Adsorption characteristics of Pb (II) onto red clay, bentonite and bone char

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Abstract. The adsorption characteristics of red clay, bentonite, bone char, modified red clay (97% red clay+3% bone char) and modified bentonite (97% bentonite+3% bone char) on Pb(II) were studied by batch test. Based on the experimental results, the Langmuir model and quasi second-order kinetic model were used to fit the experimental data. The results showed that the adsorption of Pb(II) by red clay, bentonite, and bone char is a rapid reaction process, and the adsorption capacity of bone char is significantly greater than that of red clay and bentonite. Langmuir model and quasi second-order kinetic model can be used to describe the isotherm adsorption and kinetic characteristics of red clay, bentonite and bone char, respectively. The adsorption capacity of the modified red clay or bentonite is significantly increased, and the adsorption capacity of the bentonite with 3% bone char is the best liner filler for Pb(II) pollutants.

1. Introduction

With the development of urbanization and industrialization, the heavy metal pollution of soil and water is becoming more and more serious. It is found that when the lead concentration in the environment exceeds the standard, it will directly damage the growth of plants, and even cause plant death [1]. Lead can accumulate in the environment for a long time, and enter the human body through food chain, soil, water and air [2], finally affecting human health and even life. Therefore, the problem of lead pollution cannot be ignored, which has become one of the research hotspots in the field of environmental science. Sezer et al. [3] used Ankara clay as experimental material to study the adsorption properties of various heavy metal ions. It is concluded that Ankara clay can effectively remove heavy metal ions, and can be used as landfill liner material. Bellir et al. [4] comprehensively analyzed the adsorption effect of clay on Cu by taking natural clay as test material and considering the effects of reaction time, solution pH and temperature. The results showed that clay has a strong adsorption capacity for Cu, which can be used as lining materials and alternative materials for water source protection. Du and Hayashi [5] found that Ariake clay has strong adsorption capacity for Cd and Pb, and it can effectively remove heavy metal ions in aqueous solution. Nhan et al. [6] used bentonite, lime and fly ash composite materials as test materials to analyze the adsorption properties of Pb, Zn and Fe. The results showed that the composite material can effectively remove heavy metal...
ions, and the permeability coefficient reached $10^{-8}$ m/s. Chalermyanont and Arrykul [7] carried out intermittent test, soil column test and permeability test for laterite and clay, and concluded that clay is more suitable as lining material than laterite. Al-Tabbaa and Aravinthan [8] concluded that the composite material formed by adding 6%-15% tire debris to clay is suitable for use as lining material. Bartelt-Hunt et al. [9] found that the clay added with granular activated carbon and organic bentonite can improve the adsorption performance of organic pollutants. Lu et al. [10] improved the clay by adding granular activated carbon and acidified bentonite, and studied the adsorption performance of Cr in the aqueous solution. It was found that the adsorption capacity of the improved soil improved significantly, and the permeability coefficient met the specification requirements.

In this paper, the adsorption isotherm and kinetics characteristics of Pb(II) on red clay, bentonite and bone char were studied by batch experiment. Taking red clay, red clay with 3% bone char, bentonite and bentonite with 3% bone char as the packing materials, the isothermal adsorption characteristics of Pb(II) on different materials were studied. Based on the experimental results, the Langmuir model and quasi second-order kinetic model were used to fit the experimental data.

2. Materials and method

2.1. Test material

The bone char used in the experiment was commercial bone char (purchased from Shijiazhuang Baoqian Trading Co., Ltd.), which was not polluted by lead. The bone char used in the experiment is dry powder. After being crushed by a high-speed pulverizer, it passes through a 60 mesh sieve, and it is placed in an oven with 60 °C for 24 hours, and the dried and ground bone charcoal is placed in a dryer for the test. The red clay and bentonite used in the test are all from Dalian area and are not polluted by Pb (II). The chemical composition of clay, bentonite, and bone char are shown in Table 1.

| Table 1. The chemical composition of red clay, bentonite, and bone char. |
|---------------------------------------------------------------|
| composition     | mass percent/% | composition | mass percent/% | composition | mass percent/% |
| SiO$_2$         | 49.20          | SiO$_2$     | 70.70          | CaO         | 48.9          |
| Al$_2$O$_3$     | 20.90          | Al$_2$O$_3$ | 14.30          | P$_2$O$_5$  | 47.5          |
| Fe$_2$O$_3$     | 15.70          | Fe$_2$O$_3$ | 2.94           | MgO         | 0.89          |
| CaO             | 4.34           | CaO         | 2.99           | SiO$_2$     | 0.43          |
| K$_2$O          | 4.09           | K$_2$O      | 4.38           | Al$_2$O$_3$ | 0.39          |
| MgO             | 1.75           | MgO         | 2.00           | SO$_3$      | 0.36          |
| TiO$_2$         | 1.46           | TiO$_2$     | 0.24           | Fe$_2$O$_3$ | 0.26          |
| Na$_2$O         | 1.20           | Na$_2$O     | 1.91           | Cl          | 0.08          |
| MnO             | 0.11           | BaO         | 0.20           | SrO         | 0.07          |
|                 |                |             |                | K$_2$O      | 0.06          |
|                 |                |             |                | ZnO         | 0.05          |
|                 |                |             |                | CuO         | 0.03          |
|                 |                |             |                | ZrO$_2$     | 0.02          |

