

Leaching risk of chelate induced phytoremediation of Tl contaminated soil by *Zea mays* L.

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Abstract. In this paper, the effects of EDTA and EDDS as chelating agents, chelating-induced maize remediation on Tl-contaminated soils and their heavy metal leakage characteristics under rainfall conditions were studied. The results showed that both EDTA and EDDS could promote the uptake of Tl by maize, and EDDS could further promote the transfer of Tl from maize roots to shoot, and the effect of EDTA was weaker; The content of Tl in the leachate during the leaching process obeys the linear decrease rule with increasing rainfall. Under the condition of acid rain, the concentration of Tl was higher than that of non-acid rain in the leachate of EDDS chelating induction.

Introduction

Phytoextraction is one of the typical remediation techniques for heavy metal contaminated soils due to both economic and environmentally friendly characteristics^[1].

There are two types of plant used in phytoextraction: hyperaccumulators and tolerant plants. The latter, because of the high biomass and good environmental adaptability, the total extraction of heavy metals was no less than that of hyperaccumulator, and thus more favored by the researchers, though the heavy metal enrichment capacity has been reduced compared to the former. At the same time, in order to enhanced the extraction of tolerant plants, the chelation induction measures (Referred to as chelate-induced phytoextraction) of adding chelate agent to activate heavy metals from the soil solid phase into the solution to promote plant absorption also came into being.

At present, chelate-induced phytoextraction have been extensively studied in the selection of chelating agents and tolerant plants and heavy metal contaminated soil types. (1) EDTA, EDDS is generally considered to be two very effective artificial and natural, non-degradable and biodegradable typical chelating agents, can activate a variety of heavy metals (including Cd, Cu, Pb, Zn and etc.) in the soil, and can promote the effective absorption of plants.(2) Typical tolerant plants are mainly :Maize, Vetiver grass, Cabbage and Chrysanthemum^[2-4]. Among them, the maize (such as ZhengDan 958), a kind of a well-tolerated plants, is determined to be able to "side of the production side of the repair" and is worth promoting^[5]. (3) The main types of heavy metal in the contaminated soils are focused on Cd, Pb, Cu, Zn etc. and composite contaminated^[3].

Current problems in chelate - induced phytoextraction: (1) The research about heavy metal leakage risk of chelate-induced phytoextraction is still relatively weak, mostly stay in the theoretical analysis and simple leaching experiments. Fewer researchers have conducted studies on heavy metal leakage risk of chelate-induced phytoextraction under planting conditions. (2) Heavy metal contaminated soil types include limitations, such as Tl and other typical toxic heavy metal pollution soils in chelate induced phytoextraction have not been reported.

Based on the above problems, this paper studied the effects of EDTA, EDDS as chelating agent, chelating-induced maize remediation on Tl contaminated soil and its heavy metal leakage under rainfall conditions, and provided the basis for improving phytoextraction theory and scientific guidance.

Materials and methods

Collection and preparation of soil samples

Soil samples were collected from the topsoil of red soil (0-20cm, red soil) near a pyrite in Guangdong Province, China (22° 59' 25.5" N, 112° 00' 40.5" E). Dry, remove the larger plant debris and stones, broken, over 4mm nylon sieve, packing reserve. Determination of physical and chemical properties of soil using soil agrochemical routine analysis method^[6], including: particle size components (sand, silt, clay content percentage were 51, 33, 16, respectively), dry density (1.279 g/cm³), pH (4.5), CEC (3.3 cmol/kg), organic matter (15.4 mg/kg) and fertility component (effective N, P, K were 0.084, 0.9, 12.1 mg/kg, respectively). Soil heavy metals (Tl) were digested with HNO₃-HF (5:1) system and then determined by atomic absorption spectrometry (AAS).

Greenhouse cultivation

TlNO₃ was manually added to prepare Tl contaminated soil (5 mg/kg) and loaded into experimental soil column (7 cm in diameter, 12 cm height) (300 per one). Dry and wet alternately placed 60 days after the addition of compound fertilizer (N / P₂O₅ / K₂O = 15:15:15); Select the well germination of ZhengDan 958 maize seeds planted in soil samples, depth 2 ~ 3 cm. The soil samples were then placed in a greenhouse for 30 days and the temperature was maintained at 25-35 ° C. Constant water was added daily to maintain soil moisture at around 70% of field capacity. Until the seedlings grow to seven leaf stage, adding EDTA, EDDS chelating agent to the soil column (4 mmol/kg). To make leaching experiments after two days of culture, according to Zhou (2007), the activation of heavy metals reached its maximum at the third day after the chelating agent was added^[7].

