Effects of different amendments on Lead and Cadmium in contaminated farmland soils around lead-zinc mines

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Abstract: In order to provide a theoretical reference for the passive remediation of the farmland contaminated by cadmium and lead, eighteen different materials include lime kind agent, phosphate, iron oxide and clay minerals were used as the soil heavy metal passivators. Results showed that adding the passivators Ca(OH)2, sodium pyrophosphate, CaHPO4 could significantly decrease the available cadmium in soils, and the optimal concentrations were 2%, 1% and 2%, respectively. The passivators FeCl3, NaH2PO4 and CaHPO4 could significantly decrease the available lead in soils, and the optimal concentrations were 3%, 2% and 2%, respectively.

1. Introduction
With the continuous development of social economy, the problem of heavy metal pollution in soil brought by industrial and agricultural production has become increasingly serious[1-2]. A variety of pollutants carrying heavy metal elements enter the soil environment in large quantities, such as industrial wastewater and waste residues, household wastes, agricultural sewage and chemical fertilizers and pesticides can all cause heavy metal pollution in soil[3-5]. Heavy metal pollution will reduce soil fertility and crop yield, lead to excessive content of heavy metals in agricultural products for farmland. Lead and cadmium contaminated soils are a global environmental concern that results not only in human health and ecological hazards, but also in huge economic implications with respect to reclamation and restoration costs[6-7]. Therefore, the treatment and remediation of heavy metal pollution in soil, the improvement of soil environmental quality, and the guarantee of crop safety have become urgent needs at present. It is of great significance to reduce the content of available heavy metals in soil through in-situ remediation of passivators[8].

At present, the remediation methods of heavy metal contaminated soil in farmland mainly include physical remediation, chemical remediation, bioremediation and combined remediation[9-11]. Heavy metal pollution of agricultural soil in China is characterized by large area and moderate and mild pollution. In situ passivation is widely concerned because of its simple operation, quick effect and suitability for large-scale pollution treatment[12]. Surrounding farmland location lead-zinc mine in Sichuan province, this study selects the lime class passivation agent, phosphate passivator, iron oxide passivator and gotten a total of eighteen kinds of plant-based passivation agent, passivation repair contaminated soil to the field research, aimed at screening effective and appropriate for the cadmium...
and lead pollution of soil surrounding the mining area of passivator and seems to provide a reference for restoration of cadmium lead pollution of farmland.

2. Material and method

2.1. Soil Sample

The samples were obtained from 0 cm - 20 cm below the ground surface around lead and zinc mine in Sichuan province. The soil was air dried, sieved (2mm) and mixed. Each run of experiments were conducted to 500g samples, screened through 0.149mm nylon sieve. Physical and chemical properties of soil were shown in table 1. The content of lead and cadmium exceeded the screening value of China (GB36600-2018).

| Test material | pH | Total heavy metal (mg/kg) | Cd | Pb | Cr | Hg | As |
|---------------|----|--------------------------|----|----|----|----|----|
| Soil sample   | 7.27| 21.92, 733.47, 3.53, 0.99 |    |    |    |    |    |

2.2. Soil Characterization

Soil pH was measured in a 1:2.5 (w/v) ratio of soil to distilled water using a pH-meter (HQ-40d). Soil organic matter was measured using peripheral heating method of potassium dichromate. The total amount of Cd, Pb and Cr in soil was digested by HNO₃-HCl-HF microwave, and the digestion solution was determined by atomic absorption spectrophotometer (AAS). The total amount of Hg and As in the soil were digested by HNO₃-HCl microwave, and the solution was determined by atomic fluorescence spectrophotometer (AFS). The available heavy metal was extracted by DTPA solution.

2.3. Amendments

In this study, 18 kinds of amendments were used as the experimental materials, including lime amendments, phosphate amendments, iron oxide amendments and clay minerals amendments with better passivating effects on soil cadmium and lead.

(1) Lime amendments: CaO, Ca(OH)₂, CaCO₃.

(2) Phosphate amendments: NaH₂PO₄, Na₂HPO₄, CaHPO₄, Ca₃(PO₄)₂, sodium pyrophosphate, hydroxyapatite.

(3) Iron oxide amendments: FeSO₄, FeCl₃, Fe₂O₃, FeCl₂.

(4) Clay minerals amendments: sepiolite, zeolite, bentonite, montmorillonite, attapulgite.

2.4. Selection Experiment of Amendments

The passivating agents for soil cadmium and lead were preliminarily screened through the static culture experiment. 100g of 2mm sieved soil was weighed, and 5% passivating agents were added respectively. The moisture content of the soil was adjusted to 20% with ultra-pure water, which was stirred evenly and placed in the incubator for continuous culture for 3d.

