Study on DOM adsorption behavior and influencing factors of Cd

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Abstract. In this paper, dissolved organic matter (DOM) in crop straw was used as adsorbent and Cd\(^{2+}\) was used as adsorbent to set a single factor to study the adsorption behavior of DOM onCd contamination. The optimal adsorption conditions were found, and the DOM was scanned with UV ism at the spectral level. provide a scientific basis for the later use of DOM in the treatment of Cd\(^{2+}\) in crops. The results of the single-factor test showed that the main factors affecting adsorption were DOM dose and pH. When the dosage of DOM solution was 0.25 mL, the adsorption rate of Cd\(^{2+}\) was about 72.3%, and when the addition of DOM solution reached 89.6%, the adsorption rate reached the highest point was 2 mL. When the pH is between 6 and 8, the adsorption rate of Cd\(^{2+}\) can be maintained in a highly efficient and stable state.

1. Introduction

Dissolved Organic Matter (DOM), Usually refers to that part of the organic matter that is soluble in water, and can also be defined as a continuum of organic molecules of different sizes and structures through a membrane of 0.45 μm aperture.[1] Its main ingredients are humus and non-humus hydrophilic substances [2].

Because of the complex composition and characteristics, it not only plays an important role in the improvement of fertility, but also attracts more and more attention in the degradation of soil organic pollutants, heavy metal pollution control, etc., and has become a research hotspot in the cross-cutting fields of soil science, ecological science and environmental science.[3] Is a substance considered to be potential for improving heavy metal pollution.[4,5] In recent years, relevant scholars have carried out a large number of research on DOM adsorption heavy metals, Wang Weimei, Zhou Lixiang and others[6] found that DOM’s ability to dissolve Cu is affected by the nature of its own source, Xu Hui[1] studied the effects of DOM on the environmental behavior of organic pollutants, Zeng Xibai, Yang Jiabo, etc.[7] studied the effect of DOM on the biological effectiveness of Cu in soil, and Fu Meiyun and Zhou Lixiang[8] studied the effects of DOM on soil Pb dissolved.
In this paper, the effect of DOM on the adsorption behavior of heavy metal Cd under different conditions was studied, and its migration law was comprehensively analyzed to achieve the effect of remediation of soil heavy metal Cd pollution. In order to provide a new idea for soil heavy metal pollution control and provide theoretical basis for understanding the environmental chemical behavior of heavy metals.

2. Materials and Methods

2.1. Dom、Soil Collection and Pretreatment

Take the surface layer (0–20cm) soil in the flower bed of a certain university, the basic physical and chemical properties of the soil are determined according to the soil agrochemical analysis, the results are shown in Table 1. It can be seen from table 1 that the heavy metal contents in the soil are all below the average background value of heavy metals in chinese soil,[9] according to which, the soil samples are not contaminated by heavy metals.

The soil sample was put into the bottle at a mass ratio of 1:4 to purified water, the fresh corn straw was crushed and added, then oscillated at 25℃,120 r/min for 24 h. The resulting solution was centrifuged at 3500 r·min⁻¹ for 30 min. The supernatant was used as a solubility organic matter (DOM) sample after 0.45 µm sterile microporous filter, and was stored in the refrigerator for reserve. [10]

| Tab. 1 The basic physical and chemical properties of soil |
|-----------------|-------|-------|------|------|------|
| Index | pH    | organic matter (g·kg⁻¹) | Water content (%) | Unit weight (g·cm⁻³) | Conductivity (μS·cm⁻¹) | Cd (mg·kg⁻¹) |
|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Content | 7.50~7.54 | 15.61 | 21.12 | 4.25 | 198 | ND |

2.2. Experiment design

(1) 1 mL of DOM solution was added to the Cd²⁺ solution with concentrations of 20,40,60,80,100 mg/L respectively. The pH was adjusted to 7, and then sealed and oscillated in a constant temperature 25℃, 120 r·min⁻¹ constant temperature oscillator for 11 h. After the oscillation was completed, the supernatant was separated by centrifugation at 3500 r·min⁻¹ to obtain the result analysis.

