USING ACTIVATING SUBSTANCES AND PHYTOREMEDIATION FOR THE SOIL CONTAMINATED WITH CADMIUM

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ABSTRACT

One of the key issues of concern is the development of heavy metals in the soil and the environmental pollution. The test soil was collected from a farmland in Yixing City, Wuxi City, Jiangsu Province, China. The soil was highly contaminated Cd clay soils need more washings than sandy soils for effective metal stabilization. The soil was naturally air-dried after 3 weeks of equilibration and ground on a 100-mesh nylon mesh and studying technologies of soil contaminated by cadmium, suitable for effective rehabilitation technology is very important. This model simulates soil contaminated with high levels of cadmium and tests the impact of the determinant of heavy metals in the soil and the effects of acid-to-soil testing on 5 types of "activating agents Tetrasodium Glutamate Diacetate (GLDA), Etidronic acid monohydrate (HEDP), Saponin, Wood vinegar (WV), Citric acid (CA) in heavy metals to study combinations of plants and activators in the reclaimed soil of ryegrass (Lolium perenne L), rockcrop (Sedum alfredii Hance), rape (Brassica napus L.) heavy metals contaminated soil, the following conclusions are as follows: Five activators, including CA, GLDA, WV, HEDP, and Saponin, were used to remove heavy metal cadmium from the soil of three plants (Sedum alfredii Hance, Lolium perenne L., and Brassica napus L.). Phytoremediation is a new technology used to treat the high-polluted environment. This new invention relates to heavy metal pollution control techniques, particularly the chemical method of fixing heavy-polluted soil. This includes a soil-contaminated agricultural soil of laboratory experiment with five chelators Citric acid (CA), Saponin, Tetrasodium Glutamate Diacetate (GLDA), Etidronic acid monohydrate (HEDP), Wood vinegar (WV). The extraction efficiency of Wood vinegar(WV) was higher than that of other activators, for example, WV of 50mmol L-1 can remove of cadmium, and compared with other activators, Tetrasodium Glutamate Diacetate (GLDA) has a lower leaching effect of cadmium. Both WV and Etidronic acid monohydrate (HEDP) can increase metal movement and improve their bio-potency, which can be converted by oxidation, a residual dissolving of acid. 50 mmol • L-1

HEDP and 10 mmol • L-1 WV can eliminate secondary high-efficiency and low-cost cadmium. Use better result with WV. These results have confirmed the result of the soil washing method in WV. HEDP also has a strong reduction effect, which can dissolve the oxide material on the metal surface. Plant-based phytoremediation techniques are usually defined as a reliable method of fixing heavy contaminated soils. However, the biochemical level in the soil is a limiting consumer. The major dilution and recovery technologies are the development and development of a non-hazardous, low-cost, no-pollution-free, economically-efficient process.

Keywords: Soil, Phytoremediation, activator, chelator, cadmium.

INTRODUCTION

Phytoremediation uses plants to clean up contaminated environments.[1] The heavy metal, such as Cadmium, remains in the soil and is used for agricultural purposes in mining and urban areas. One such technique is phytoremediation, which exploits the ability of certain plants to accumulate a large amount of the heavy metals. Phytoremediation is the method by which plants are used to sequester, remove, or accumulate different heavy metals from the environment.[2] Phytoremediation is defined as using plants to make soil contaminant nontoxic.[3] Heavy metal contamination of soil is a major concern in all parts of the world, in particular in emerging countries where there is an increasing need for soil for food.[4] Fossilization can be contaminated with soil or static water in any place where chronic pollution occurs.[5][6] Examples of successful use of phytoremediation include the abandonment of abandoned metal mines and the generation of polychlorinated biphenyls and the reduction of waste rock tailings to minimize the impact of soil, water, and air pollutants on the ground.[7] Pollutants such as metals, pesticides, solvents, explosives, crude oils and their derivatives have adversely affected worldwide firms projects.[8] Over the past 20 years, the technology has become increasingly popular and has been working in areas with cadmium, and lead, arsenic, and arsenic contaminated soil. It is advantageous to consider environmental issues.[9] One of the main weaknesses of the controllers is long-term commitments, which can be fixed under normal conditions of plant growth. In this paper 5 chelates (CA, WV, GLDA, HEDP, Saponin) is used for increasing biological resources of cadmium in soil.[10]