The physical behaviors of lining material are shown in Table 2. The clay lining and bentonite lining materials were improved with bone char (97% clay and 3% bone char; 97% bentonite and 3% bone char).

| Table 2. Physical parameters of landfill liner materials. |
|----------------------------------------------------------|
| liner materials                | $w_l$ | $w_p$ | $I_p$ | $\rho_{\text{max}}$ (g/cm$^3$) | $w_{\text{opt}}$ | $e$ | $G_e$ |
| red clay                      | 33.4  | 17.1  | 16.3  | 1.83                          | 16.8             | 0.45 | 2.66  |
| 97% red clay+3% bone char     | 33.6  | 17.0  | 16.6  | 1.78                          | 16.5             | 0.47 | 2.62  |
| bentonite                     | 99.7  | 41.0  | 58.7  | 1.12                          | 38.5             | 1.15 | 2.42  |
| 97% bentonite+3% bone char    | 99.3  | 41.2  | 58.1  | 1.10                          | 38.1             | 1.17 | 2.39  |
2.2. Test method
The movement of heavy metal Pb(II) in liner materials of landfill was analyzed by soil column test. The soil column model test equipment is a self-made plexiglass column. The lining materials used in indoor soil column test are natural red clay, red clay with 3% bone char, natural bentonite and bentonite with 3% bone char. The permeability coefficient, initial concentration of Pb(II) solution, pollutant time of lining materials are list in Table 3.

Table 3. Test scheme.

| liner materials                  | k/(cm/s) | Pb(II) concentration/(mg/L) | T/(d) |
|---------------------------------|----------|-----------------------------|-------|
| red clay                        | 2.63×10^{-8} | 250                         | 350   |
| 97% red clay+3% bone char       | 2.88×10^{-8} | 250                         | 350   |
| bentonite                       | 3.37×10^{-9} | 250                         | 350   |
| 97% bentonite+3% bone char      | 4.05×10^{-9} | 250                         | 350   |

3. Results and discussion
During the experimental, the solid-liquid ratio \( r = 1 \) g/L, reaction time is 12 h, control temperature is 20 °C, the isothermal adsorption characteristics and kinetic characteristics of bone char, natural red clay and natural bentonite for Pb(II) were studied, the test results as shown in Figure 1 and Figure 2. The results showed that the order of adsorption capacity of three adsorbents for Pb(II) was bone char > bentonite > red clay, which further indicated that bone char could be used as modified materials of natural red clay and bentonite, while the adsorption of three adsorbents for Pb(II) was a rapid adsorption process.

![Figure 1. Adsorption isotherms of Pb(II) onto different adsorbents.](image1)

![Figure 2. Adsorption kinetics of Pb(II) onto different adsorbents.](image2)

The Langmuir model and quasi-second-order kinetic model were used to fit the test data of bone char, natural red clay and natural bentonite (Figure 3). The results showed that the fitting effect of Langmuir model and quasi second-order kinetic model were very good, and the determination coefficient \( R^2 \) is greater than 0.99. The model parameters of three adsorbents are listed in Table 4.
In Langmuir model, the $Q$ value of the model parameter can reflect the adsorption capacity of the adsorbents. As listed in Table 4, it can be seen that $Q_{\text{bone char}} > Q_{\text{bentonite}} > Q_{\text{red clay}}$, indicating that the adsorption capacity of bone char to Pb(II) is better than that of natural red clay and natural bentonite. Therefore, it is feasible to further reduce the migration of Pb(II) in the lining system by using bone charcoal as the improved material and improving the adsorption performance of natural red clay and natural bentonite.

When Pb(II) contaminant transported in the liner of landfill, the adsorption of liner material to contaminant should be considered. During the test process, the solid-liquid ratio $r=100$ g/L, 5 g of soil was weighed and placed in a conical flask, adding 50ml of Pb(II) solution with different initial concentrations, respectively. The temperature was controlled at 20 °C, and oscillate at constant temperature for 12 h. The isothermal adsorption curves of lining materials to Pb(II) as shown in Figure 4. It can be seen that the adsorption capacity of modified red clay or bentonite is significantly greater than that of natural red clay or bentonite, and the adsorption of Pb(II) is a rapid adsorption process.

Langmuir model was used to fitting the isothermal adsorption characteristics of four liner fillers. As listed in Table 5, it can be seen that $Q_{\text{modified bentonite}} > Q_{\text{bentonite}} > Q_{\text{modified red clay}} > Q_{\text{red clay}}$, indicating that the adsorption performance of bentonite with 3% bone charcoal is significantly better than the other fillers, which is the optimal liner filler for Pb(II) pollutants.
4. Conclusions

(1) The adsorption of Pb(II) onto red clay, bentonite, and bone char is a rapid reaction process, and the adsorption capacity of bone char is greater than that of red clay and bentonite, which indicates that the bone char can be used as an improved material.

(2) Based on test results, the Langmuir model and quasi second-order kinetic model can be used to describe the isotherm adsorption and kinetic characteristics of red clay, bentonite and bone char, respectively.

(3) The adsorption capacity of modified red clay or bentonite is significantly increased, and the adsorption capacity of the bentonite with 3% bone charcoal is the best liner filler for Pb(II) pollutants.

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