 32.04% compared with that at pH=4.

4. Discussion

The removal rate of Cu$^{2+}$ and Cd$^{2+}$ increases with the amount of added insect feces increases. Because when the amount of insect feces increases, the number of adsorption sites provided by insect feces as adsorbent also increases [6], and the electrostatic adsorption on metal ions is enhanced, which promotes the adsorption process [7]. In addition, the adsorption capacity of both insect feces on Cd$^{2+}$ is greater than that of Cu$^{2+}$ [8], which may be because the hydration radius of Cd$^{2+}$ is greater than that of Cu$^{2+}$, and the ability of Cd$^{2+}$ to White grubs feces the binding sites on the surface of the feces is better than that of Cu$^{2+}$ under the same conditions, so the removal effect of Cd$^{2+}$ is better [9]. In terms of the adsorption performance on Cu$^{2+}$, BSFL feces adsorption performance is greater than White grubs feces, this may be related to its shape[10], White grubs feces are granular, BSFL feces fine granular, thus the BSFL feces intergranular pore between also is bigger, so it can provide more adsorption sites for adsorption process, more conducive to the combination on heavy metal ions and adsorption sites [11]. However, the absorbing ability of BSFL feces on Cd$^{2+}$ is less than that of White grubs’ feces, which may be because some ions on the feces surface of BSFL have competitive adsorption with Cd$^{2+}$. Through the study of Ma Mengyuan et al. [12,13], it was found that due to the interaction of heavy metal ions on the surface of the adsorbent, precipitation was generated, which further affected the adsorption performance.

Under acidic conditions, both insect feces had good adsorption effects, and the adsorption effects decreased significantly with the increase of pH. Adsorption of insect feces on heavy metal ions gradually decreased with the increase of pH. Acid environment is conducive to humic acid for the adsorption of humic acid to heavy metals. When pH increased, the Cu$^{2+}$ and Cd$^{2+}$ ions in solution is hydrolyzed into hydroxyl state (MOH$^-$), the ion than free ion adsorption [14], more likely to be, in turn, reduces the
insect feces for ion adsorption. On the other hand, when the environment is more alkaline, Cu$^{2+}$ and Cd$^{2+}$ itself could also form precipitation, so it is difficult to distinguish between heavy metal ions in alkaline environment that was feces adsorption or its deposition [15], remains to be further studied.

5. Conclusion
The adsorption effect showed a significant upward trend with the increase of the amount of insect feces, and the adsorption effect was the best when the addition amount of White grubs feces and BSFL feces was 2g and 4g, respectively. With increasing of concentration Cu$^{2+}$ and Cd$^{2+}$, the adsorption quantity of Cu$^{2+}$ and Cd$^{2+}$ increased, adsorption quantity of BSFL feces for Cu$^{2+}$ was more than White grubs feces, while for Cd$^{2+}$ was less than White grubs feces when concentration of Cd$^{2+}$ was over 10mg/g. Under acidic conditions, White grubs feces and BSFL feces had better adsorption effect, and the adsorption rate of White grubs feces and BSFL feces on Cu$^{2+}$ and Cd$^{2+}$ decreased significantly with the increase of pH.

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