The invention relates to soil heavy metal pollution treatment technology and discloses a chemical elution method for repairing heavy metal contaminated soil.[11] The invention uses iron sulfate solution to continuously elute and fluorocarbon surfactant and water to leach heavy metals into the soil, increase the removal efficiency of heavy metals, and the removal rate of cadmium in contaminated soil reaches 90%.[12] The invention overcomes the problems of high cost of reagents in the existing methods for leaching heavy metals into the soil, generating secondary pollution, and then dealing with the difficult problem.[13] The invention adopts iron sulfate and fluorocarbon surfactant solution continuous elution method, which can

reduce the concentration of eluent and improve the eluant efficiency.[14] Meanwhile, it has the advantages of simple operation, avoiding secondary contamination of eluent, effectively eliminating heavy metals, and improving the soil.[15] A fluorocarbon surfactant used in the invention can easily degrade, and its degradation products can become plant nutrition.[16]

MATERIALS AND METHODS

Soils treatments and chelating agents:

Selected soil: The test soil was collected from a farmland in Yixing City, (Wuxi City, Jiangsu Province). The soil was highly contaminated Cd clay soils need more washings than sandy soils for effective metal stabilization.

To simulate a single Cd pollution: The soil corresponding to the level of Cd pollution in (highly contaminated). And all soil samples were dried in the air and after 3 weeks of equilibration sieved through a 2-mm nylon mesh prior to the extraction experiments [17]

Activators: Citric acid (CA), wood vinegar (WV), GLDA, HEDP, and Saponin, all of which were of analytical grade (AR), were purchased from Guangdong Xilong Chemical Co., Ltd. Cd standard solution (1000 mg • L-1) was produced by National Standards Research Center and purchased from Shanghai Reagent Co., Ltd. All experimental water is deionized water with a resistivity of 18.2 MΩ • cm-1.

Some physical and chemical properties of the soil presented in Table 1 were measured by standard methods of the People's Republic of China.[18]

Extraction experiments:

The effect of cd-extraction on five different chlorinated compounds was carried out in 50 ml of polyethylene pipes (Table 1). Sample test 5: (5 g) high contamination) 25 ml of extraction soil (5 g) extraction, shake for 180 minutes for 180 minutes for 25 minutes and then take centrifuge for 10 minutes for 4000 minutes and then 25 ml of residual water will be drained and centrifuged. Filter and remove mixtures with 0,45 μm membrane and measure the concentration of Cd. Four duplication copies were made for each specimen. (Table 1)

Chelant	Water	CA (mmol· L-1)	WV (% weight)	GLDA (mmol ·L-1)	HEDP (mmol· L-1)	Saponin (mmol· L-1)
Concentration	-	10 20 50	0.5 1.0 2.5	10 20 50	10 20 50	10 20 50

Table 1: Comparison of chelators in the high contamination level of Cd-contaminated soils

Sequential extraction experiments:

Referenced by BCR sequential extraction [19] to compare the highly-contaminated soil samples to compare and analyze changes in the fractions of the heavy metals fraction in the material.[20] Four steps and defined metal fractions are shown in (Table 2.)

Experiment	Fraction	Agents and procedures	Extraction time（h）
Step1	Acid soluble state	40 mL HOAc (0.11 M) 16 mL deionized water	16
Step2	Reducible state	40 mLNH2OH·HCl (0.1 M, pH 2) 16 mL deionized water	16
Step3	Oxidizable state	10mLH2O2 (30%, pH2) heat to 85℃ for1h and add 10 mL H2O2 (30%, pH2) heat to 85℃ for1h and then add 50 mL NH4OAc (1M,pH2)	1 1 16
Step4	Residual state	HCl–HNO3–HF–HClO4	4-6

Table 2: Chemical reagents and analytical conditions for the modified BCR sequential extraction

During the operation, sequential extraction tests were performed on a soil sample of 0.5 g. Centrifuge suspended centrifuges for each experiment, then filtered by a 0.45μm membrane, then the residue was extracted with extraction substances used during subsequent stages of extraction. The filter is acidified to pH <2 before further analysis.