Leaching experiment

According to Yunfu City, Guangdong Province, the characteristics of the chemical composition of rainfall, Reference method [8], to configure simulated rainfall reserve (pH of acid rain and non-acid rain were 4.5 and 6.5, respectively).

Soil column reached the saturated state before the start of rainfall leaching, Simulated rain intensity reference to the Chinese 12 hours rainstorm standard (50mm), 10ml each time, rainfall 5 times, a total of 250ml. Collecting the leachate successively in the leaching process. After leaching, harvest maize on the ground and the underground, respectively, Washed and placed in the oven at 70°C drying to constant weight, weighing. Using HNO₃-H₂O₂ to digestion, filtration, determination of heavy metal content in plants by AAS.

Design of leaching experiment: Design five kinds of experimental program, Non-acid rain + no chelating agent + no maize (CK0), Non-acid rain + no chelating agent + maize (CK), Non-acid rain + EDTA + maize (A), Non-acid rain + EDDS + maize (B), acid rain + EDDS + maize (C). Each program sets 3 repetitions.

Monitoring indicators: leachate pH, Tl content; plant Physiological Index (height, leaf length, leaf width, stem diameter, stem length, dry weight) and heavy metals content (on the ground and the underground).

Data processing and statistical methods

Calculation of plant extraction efficiency. Including bioconcentration factors (BCF) and Transfer coefficient (TF), is the ratio of the content of heavy metal of the shoot content to the soil content and the ratio of the content of heavy metal of the shoot content to the underground, respectively. Origin software package 8.0 was used for data mapping and regression analysis.

Results and discussion

Physiological characteristics of maize

The test results of plant physiological indicators about three experimental plans in Table 1.

From the table, there was no significant difference between the blank(CK) and the treatment with chelating agent(A,B), indicating that the maize had good adaptability to the content of EDTA and EDDS.

Table 1 Effects of chelate treatments on phytoextraction in Zea mays

Treatment	Height (cm)	Leaf length (cm)	Leaf width (cm)	Stem diameter (cm)	Stem length (cm)	Shoot DW (g)	Total DW (g)
CK	69.8±1.3	51.0±0.5	2.5±0.1	1.2±0.1	21.2±0.3	1.4500±0.2137	1.7867±0.1552
A	69.7±0.5	49.5±2.3	2.8±0.8	1.2±0.1	21.3±0.3	1.4237±0.1356	1.7577±0.2274
B	69.0±0.7	50.0±1.2	2.2±0.4	1.3±0.1	22.3±0.8	1.3840±0.1420	1.7269±0.1837

Characteristic of Tl phytoextraction by Z.mays

The results of several scheme of phytoextraction about Tl are shown in Table 2.

Table 2 Effects of chelate treatments on phytoextraction in Zea mays

Treatment	Shoot concentrations (mg·kg ⁻¹)	BCF	TF
CK	114.755±20.029	22.951	0.395
A	119.053±8.089	23.811	0.370
B	130.043±4.387	26.009	0.442

From the table,bioconcentration factors of scheme A and B which adding chelating agent is higher than CK , indicating that the chelating agent promoted the absorption of Tl on maize, and the effect of EDDS was

better than EDTA.The transfer coefficient of EDDS was greater than that of the control group(CK),indicating that EDDS further promoted the transfer of Tl from the roots to the shoots ; The transfer coefficient of EDTA was less than that of the control group(CK), which indicated that the transfer of Tl with EDTA was weak. The transfer performance of Tl with EDTA is different from the results about Pb, Cd^[9,10],it was related to different types of heavy metal.

