

The Passivation Effect on Cd of Mixing of Hyperaccumulated Plant Straw and Phosphate Rock Powder in Cd Polluted Soil

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Abstract. Soil culture experiments were carried out to study the effects of the mixture of cadmium (Cd) hyperaccumulator straw (*Solanum nigrum* L., *Amaranthus chinense* L., and *Siegesbeckia orientalis* L.) and phosphate rock on soil pH, available Cd content and soil nutrients in Cd polluted soil. The results showed that: (1) The soil pH was increased to a certain extent by three kinds of compound materials. (2) The contents of available potassium (AK) and available phosphorus (AP) in soil were increased to a certain extent by the three compounding materials, but there was no significant effect on total nitrogen (TN). And 2% phosphate rock powder and 1% *Amaranthus chinense* L. had the greatest increase in AP, reaching 49.28%, and 2% phosphate rock powder and 1% *Siegesbeckia orientalis* L. had the greatest increase in AK, reaching 136.23%. (3) The available Cd content in soil was reduced by three kinds of compound materials. The decrease of available Cd was the greatest in 2% phosphate rock powder and 1% *Solanum nigrum* L. straw mixed, which was 12.71%. In summary, the combination of Cd hyperaccumulator straw and phosphate rock powder can effectively passivate Cd in soil and improve soil nutrient content, and 2% phosphate rock powder and 1% *Solanum nigrum* L. straw are the best.

1 Introduction

Cadmium (Cd) pollution in soil has become a global environmental problem. In 2014, the Chinese Ministry of Environmental Protection and the Ministry of Land and Resources jointly issued a national soil pollution bulletin, which showed that the total over-standard rate of soil in China was 16.1% [1,2]. Among them, inorganic type was the main pollution type, and heavy metals such as cadmium (Cd), lead (Pb), mercury (Hg) were the most serious. Among many heavy metal pollutants, Cd has attracted much attention because of its mobility and high toxicity. Cd is easily absorbed and accumulated by plants. When the concentration of Cd in plants reaches a certain level, it will affect the growth and development of plants and ultimately affect the yield and quality of crops. If people eat too much Cd containing food, it will damage the respiratory system, cardiovascular system, immune system, and then threaten people's life and health. Therefore, how to effectively improve and utilize Cd contaminated soil is of great significance to human development.

Reducing the bioavailability of Cd in soil by in-situ passivation remediation technology shows its unique advantages in two key issues: efficiency and cost of remediation. And it has little disturbance to soil and is suitable for remediation of large area Cd polluted soil. It is widely regarded as an effective ecological control measure [3,4]. Hyperaccumulated plants which can enrich heavy metals in excess, are mainly used for

phytoremediation at present, but there are few reports on the passivation remediation with the mixture of straw and phosphate rock powder. In this experiment, the straw of *Solanum nigrum* L., *Amaranthus chinense* L., *Siegesbeckia orientalis* L and phosphate rock powder were used as materials to study the passivation effect of hyperaccumulator straw and phosphate rock powder on Cd in polluted soil, in order to provide a theoretical basis for the in-situ passivation remediation technology of Cd polluted soil.

2 Materials and Methods

2.1 Materials

The straw of *Solanum nigrum* L., *Amaranthus chinense* L., and *Siegesbeckia orientalis* L.: Straw was collected from Chongzhou Base of Sichuan Agricultural University and was not polluted by heavy metals. The plant straw was dried and pulverized with a micro-plant sample pulverizer (pore size of 1 mm).

Phosphate rock powder: Phosphate rock powder was purchased from Sichuan Jinxin Mineral Products Co., Ltd., after grinding, pass through 100 mesh sieve.

Cd polluted soil: The soil was collected from the 0-20 cm surface soil of Chongzhou Base of Sichuan Agricultural University, and added with Cd²⁺ solution (formed with CdCl₂•2.5H₂O). The mixture was mixed well, and equilibrated for 30 days at room temperature.

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The basic physical and chemical properties of Cd polluted soil are shown in Table 1.

Table1. The basic physical and chemical properties of Cd polluted soil. ($\text{mg} \cdot \text{kg}^{-1}$)

pH	AP	AK	TN	Cd
6.49	38.47	78.93	758.84	3.71

2.2 Experimental Design

Using indoor culture experiments, 300 g of Cd polluted soil was weighed and placed in a 500 ml plastic bottle. And adding 2% phosphate rock powder and 1% *Solanum nigrum* L. straw (TL), 2% phosphate rock powder and 1% *Amaranthus chinense* L. straw (TZ), 2% phosphate rock powder and 1% *Siegesbeckia orientalis* L. straw (TX) respectively. At the same time, the control (CK) was set without adding any substance. And each treatment was repeated 3 times. Water was added to the culture bottle according to 65% of the field water holding capacity, sealed with plastic film, and left a few holes in the middle of the plastic film. The entire culture process was maintained at room temperature ($25\text{ }^{\circ}\text{C}$) and the soil moisture was maintained at about 65% of the field water holding capacity. After 60 days of culture, soil samples were taken, air-dried and sieved, and various indicators were determined.