Analytical methods:

Cd was performed using the Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer with AS-90 Plus Autosampler and PC.[21]

Water Out		Water In	
Furnace Cooling System		*Furnace Gasses*	
Recommended Pressure	*Max Pressure*	*Recommended Pressure*	*Max Pressure*
350 kPA ± 10%, 3.5 bar ± 10%, 51.0 psig ±10%	400 kPA ± 10%, 4.0 bar ± 10%, 58.0 psig ±10%	350 kPA ± 10%, 3.5 bar ± 10%, 51.0 psig ±10%	400 kPA ± 10%, 4.0 bar ± 10%, 58.0 psig ±10%

Table 3: Perkin Elmer AS 90 plus Autosampler Details

Cd analysis was carried out in accordance with using a Perkin Elmer model AA-400 spectrophotometer (Perkin Elmer Corporation, USA). The detection limit for Cd was 0.020 mg·kg-1. And the ashing temperature and atomization temperature on the determination of cadmium are 350℃ and 1500℃, respectively. For quality control, geochemical standard reference sample soil GBW07405 (GSS-5) were purchased from IGGE, China. Recovery rates of 95 % ± 5% were obtained using standard methods described above.[22]

Statistical analysis was performed using the GraphPad Prism 5 for Windows Evaluation Version.[23] Data are presented as mean values ± standard deviation (SD) of 4 replicates. Mean values were compared by one-way analysis of variance followed by LSD test at the 5% level.

RESULT AND DISCUSSION

Figure 1, Shows the use of five kinds of activators, including Citric acid, Wood vinegar, GLDA, HEDP and Saponin to extract the soil heavy metal cadmium (highly polluted). The results showed that the leaching efficiency of the five activators increased with the increase of the concentration of activator, WV> HEDP > CA >GLDA> Saponin, in the control experiment almost cadmium removal.

The extraction efficiency of WV was higher than that of other activators, for example, WV of 50 mmol L-1 can remove 69.08% of cadmium, compared with other activators, GLDA has a lower leaching effect of cadmium.

The result of the removal of five types of stimulants such as CA, wood vinegar, GLDA, HEDP, Saponin can reach cadmium 80%. In contrast, the dehumidification rate decreased to 69.08% when it was 50mmol.L-1. As a result, moderate citric acid has a negative effect on limiting the heavy metals contained in the soil.

As shown in Figures 1, Simultaneously the cadmium-polluted by these elements, 50mmol.L-1 HEDP cadmium removal rates are 38.96%.

For CA, the removal of 10 mmol.L-1 cadmium is 19.28%. In the case of cadmium in the soil, the HEDP is removed at 34.94% at 10 mmol.L-1, and at 45.18% 20mmol.L-1, 50mmol.L-1, it is removed. Saponin is smaller in appearance than HEDP. the evaporation of the cadmium and increases the acidity of HEDP as causes the removal of the cadmium. The higher the HEDP content, the greater the limiting strength of the removal of the cadmium.
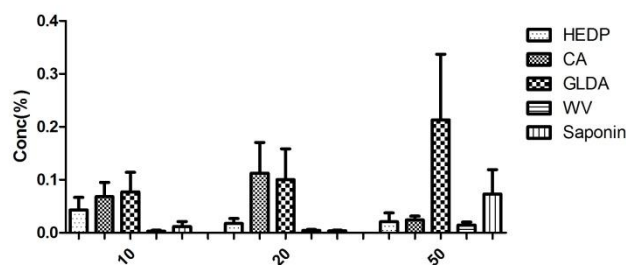

Figure 1: Leaching rate of Cd-contaminated in soils with different concentration of CA, WV, GLDA, HEDP, and Saponin. Values shown are the mean ± SD (n=3)

Active agent and plant combined remediation technology are suitable for various types of heavy metal contaminated soil, but different activators and plant combined remediation methods have different effects on the removal of heavy metals in soil.[24][25]

Figure 2, In the soil, Cd mainly exists in acid solubility and reducible state, the ratio of these two parts is 73.67%. By elution experiments, the removal of cadmium was mainly while the removal of cadmium in oxidizing and residual forms was very small.

As compared with other activators, the extraction efficiency of Cd by Saponin is higher, 32.78% cadmium can be removed [26]by 10 mmol · L-1, Acid and reducible Cd were the main components. This may be that Saponin can effectively remove acid soluble and reducible Cd by reducing soil pH. [27]At the same time, the graph shows that Saponin can also remove the oxidizable and residual Cd in some degree, The residual state, also known as an unavailable state, is not easily released by the soil, and the oxidized metal can be released under strongly oxidizing conditions.The graph shows that increasing the concentration of Saponin does not significantly increase the removal efficiency of cadmium, so in practical application, 10 mmol · L-1 Saponin can be used, taking into account the economic cost of the activator.