2.5. Optimization of Amendments Application Conditions

The amendments with better passivating effect on soil cadmium and lead were selected from 18 test amendments by screening test. The optimal application conditions of amendments were studied through further static culture experiment. The tests were conducted in 500 mL polyethylene bottles. The bottles containing 50g soils and different concentrations (0%, 0.5%, 1%, 2%, 3% adn 5%) of amendments. The moisture content of the soil was adjusted to 20% with ultra-pure water, which was stirred evenly and placed in the incubator for continuous culture for 3d.
3. Results and Discussion

3.1. Effects of Different Amendments on Cadmium Effective State Content in Soil

After the addition of amendments, the available cadmium content in most of the treated soils decreased in different degrees. The best amendments was lime passivator, the concentration of available cadmium was 0.58 mg/kg after adding CaOH three days. The highest immobilization efficiency of cadmium for CaOH was 70.41%. The concentration of soil cadmium increased significantly after adding FeCl₃ and FeSO₄, which illustrate that the two reagents has no effect on passivating soil cadmium, but exciting cadmium in soil. The available cadmium content in soils decreased by CaHPO₄ and sodium pyrophosphate treatments. The concentration of available cadmium decreased to 0.92 mg/kg adding sodium pyrophosphate 3 days later, which decreased to 1.19 mg/kg by CaHPO₄. Effective of iron oxides amendments and clay minerals amendments was poor in this study.

![Figure 1. Effects of different amendments on Cd effective state content in soil.](image)

(Treatments: 1: CaO, 2: CaCO₃, 3: Ca(OH)₂, 4: FeSO₄, 5: FeCl₃, 6: Fe₂O₃, 7: FeCl₂, 8: NaH₂PO₄, 9: Na₂HPO₄, 10: sodium pyrophosphate, 11: hydroxyapatite, 12: Ca₃(PO₄)₂, 13: CaHPO₄, 14: montmorillonite, 15: zeolite, 16: sepiolite, 17: attapulgite, 18: bentonite, 19: CK.)

3.2. Effects of Different Amendments on Lead Effective State Content in Soil

The passivation effects of different amendments on soil available lead are shown in Figure 2. After the addition of amendments, concentration of available lead decreased in most of the treated soils. The best amendments of iron oxide passivators was FeCl₃, which the concentration of available lead decreased 62.5% after three days. The available lead content in soils decreased by CaHPO₄ and NaH₂PO₄, the soil available lead decreased form 119.06 mg/kg to 37.74 mg/kg and 70.08 mg/kg by NaH₂PO₄ and CaHPO₄, respectively. The concentration of soil lead increased significantly after adding sodium pyrophosphate, meanwhile the lime amendments and clay mineral amendments in this study have no significant effect on soil available lead.
3.3. Effects of Different Treatments on Cadmium Effective State Content in Soil

Based on the experimental results, three kinds of passivation reagents with better effect on soil cadmium were selected. The best amendment for cadmium contaminated soil was CaOH, followed by sodium pyrophosphate and CaHPO4. Different concentrations of CaOH, sodium pyrophosphate and CaHPO4 were used and the results are shown in Figure 3. The concentration of available cadmium decreased with increasing CaOH, sodium pyrophosphate and CaHPO4 concentration from 0.5% to 5% in a logarithmic pattern. The concentration of available cadmium was 1.16 mg/kg, 0.98 mg/kg, 0.45 mg/kg, 0.38 mg/kg and 0.36 mg/kg when the concentration of CaOH was 0.5%, 1%, 2%, 3%, and 5%, respectively. But when the dose of amendment was enough for the requirement of soil, the influence was very slight. The critical level of CaOH, followed by sodium pyrophosphate and CaHPO4 in this study was 2%, 1% and 2%.

3.4. Effects of Different Treatments on Lead Effective State Content in Soil

The application of amendments significantly decreased soil available lead, and the best amendments of lead was FeCl3, NaH2PO4 and CaHPO4. Different concentrations of FeCl3, NaH2PO4 and CaHPO4 were used and the results are shown in Figure 4. The concentration of available lead decreased with increasing FeCl3, NaH2PO4 and CaHPO4 concentration from 0.5% to 5% in a logarithmic pattern. The concentration of available lead was 72.66 mg/kg, 64.65 mg/kg, 45.61 mg/kg, 46.28 mg/kg and 37.74 mg/kg when the concentration of NaH2PO4 was 0.5%, 1%, 2%, 3%, and 5%, respectively. But when the dose of amendment was enough for the requirement of soil, the influence was very slight. The concentration of available lead was 89.03 mg/kg, 78.50 mg/kg, 64.88 mg/kg, 51.24 mg/kg and 44.63 mg/kg when the concentration of NaH2PO4 was 0.5%, 1%, 2%, 3%, and 5%, respectively.
FeCl₃ was 0.5%, 1%, 2%, 3%, and 5%, respectively. 2%.

Figure 4. Effects of different adding amount amendments on Pb effective state content in soil.

4. Conclusions
In the incubation experiments, effectiveness of 18 amendments passivating cadmium and lead from contaminated soil was examined in the soil incubation experiment. The best amendment for cadmium contaminated soil was CaOH, and the best additive amount of CaOH was 2% for cadmium contaminated soils. The best amendment for lead contaminated soil was NaH₂PO₄, and the best additive amount of NaH₂PO₄ was 2%. The best amendment for cadmium-lead-contaminated soil was CaHPO₄, and the best additive amount of CaHPO₄ was 2%.

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