Effect of Citric Acid on immobilization of Heavy Metals

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Abstract: Heavy metal pollution of soils has become increasingly serious, and chemical immobilization is usually used to remediate heavy metal contaminated soil. With changing environmental conditions, the immobilization heavy metal may be released again, which is a risk to ecological environment and human health. In the study, sepiolite is applied to the heavy metal contaminated soil (0.5%, 2%, 5%), training for 60 days, adding 2mmol/Kg, 10mmol/Kg and 20mmol/Kg citric acid into the contaminated soil. This research adopted characteristic leaching procedure (TCLP) to evaluate the remedation effect and BCR to analysis the change of heavy metal species of soil. The results show that, no adding citric acid, the content of TCLP-Cd decreased with the increase of sepiolite addition ratio. When the sepiolite addition ratio was 5%, TCLP-Cd is lower than its of TCLP international standards. It shows that sepiolite can effectively remediate heavy metals in soil. When the proportion of sepiolite is constant, low concentration of citric acid is helpful to remediation, while high concentration of citric acid is not conducive to remediation of heavy metals. BCR method showed that the exchangeable content increased with the increase of citric acid concentration, but the oxidizable content decreased, indicating that citric acid could increase the bioavailability of heavy metals.

1. Introduction
With the rapid development of industry and agriculture, mining, mineral smelting and wastewater irrigation have led to heavy metal pollution in soil[1], heavy metal pollution of soil is becoming more and more serious. Heavy metals of soil can accumulate in plants, and through the role of the food chain, it will do harm to the ecological environment and human health. Therefore, the remediation of heavy metals contaminated soil has attracted more and more attention from researchers at home and abroad[2]. At present, the remediation methods of heavy metals in soil mainly include physical method (deep plough, covering soil), chemical method (immobilization remediation, leaching method) and biological method (phytoremediation and microbial remediation)[3]. Chemical stabilization is low-cost and simple operation, which is widely used[4]. Chemical stabilization is to add passivators into contaminated soil, which react with heavy metals through complexation, precipitation and ion exchange to fix heavy metals of soil, reducing the migration and the bioavailability of heavy metals[5].

Sepiolite, Mg₈Si₂O₅(OH)₄(H₂O)₄·8H₂O, which is widely used in remediation of heavy metal contaminated soil due to its low-cost, rich content and large specific surface area[3]. Sun et al. showed that the sepiolite was applied into contaminated soil, concentrations of cadmium and lead in the shoots decreased by 46.2% and 65.8% respectively, which significantly reduced the concentration of heavy metals in plants[6]. Li and Xu et al. showed that sepiolite could reduce exchangeable cadmium in soil by 12.5% - 18.2%, and significantly reduce the content of available cadmium[7]. Sun et al. also showed that sepiolite significantly reduced TCLP-Cd content and cadmium concentrations in shoots[8]. These studies show that sepiolite can change the form and availability of heavy metals of soil, decreased the concentration of heavy metals in plants, and thus reduce the bioavailability of heavy metals in soil.
Although sepiolite can reduce the migration and bioavailability of heavy metals by changing the form and effective state of heavy metals, the total amount of heavy metals in soil has not changed, and the form and availability of heavy metals will change with the change of environmental conditions. Small molecular organic acids secreted by roots in soils can change the environmental conditions of soil[9], and then affect the form and availability of heavy metals, so that passivated heavy metals may be released again and may be threaten to human health and ecological environment safety. Therefore, in this study, sepiolite was used as passivator, citric acid was added to simulate the change of environmental conditions, to study the stability of passivation repair and prevent the harm of heavy metal release.

2. Materials and methods

2.1 Test soil and passivators
The soil was collected from a farmland soil polluted by Cd and Pb in Dali, pH value is 7.65, it is a neutral soil. Total Cd and Pb were 5.50 mg/Kg and 191.00 mg/Kg, respectively. The sepiolite sample used in this study comes from a company.