Similar to Saponin, CA also removed acid soluble and reducible cadmium. 10 mmol · L-1CA can remove 42.54% acid-soluble and reducible Cd. The removal rate of cadmium by HEDP was relatively small, and the

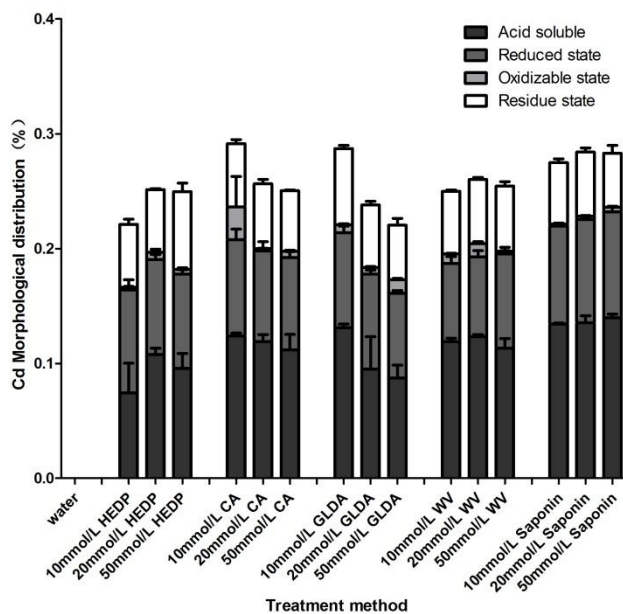removal of reducible cadmium was the main, but the acid soluble cadmium was not decreased as expected.

Figure 2: Sequential extraction steps of Cd in highly-contaminated soils after oscillating. Values shown are the mean ± SD (n=3)

CONCLUSIONS

From the results of the laboratory analysis, soil washings showed that phytoremediation was effective and WV washes away from heavy metals. Depending on pollution, the chelator used for soil is a technology that can be environmentally friendly, harmless, and polluted. Due to the fact that only one type of heavy metal or cadmium is contaminated, these five types of activators are generally eliminating heavy metals at the same level.

❖ GLDA is better than Saponin's ability to change the cadmium state.

❖ WV of -2.5% is more effective in cleaning the cadmium.

❖ HEDP reduces the coefficient of accumulation and transferability in cadmium soil.

❖ CA is good for cadmium restriction.

❖ Saponin may limit the cadmium when cadmium pollution in the soil is low, but there is less capacity to limit polluted soil cadmium.

As an acid organophosphate inhibitor, HEDP can not only reduce the release of heavy metals from soil pH but also form stable chelates with Fe, Cu and Zn ions. [28] HEDP also has a strong reductive effect, which can dissolve the oxide material on the surface of the metal.

The results of BCR showed that HEDP mainly removed the reducible Cd, and the reducible Cd extracted from HEDP of 10 mmol · L-1 accounted for 35.22% of the total removal rate. With the increasing of HEDP concentration, the cadmium in the acid-soluble state changed obviously, The acid-soluble Cd extracted by HEDP accounted for 24.53% of the total form Cd removal rate when 50 mmol · L-1 was 50 mmol · L-1.

REFERENCES

1. E. P. A. EPA, "A Citizen's Guide to Phytoremediation," *Engineering*, pp. 1–6, 2012.

2. E. Masarovi and K. Krá, "Plant-Heavy Metal Interaction: Phytoremediation, Biofortification and Nanoparticles," *Intech Open*, pp. 78–102, 2010.

3. M. Komárek, "Is There a Future for Chelant-Enhanced Phytoextraction of Metals from Contaminated Soils ?," pp. 467–470, 2010.

4. WHO, "Our Planet, Our Health, Our Future," *Public Heal. Environ. Dep.*, p. 64, 2012.

5. M. Lambert and B. a Leven, "New Methods of Cleaning Up Heavy Metal in Soils and Water Innovative Solutions to an Environmental Problem," *Environ. Sci. Technol. Briefs Citizens*, pp. 1–3, 2000.

6. M. B. Hinojosa, J. A. Carreira, R. García-Ruíz, and R. P. Dick, "Soil moisture pre-treatment effects on enzyme activities as indicators of heavy metal-contaminated and reclaimed soils," in *Soil Biology and Biochemistry*, 2004, vol. 36, no. 10, pp. 1559–1568.