2.3 Experimental Methods

Soil pH was determined by potentiometry at a soil-liquid ratio of 1:2.5 [5]. Total nitrogen (TN) content in soil was determined by Semi-micro Kjeldahl method [5]. Available phosphorus (AP) content in soil was determined by NaHCO_3 extraction- Mo-Sb colorimetry [5]. Available Potassium (AK) in soil was determined by NH_4OAC Extraction-Flame Spectrophotometry [5]. Available Cd in soil was determined by DTPA solution Extraction-Atomic Absorption Spectrometry [5].

2.4 Statistic Analyses

Statistical analyses were performed using Microsoft Excel 2016 and SPSS 22.0 statistical software. Data were analyzed by one-way ANOVA with least significant difference (LSD) at 5% confidence level.

3 Results and Discussion

3.1 Effect of Passivator on Soil pH

As shown in Fig.1, the addition of different passivators increased the soil pH, and TX treatment pH value increased the most, and TL, TZ treatments slightly lower. The main reason for the increase of soil pH value after adding passivator is the alkalinity of phosphate rock powder, which can neutralize acid ions after applied to soil [6].

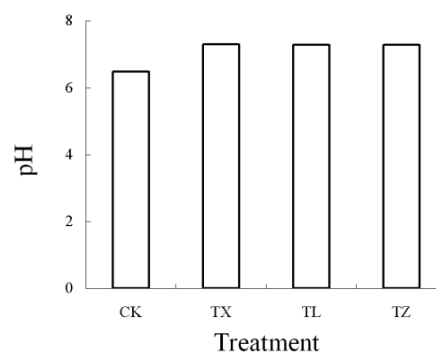


Fig. 1. pH in Cd polluted soil

3.2 Effects of Passivators on Soil Fertility

There was no significant difference in TN content in soil between treatment with different passivators and CK (Table 2). AP content is 24.63%~49.28% higher than CK, TL and TZ treatments were significantly higher than CK, and the TZ treatment increased the most, reaching 49.28%. AK content of all treatments was higher than CK, and the TX treatment had the highest AK content, which was 1.36 times higher than CK. The reason for the increase of soil nutrients is that straw contains certain K and P elements, which become mineral nutrients through the mineralization process, thus increasing the content of AP and AK in soil [7]. On the other hand, phosphate rock powder is a slow-release fertilizer of phosphorus, which can stably provide P element for plants [8].

Table 2. Comparison of soil fertility under different treatments

Treatments	TN ($\text{mg} \cdot \text{kg}^{-1}$)	AP ($\text{mg} \cdot \text{kg}^{-1}$)	AK ($\text{mg} \cdot \text{kg}^{-1}$)
CK	757.35±11.69a	53.64±2.48b	75.06±14.49c
TX	705.13±24.32a	66.85±4.92ab	177.03±25.39a
TL	774.95±46.83a	78.85±15.15a	123.25±26.70b
TZ	777.13±57.87a	80.08±4.60a	165.94±49.43a

Note: Different letters in each column indicate significant differences ($P < 0.05$) among different treatments.

3.3 Effects of Passivators on Soil Available Cd

As shown in Fig. 2, available Cd content in soil treated with different passivators was significantly lower than of CK. Compared with CK, TX, TL and TZ treatments decreased by 7.59%, 12.71% and 8.22%, respectively. It showed that the best passivation effect of Cd in soil was the mixture of 1% *Solanum nigrum* L. straw and 2% phosphate rock powder.

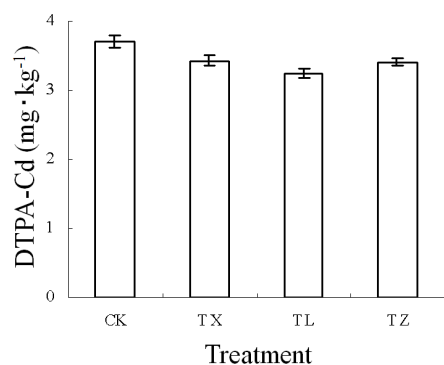


Fig. 2. Cd content in Cd polluted soil

Soil pH is an important factor affecting the distribution of heavy metals in soil. With the increase of pH in soil, the availability of heavy metal decreases, and soil adsorption of heavy metals is also gradually strengthened. When organic-inorganic passivator was applied to soil, the pH in soil was increased, and the absorption of heavy metals by soil colloids was promoted, that is, the transformation of exchangeable Cd to carbonate-bound Cd, organic Cd and iron-manganese oxidized Cd was promoted, thus the effective Cd was reduced. On the other hand, phosphorus-containing substances such as phosphate rock powder or straw can form precipitation with heavy metals or directly adsorb heavy metals on the surface of phosphate to stabilize Cd, thereby fixing the effective Cd in soil and reducing the activity of Cd.