2.2 Experimental design
Accurately weigh 400 g soil sample in a flowerpot with 8 cm in height and 5 cm in diameter; (1) 0.5%, 2%, 5% sepiolite were added to the soil, which were recorded as S1, S2, S3 and S4 respectively; (2) no adding sepiolite, which was recorded as CK. Setting up three parallel samples and maintaining 20% field water capacity. After 60 days of incubation, adding 2 mmol/Kg, 10 mmol/kg and 20 mmol/kg citric acid into the soil, samples were taken after one week of incubation.

2.3 Analysis method
The soil sample were digested with a solution of HNO3-HCl-HF-HClO4 and atomic absorbance spectrophotometry, prior to determinations of Cd and Pb in solution. Soil Cd and Pb fractionation was performed using BCR. The pH value of soil was determined as 1:2.5 ration of soil mass to water volume using a pH meter.

2.4 Statistical analysis
The means and standard deviations were calculated using Excel 2016. Two ways analysis of variance was carried out with SPSS17.0, using Origin 8.0 software to draw.

3. Results and discussion

3.1 Effects of citric acid and sepiolite on extractable heavy metals from soil by TCLP

3.1.1 Extracted Cd from TCLP
No adding citric acid, the content of TCLP-Cd in soils decreases with the increase of sepiolite proportion from table 1. Adding 2% and 5% sepiolite, the content of TCLP-Cd is 0.47mg/kg and 0.48 mg/kg, respectively, which are lower than international standards, and when the concentration of citric acid is constant, the content of TCLP-Cd decreases with the increase of sepiolite addition ratio, indicating that sepiolite can effectively immobilize Cd of soils. The concentration of citric acid was 2 mmol/kg and 10 mmol/Kg, the content of TCLP-Cd in sepiolite-treated soil was lower than international standard, but when the concentration of citric acid was 20 mmol/Kg, the content of heavy metals in sepiolite-treated soil was 0.5076 mg/Kg~0.5001 mg/Kg, which was higher than international standard. It indicated that high concentration of citric acid had a great influence on heavy metals in soil. This may be because low concentration of citric acid can adsorb on sepiolite and soil, increasing the adsorption sites of heavy metals, while high concentration of citric acid will bring a large number of hydrogen ions, which will lead to desorption reaction of heavy metals in soil, thus increasing the concentration of heavy metals.
Table 1. Extracted Cd Content in TCLP (mg/Kg)

| Citric acid concentration | 0      | 2mmol/Kg | 10mmol/Kg | 20mmol/Kg |
|---------------------------|--------|----------|-----------|-----------|
| CK                        | 0.5229 | 0.5139   | 0.567     | 0.5883    |
| 0.5%HP                    | 0.5025 | 0.42     | 0.4191    | 0.5076    |
| 2%HP                      | 0.4698 | 0.4524   | 0.48      | 0.5052    |
| 5%HP                      | 0.48   | 0.4791   | 0.4515    | 0.5001    |
| International standard of TCLP | 0.5  | 0.5      | 0.5       | 0.5       |

3.1.2 Extracted Pb from TCLP

No adding citric acid, the content of TCLP-Pb in soils decreases with the increase of sepiolite proportion from table 2, from 6.502 mg/kg without sepiolite to 5.992 mg/kg, decreased by 7.84%. It shows that sepiolite can immobile Pb of soil. When the concentration of citric acid is constant, the content of TCLP-Pb decreases with the increase of sepiolite addition ratio. The concentration of citric acid is 20 mmol/kg and the proportion of sepiolite is 0.5%~5%, the content of TCLP-Pb changes from 11.416 mg/kg without sepiolite to 6.67~5.678 mg/Kg, effectively reducing the concentration of TCLP-Pb, but higher than international standards. This indicates that when using sepiolite to remediate Pb, it should be noted that heavy metals of soil may be released again with the change of environmental conditions.