7. H. M. Anawar, F. Akter, Z. M. Solaiman, and V. Strezov, "Biochar: An Emerging Panacea for Remediation of Soil Contaminants from Mining, Industry and Sewage Wastes," *Pedosphere*, vol. 25, no. 5, pp. 654–665, 2015.

8. T. Komives, G. Gullner, A. Bittsanszky, S. Pascal, and F. Laurent, "Phytoremediation of persistent organic pollutants," *Cereal Res. Commun.*, vol. 37, no. SUPPL.1, pp. 537–540, 2009.

9. O. V. Singh and R. K. Jain, "Phytoremediation of toxic aromatic pollutants from soil," *Applied Microbiology and Biotechnology*, vol. 63, no. 2. pp. 128–135, 2003.

10. S. P. McGrath, F. J. Zhao, and E. Lombi, "Plant and rhizosphere processes involved in phytoremediation of metal-contaminated soils," *Plant Soil*, vol. 232, no. 1–2, pp. 207–214, 2001.

11. Irena Sherameti • AjitVarma, *Heavy Metal Contamination of Soils Monitoring and Remediation*, vol. 44. 2015.

12. R. J. Abumaizar and E. H. Smith, "Heavy metal contaminants removal by soil washing," vol. 70, no. 1–2, p. 16, 1999.

13. G. Koptsik, S. Koptsik, G. Spiers, and P. Beckett, "Chapter 18 – Restoration of Smelter Industrial Barrens Following Pollution Reduction Drives Economic Recovery," in *Environmental Materials and Waste*, 2016, pp. 463–483.

14. D. M. Lemal, "Perspective on Fluorocarbon Chemistry," *Journal of Organic Chemistry*. 2004.

15. M. Gavrilescu, "Removal of heavy metals from the environment by biosorption," *Engineering in Life Sciences*. 2004.

16. M. Ghosh and S. P. Singh, "A review on phytoremediation of heavy metals and utilization of its byproducts," *Applied Ecology and Environmental Research*, vol. 3, no. 1. pp. 1–18, 2005.

17. Z. a Ahnstrom and D. R. Parker, "Cadmium reactivity in metal-contaminated soils using a coupled stable isotope dilution-sequential extraction procedure.," *Environ. Sci. Technol.*, vol. 35, no. 1, pp. 121–126, 2001.

18. Y. Wei, Z. Zhou, and G. Liu, "Physico-chemical properties and enzyme activities of the arable soils in Lhasa, Tibet, China," *J. Mt. Sci.*, 2012.

19. K. F. Mossop and C. M. Davidson, "Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments," *Anal. Chim. Acta*, vol. 478, no. 1, pp. 111–118, 2003.

20. J. Qian, X. Q. Shan, Z. J. Wang, and Q. Tu, "Distribution and plant availability of heavy metals in different particle-size fractions of soil," *Sci. Total Environ.*, 1996.

21. A. Supplies, "Agilent Supplies FOR PerkinElmer AA SPECTROMETERS."

22. L. S. Cornish, Y. P. Ma, S. C. Chan, T. T. Wong, C. F. Ng, and C. K. Chan, "Signal Averaging Computer System for Perkin-Elmer 577 Infrared Spectrophotometer," *Comput. Chem.*, 1987.

23. GraphPad Software Inc, "GraphPad Prism User Guide," p. 452, 2014.

24. M. Sa??lam, K. ??a??atay Selvi, O. Dengiz, and F. E. G??rsoy, "Affects of different tillage managements on soil physical quality in a clayey soil," *Environ. Monit. Assess.*, 2015.

25. O. Kara and M. Baykara, "Changes in soil microbial biomass and aggregate stability under different land uses in the northeastern Turkey," *Environ. Monit. Assess.*, 2014.

26. C. WANG, X. HU, M. CHEN, and Y. WU, "Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants," *J. Hazard. Mater.*, 2005.

27. I. Mohamed, G. shi Zhang, Z. guo Li, Y. Liu, F. Chen, and K. Dai, "Ecological restoration of an acidic Cd contaminated soil using bamboo biochar application," *Ecol. Eng.*, 2015.

28. I. Ahumada *et al.*, "Determination of the bioavailable fraction of Cu and Zn in soils amended with biosolids as determined by diffusive gradients in thin films (DGT), BCR sequential extraction, and ryegrass plant," *Water. Air. Soil Pollut.*, 2011.