(2) The Cd²⁺ solution with a concentration of 100 mg/Ll was adjusted to its pH of 6,7,8,9 and then added 1 ml of DOM solution respectively. after sealing, the cd² solution was put into a constant temperature 25℃, 120 r·min⁻¹ constant temperature oscillator for oscillation for 11 h. after the oscillation was completed, the supernatant was separated by centrifugation at 3500 r·min⁻¹ for the result analysis.

(3) Take the Cd²⁺ solution with the same pH of 7 and the concentration of 100 mg/L, add the solution of 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00 mL DOM respectively, and put the oscillation in the constant temperature 25℃, 120 r·min⁻¹ constant temperature oscillator for 11 h after the oscillation is completed, centrifuge the separation in 3500 r·min⁻¹ to get the supernatant for the result analysis.

A blank control group was set up for each of the above experiments. According to the change of Cd²⁺ mass concentration before and after adsorption, the equilibrium adsorption amount and adsorption rate were obtained.

2.3. Indicators and Methods

The DOC was measured using a total organic carbon analyzer; the UV spectral analysis was performed using a UV-vis spectrophotometer with a scanning wavelength of 200-700 nm and a scanning interval of 0.5 nm; and the concentration of Cd²⁺ in the solution was determined by an atomic absorption spectrophotometer.
2.4. Statistical analysis of data
The experimental data were analyzed by Microsoft excel2013, Origin8.5 and other software.

3. Interpretation of result

3.1. Ultraviolet Spectrum Analysis of DOM
The UV spectra of DOM under different pH treatments are shown in figure 1. Overall, as the UV absorption wavelength increases, the absorption intensity first increases sharply and then decreases steadily, to 600 nm and then the UV absorbance approaches 0. Under different pH conditions, the UV spectral maximum absorption wavelength $\lambda_{\text{max}}$ is located at 244 nm (pH 6), 229 nm (pH 7), 236.5 nm (pH 8) and 245 nm (pH 9), corresponding to a maximum absorbance were 1.8632, 1.6458, 1.7904 and 1.8446 respectively. Meanwhile, a more obvious absorption platform appears near the 345 nm (pH 6) and 355 nm (pH 9) regions. It is generally believed that the uv absorption peak near 240 nm originates from the strong absorption generated by the $\pi-\pi^*$ transition, which can be attributed to the k absorption band in the uv spectrum. When the pH value is nearly neutral, the $\lambda_{\text{max}}$ value is minimal (229 nm); under acidic (pH 6) and alkaline (pH 8 and 9) conditions, the $\lambda_{\text{max}}$ value all moves in the direction of long wavelength. It is speculated that a hydrogen bond may be formed between the solvent molecule and the DOM molecule due to the influence of the acidity and alkalinity of the solution, or the dipole of the polar solvent molecule increases the polarity of the DOM molecule, that is the solvent effect occurs, resulting in the absorption wavelength red shift and the $\lambda_{\text{max}}$ absorbance increase.

![Fig.1 Ultraviolet spectrum of DOM in straw humus at different pH](image)

3.2. Effects of Different Cd$^{2+}$ Concentrations on DOM Adsorption Behavior
DOM adsorption at different Cd$^{2+}$ concentrations is shown in Fig.2. With the increase of Cd$^{2+}$ concentration, the adsorption capacity and its positive correlation trend increased, but the removal rate of Cd$^{2+}$ gradually decreased. When Cd$^{2+}$ was 20 mg/L, the removal rate was the largest at 86.4%, When Cd$^{2+}$ was 40 mg/L, and the adsorption capacity was low at this time, only 4.11 mg·g$^{-1}$. The removal rate dropped to 80.1%. Then, with the increase of concentration, the removal rate gradually decreased, but the trend was gentle. When Cd$^{2+}$ was 100 mg/L, the removal rate dropped to 79.1%, and the adsorption rate reached the highest large value 19.77 mg·g$^{-1}$. this is because as the adsorption continues, the adsorption sites continue to decrease. although the adsorption capacity will increase with the increase of adsorbate concentration, the removal rate will decrease due to the greater increase of adsorbate concentration. [11]
3.3. Effect of DOM on adsorption of Cd$^{2+}$ under different pH conditions