Adding alkaline substances such as lime, phosphate rock powder or straw into the soil can effectively improve the pH value of the soil. In this experiment, the pH values of the three passivators were significantly higher than those of CK group, and the combination of Siegesian straw and phosphate rock powder had the greatest increase in pH. The main reason is that inorganic substances such as phosphate rock powder are alkaline and can neutralize acidifying ions when applied to soil. At present, the mixture of organic and inorganic substances is often used as passivator in the passivation remediation of heavy metal soil. These substances can effectively alleviate heavy metal pollution in soil through a series of chemical actions. People found that among the 15 passivator combinations, the combination of quicklime + passivator 4 + organic fertilizer had the most obvious effect on the increase of soil pH, and the decrease of exchangeable Cd was also the largest. And the combination of activated carbon and phosphate rock powder can effectively reduce the content of available Cd in soil. People also found that the mixture of lime, zeolite, superphosphate and biomass charcoal in a certain proportion, can effectively reduce the content of available Cd in soil by increasing soil pH. Similar to the results of previous experiments, in this experiment, compared with CK group, the total Cd content of the treatment with different passivators did not change significantly and the effective Cd content decreased to a certain extent, and there were significant differences with CK group. Among them, the effective Cd of the combination of *Solanum nigrum* straw and phosphate rock powder decreased the most, and the passivation

effect was the best. Soil pH is an important factor affecting the distribution of heavy metals in soil. Many studies have shown that the activity of heavy metals in soil is closely related to soil pH. With the increase of soil pH, the availability of various heavy metals decreases, and the adsorption of heavy metals in soil is gradually strengthened. When inorganic and organic passivators are mixed into the soil, the physical and chemical properties of the soil are changed, the absorption of heavy metals by soil colloids is promoted, and the precipitation is promoted, that is, the transformation of exchangeable Cd into carbonate-bound Cd (Cb-Cd), organic Cd (OMb-Cd) and iron-manganese oxidized Cd (Fe-Mnb-Cd), and the transformation of exchangeable Cd into carbonate-bound Cd (Cb-Cd), organic Cd (OMb-Cd) is promoted. The effective Cd and soil toxicity decreased. On the other hand, when phosphate rock powder, a phosphorus containing substance, is added to the soil, it can form precipitation with heavy metals or directly adsorb heavy metals on the surface of phosphate to stabilize Cd. In addition, organic substances such as straw and biomass charcoal have strong adsorption and ion exchange effects on heavy metal ions, which can fix the effective Cd in soil and reduce the activity of Cd.

Soil fertility (such as TN, AP, organic matter content, etc.) is very important for plant growth and development. The content and activity of heavy metals in soil are related to these soil nutrients. People found that straw returning can effectively improve the content of soil organic matter and AK, and the content of soil organic matter and AK is proportional to the amount of straw returning. A previous study found that different kinds of phosphate rock powder could increase the contents of AP, AK and TN in soil after application. Similar to the previous research results, in this experiment, the content of AP and AK in soil was significantly increased by the combination of super-enriched plant straw and phosphate rock powder. Compared with CK group, the combination of *Siegesia sinensis* and phosphate rock powder had the greatest increase in AK, reaching 344.03 mg kg⁻¹, while the combination of amaranth and phosphate rock powder had the greatest increase in AP than CK group. On the one hand, the reason for the increase of soil nutrients is that the super-enriched plant straw contains certain K and P elements, which become mineral nutrients through the mineralization process, thus increasing the content of AP and AK in soil; on the other hand, phosphate rock powder is a slow-release fertilizer of phosphorus, which can provide P elements for plants steadily and apply it to the soil at the same time. After soils, it can also promote plant uptake of N, P and K to a certain extent, and increase crop yield. The increase of nutrients in soil, especially P element, increases the content of phosphate in soil, makes heavy metals adsorbed by phosphate, and reduces the activity of Cd.

4 Conclusion

Different passivator treatments can increase the content of AP and AK in soil, increase pH and reduce the content of available Cd in soil, and have a good passivation

effect on Cd in Cd polluted soil. And the mixture of 1% *Solanum nigrum* L. straw and 2% phosphate rock powder have the best effect.

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