Changes of Tl concentration in leachate

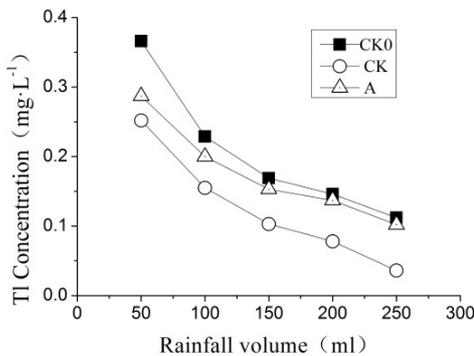


Fig.1 Changes of Tl concentration in leachate(CK0, CK,

related to the absence of maize absorption;CK is the lowest,related to maize absorption;A is higher than CK, related to EDTA activation of Tl into soil solution.The content of Tl in the leachate decreased with the increase of rainfall, and obeyed the law of linearly decreasing(CK0:y = -0.0012x+0.3812 R²=0.8729; CK:y=-0.0009x+0.3062 R²=0.9188; A:y=-0.001x+0.2947 R²=0.9287),The Tl concentration decline rate of unit rainfall(CK0,CK,A) was 0.0012、0.0009、0.001 mg/L,respectively.

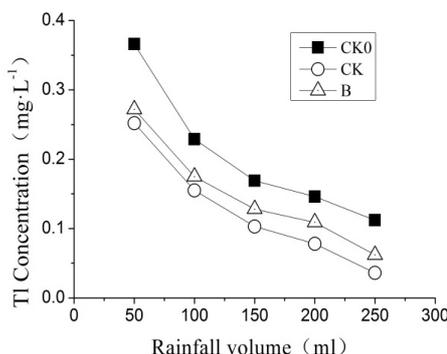


Fig.2 Changes of Tl concentration in leachate(CK0, CK, B)

The results of the change of heavy metals in the leachate of several schemes are shown in Figure 1-3.

As can be seen from Figure 1:The order of heavy metal content of leachate from high to low in leaching process was CK0(non-acid rain+no chelating agent+ no maize)>A(non-acid rain+EDTA + maize)>CK(non-acid rain+no chelating agent+ maize),which reflects the effects of maize absorption and chelating agent activation on the concentration of heavy metals in the soil solution.CK0 is the highest, mainly

related to the absence of maize absorption;CK is the lowest,related to maize absorption;A is higher than CK, related to EDTA activation of Tl into soil solution.The content of Tl in the leachate decreased with the increase of rainfall, and obeyed the law of linearly decreasing(CK0:y = -0.0012x+0.3812 R²=0.8729; CK:y=-0.0009x+0.3062 R²=0.9188; A:y=-0.001x+0.2947 R²=0.9287),The Tl concentration decline rate of unit rainfall(CK0,CK,A) was 0.0012、0.0009、0.001 mg/L,respectively.

Form Figure 2:For the non-acid rain condition, EDDS induced extraction,the order of Tl content in the leachate from high to low and the change of Tl content in the leachate with the rainfall were in agreement with EDTA induction.Linear variation equation is y = -0.001x +0.2777 R² = 0.9372,the Tl concentration decline rate of unit rainfall was 0.001mg/L.

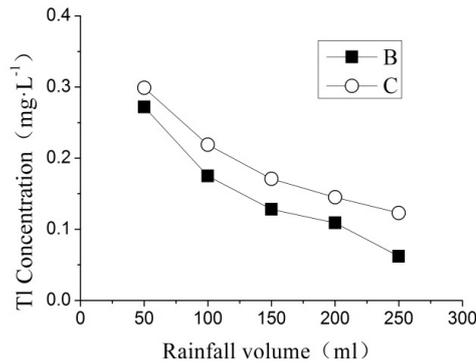


Fig.3 Changes of TI concentration in leachate(B,C)

Form Figure 3:For the acid rain condition, EDDS induced extraction, TI content in the leachate is higher than non-acid rain condition, reflecting the acid rain to further promote the activation of TI. The change of TI content in the leachate with the rainfall were in agreement with the non-acid rain condition of EDDS induction. Linear variation equation is $y = -0.0009x + 0.3188$ $R^2 = 0.9265$, the TI concentration decline rate of unit rainfall was 0.0009 mg/L.

Conclusions

EDTA and EDDS could promote the uptake of TI by maize, and EDDS could further promote the transfer of TI from maize roots to shoot, and the effect of EDTA was weaker. The content of TI in the leachate of the leaching process obeys the linear decrease rule with increasing rainfall. Under the condition of acid rain, the concentration of TI was higher than that of non acid rain in the leachate of EDDS chelating induction.

Acknowledgements

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