Study on Migration and Transformation of Cd in BHMTPMPA Remediation Soil

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Abstract. Organic phosphonic acid has good chelation ability, easy biodegradation, and belongs to environmental friendly reagent. It can be used as eluent to remediate soil contaminated by heavy metal Cd. This paper studied the migration and transformation process of Cd in organic phosphonic acid BHMTPMPA remediation soil. The results showed that the concentration of exchangeable Cd in 1-7 layer of soil column was significantly higher than that in control, and the concentration of exchangeable Cd in 8-10 layer was not significantly different. The activation effect of BHMTPMPA on Cd in soil column is mainly concentrated in the depth of 0-70 cm soil layer. The exchangeable states in layer 2 Cd the highest concentration, and the exchangeable states in other soil layers Cd no obvious migration occurs, which indicated that the migration mainly occurred in the depth of 0-20 cm soil layer, and the Cd of other forms in the soil column did not occur obvious migration phenomenon.

1. Introduction
In the early stages of soil leaching and chelation-induced plant extraction, chelating agents widely used by researchers usually have poor biodegradability, and heavy metals activated by these chelating agents are at risk of percolating deep into the soil, while will cause further pollution to the soil environment. So the biodegradable chelating agent with strong chelating ability and will not cause deeper harm to the environment is the key factors in soil remediation research [1~4]. Organic phosphonic acid has good chelation ability and excellent chelation ability to many heavy metal [5~7]. Organic phosphonic acid is biodegradable and can be degraded by microorganisms [8~9], which belongs to the environmental friendly reagent, which can be used as eluent to remediate the soil contaminated by heavy metal Cd. This paper studied the migration and transformation process of Cd in organic phosphonic acid BHMTPMPA remediation soil, by analyzing the change of concentration of different morphological Cd in different soil depth, to elucidate Cd migration patterns in organic phosphonic acid BHMTPMPA remediation soils.
2. Materials and methods
Experimental soil collected from Qipanshan non-polluting topsoil in Shenyang, which collected soil samples in the range of 0-20 cm soil depths. After removing the plants, animals and gravel from the collected soil samples, the soil samples were air-dried, mixed evenly and then sifted over 10 mesh, and stored in a dry place. After 40 mesh sieve, cadmium chloride was added and mixed together as experimental soil.

The Cd concentration of heavy metals in artificially polluted soil was set to 6 mg/kg, which was generally consistent with the pollution degree and level Cd heavy metals in Zhangshi Irrigation District, Liaoning Province. The total height of the sample is 100 cm, separated by nylon mesh every 10 cm. Each pillar contains 10 layers (0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, 90-100 cm). Organic phosphonic acid BHMTPMPA was added to the soil column, and distilled water was added to the control group. The ratio of organic phosphonic acid to soil Cd molar concentration is 50:1. The organic phosphonic acid leaching solution was added to the soil column at a constant flow rate until the soil at the bottom of the soil column was infiltrated by the leaching solution. At the end of the soil column washing experiment, the soil samples in each soil column were removed layer by layer. Take a portion of the soil from each layer of soil, which was air dried, shredded, sifted, packaged and set aside. The different morphological Cd in soil were extracted by tesserier chemical extraction method [10].

3. Results and Discussion

3.1. Concentration variation of exchangeable Cd in different soil layers
As shown in figure 1, it can be seen that after the addition of organic phosphonic acid BHMTPMPA, compared with the control group, the exchangeable Cd concentration in different depth soil layer is different compared with the control group. The exchangeable Cd concentrations in layers1-7 were significantly higher than that in the control, and layers 1-6 reached extremely significant levels. The exchangeable Cd in BHMTPMPA remediation soil gradually decreased with the deepening of soil layer, and there was no significant difference in the exchangeable state Cd concentration in layer 8-10 compared with the control.

![Figure 1. Variation of the concentration of exchangeable Cd in BHMTPMPA remediation soils.](image-url)
3.2. Concentration variation of carbonate bound Cd in different soil layers
As shown in figure 2, no carbonate bound Cd was detected in layers 1 to 6 of the soil column after adding organic phosphonic acid BHMTPMPA. The results showed that under the activation of BHMTPMPA, the carbonate bound state Cd was transformed into more active exchangeable state. The concentration of activated carbonate bound state Cd in layer 7 is significantly lower than that in control group, which indicates that there are a large number of carbonate bound states Cd transformed to exchangeable state. Carbonate binding states Cd concentrations in layers 8, 9, and 10 were not significantly different from those in control, nor did they accumulate migration, indicating that the carbonate bound states Cd in these three layers did not migrate downward and transformed, BHMTPMPA only affected the soil column 0-70 cm. Li Yuhong and other studies showed that under the action of exogenous organic acids, the morphological changes of heavy metal Cd in soil was significantly affected, which promoted the transformation of Cd from stable morphology to active exchangeable state, and the concentration of exchangeable state increased significantly [11]. Compared with iron-manganese oxides, organic compounds, carbonate bound Cd are more readily converted. As a result, it preferentially converts Cd exchangeable state.

![Figure 2](image)

Figure 2. Variation of the concentration of carbonate bound Cd in BHMTPMPA remediation soil

3.3. Concentration variation of ferromanganese oxide bound Cd in different soil layers
Figure 3 showed in the soil column treated with BHMTPMPA, ferromanganese oxide bound Cd was not detected at layers 1 to 4, ferromanganese oxide bound Cd in 1-4 layers was fully activated. At layer 5, the bound Cd of ferromanganese oxide was significantly lower than that of control group, a majority of ferromanganese oxide bound Cd was transformed. However, the bound Cd of ferromanganese oxide in layer 6 was significantly lower than that in control group. Concentrations of ferromanganese oxide Cd in layers 7, 8, 9 and 10 were not significantly different from those in control, and no accumulation of migration, the results showed that ferromanganese oxide binding Cd was not activated in 7, 8, 9 and 10 layers, no morphologic transformation occurred and no downward migration occurred.
3.4. Concentration variation of organic binding Cd in different soil layers
Figure 4 showed that in the BHMTPMPA treatments, no organic binding Cd was detected in layer 1 and 2 of soil column, and it showed that the organic bound state Cd was completely transformed. Compared with the control group, the organic binding Cd in layers 3 and 4 were significantly lower than that in control, indicating that most organic bound Cd underwent morphological transformation; In the 5, 6, 7, 8, 9 and 10 layers, there was no significant difference between BHMTPMPA treatments and control, and no accumulation of migration, indicating that the organic bound states Cd in layers 5 to 10 did not transform to other forms and did not migrate downward.

3.5. Concentration variation of residue Cd in different soil layers
Figure 5 showed that after adding organic phosphonic acid BHMTPMPA, concentrations of residue Cd in layers 1 to 10 of soil column were not significantly different from those in the control group. And each layer had no accumulation of migration Cd, indicating that the residual residue states Cd hardly migrated downward in each soil layer and were not transformed into other forms.
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Figure 5. Variation of residue Cd concentration in BHMTMPA remediation soil

4. Conclusion
After adding organic phosphonic acid of BHMTMPA, the exchangeable Cd concentrations were significantly higher than those of the control in 1-7 layers. And there was no significant difference in the exchangeable Cd concentrations in layers 8-10. The results showed that BHMTMPA activated Cd in soil column was mainly concentrated in 0-70 cm soil depth. The highest exchangeable state Cd concentration was in layer 2, exchangeable Cd in other soil layers did not migrate significantly, indicating that migration occurred mainly in the depth 0-20 cm soil layers, and there was no obvious migration of Cd in other forms of soil column.

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