At 25°C, Cd$^{2+}$ concentration was 100 mg/L and DOM solution volume was 1 mL. The reaction results were shown in Fig.3. According to figure 3, the adsorption rate of Cd$^{2+}$ by DOM was low at pH was 4 and 5, maintained at about 58%. When the solution pH was 6, the adsorption rate increased significantly, and at this time the adsorption rate was about 84%. When the solution pH was greater than 6, the adsorption rate continued to increase, but the trend was gentle. When the pH of the solution is 8, the adsorption rate reaches the maximum, which is about 98%. It can be seen that pH has a significant effect on the adsorption of Cd$^{2+}$. Under alkaline conditions, DOM solution after that, the adsorption rate of Cd$^{2+}$ increased significantly. Therefore, in order to ensure the good effect of DOM solution when adsorbing Cd$^{2+}$ in the soil, the acidity of the soil should be determined first, and the acid soil should first adjust the soil pH to more than 6 before the adsorption test.
3.4. Effect of DOM Solution on Adsorption of Cd$^{2+}$

At 25℃, Cd$^{2+}$ concentration was 100 mg/L and pH was 7, the reaction results were shown in figure 4.

From figure 4, it can be seen that with the increasing dose of DOM solution, the adsorption capacity of Cd$^{2+}$ also increased, and the removal rate also increased linearly. When the DOM solution added 0.25 ml, the adsorption rate of Cd$^{2+}$ was about 72.3%, and the adsorption rate reached the highest point of 89.6% when the DOM solution added 2 mL. The reason for the rise of the analysis curve may be that the increase in the addition of DOM solution increases the adsorption sites in the soil components, and the DOM in the solution reacts with metal ions to form metal complex precipitates that are insoluble in water. Cd$^{2+}$ by DOM the effect is great, and the adsorption rate increases obviously with the increase of DOM.

The reason for this phenomenon may be that first Cd$^{2+}$ is adsorbed mainly by free and unstable components in the presence of DOM solution, and the content of DOM in the solution increases with the increase of DOM solution addition, and the adsorption point in the soil gradually reaches saturation, at which time the improvement of Cd$^{2+}$ adsorption rate is relatively slow.

![Fig.4](image)

**Fig.4** Effect of the amount of straw humus on the removal effect of Cd$^{2+}$

4. Conclusion

Using dissolved organic matter (DOM) in crop straw as adsorbent and Cd ions as adsorbate, a single influencing factor was set up to study the adsorption behavior of Cd contamination by DOM. After data processing and research, the following conclusions were finally drawn.

1. In a certain range, straw soluble organic compounds can promote the adsorption of Cd$^{2+}$ by organic-inorganic complexes, and the adsorption rate becomes larger with the increase of DOM volume. When the pH was about 7, 2 mL of DOM was added to 12.5 mL of 100 mg/L Cd$^{2+}$ solution, and finally the adsorption rate of 89.6%.

2. After adding DOM solution, the adsorption of Cd$^{2+}$ was also affected by pH. with the increase of pH, the adsorption rate of Cd$^{2+}$ increased significantly. when pH is less than 6, the adsorption effect of dom is not very obvious. when pH is greater than 6, the addition of DOM solution can significantly improve its adsorption rate of Cd$^{2+}$ in solution. In order to ensure the good effect of DOM solution adsorption of Cd$^{2+}$ in the soil, the pH of the soil should be determined first, and the acid soil should first adjust the soil pH to more than 6 before the adsorption test.
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