Table 2. Extracted Lead Content in TCLP (mg/Kg)

| Citric acid concentration | 0      | 2mmol/Kg | 10mmol/Kg | 20mmol/Kg |
|---------------------------|--------|----------|-----------|-----------|
| CK                        | 6.502  | 7.272    | 10.64     | 11.416    |
| 0.5%HP                    | 6.268  | 6.854    | 8.13      | 6.67      |
| 2%HP                      | 6.112  | 6.256    | 6.424     | 6.156     |
| 5%HP                      | 5.992  | 6.158    | 7.89      | 5.678     |
| International standard of TCLP | 5   | 5        | 5         | 5         |

3.2 Effects of citric acid and sepiolite on speciation of heavy metals of soil

3.2.1 The form of Cd

Fig 1 (a) shows that the exchangeable cadmium content increases with the increase of citric acid concentration of soils without sepiolite. When the proportion of sepiolite is constant, exchangeable cadmium decreases firstly and then increases with the increase of citric acid concentration. When the concentration of citric acid is 2 mmol/kg and the proportion of sepiolite is 0.5%~5%, the exchangeable cadmium decreases from 1.49~1.57 mg/kg without citric acid to 1.45 mg/Kg~1.36 mg/kg, with a decrease of 3.00%~13.01%. However, with the increase of citric acid concentration, the content of exchangeable cadmium increased. When citric acid concentration was 20 mmol/kg, the exchangeable cadmium increased from 1.49-1.57 mg/kg without citric acid to 1.45 mg/Kg-1.36 mg/kg, with an increase of 18.30%~21.25%, which was consistent with the change of TCLP-Cd. The results show that low concentration of citric acid is helpful to the heavy metals immobilization, while high concentration of citric acid is not conducive to immobile heavy metals. From Fig. 1 (b) and (d), it can be seen that the reducible cadmium decreases with the increase of citric acid concentration, but the decrease is not significant, and the residual state has no significant change. In Fig. 1 (c), citric acid significantly reduced the content of oxidizable cadmium. When citric acid concentration was 20 mmol/kg, it decreased from 0.41-0.57 mg/kg without citric acid to 0.25 mg/Kg-0.38 mg/Kg, a decrease of 33.45%~37.62%.
3.2.2 The form of Pb
At figure 2 (a), the exchangeable lead increases from 20.05 mg/kg to 30.00 mg/kg, increased by 46.34% with the increase of citric acid concentration in CK. When citric acid concentration is 20 mmol/kg, the exchangeable lead increases from 20.05 mg/kg without citric acid to 30.00 mg/kg. When citric acid concentration is constant, the content of exchangeable lead decreases with the increase of citric acid addition ratio. When citric acid concentration is constant, the content of exchangeable lead decreases first and then increases with the increase of citric acid concentration. From Fig 2 (b), it can be seen that the reducible cadmium decreases, but the decrease is not significant. Figure 2 (c) shows that when the proportion of sepiolite is constant, the content of oxidizable lead decreases with the increase of citric acid concentration, and the concentration of citric acid is constant, the content of oxidizable lead decreases with the increase of sepiolite proportion. However, when citric acid concentration was 20 mmol/kg, sepiolite addition ratio had no significant effect on it.
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Figure 2. Effects of citric acid and sepiolite on the form of lead((a) is exchangeable cadmium; (b) is reducible cadmium; (c) is oxidizable cadmium;(d) is residual cadmium;)

4. Conclusion
(1) When sepiolite is added in a certain proportion, the exchangeable cadmium and lead increased with the increase of citric acid concentration, while the oxidizable cadmium and lead changed in the opposite direction; When the concentration of citric acid is constant, it decreases with the increase of sepiolite addition ratio, which indicates that sepiolite has passivation effect on cadmium and lead immobilization, and the addition of citric acid increases the activity of lead and cadmium.

(2) Heavy metals were extracted by TCLP, and sepiolite was added in a certain proportion, when the concentration of citric acid is 2 mmol/kg, the content of TCLP-Cd decreases, which is lower than that without citric acid. But when the concentration of citric acid is 10 mmol/Kg~20 mmol/kg, TCLP-Cd increases with the increase of citric acid concentration. This indicates that low concentration of citric acid is helpful to the cadmium immobilization, while high concentration of citric acid is not conducive to the heavy metals immobilization.

(3) When sepiolite was added in a certain proportion, the content of lead extracted by TCLP method increased with the increase of citric acid concentration, and exceeded the international standard of TCLP. It is unfavorable for sepiolite passivation to repair lead when environmental conditions change.

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