Remediation of Heavy Metal Contamination in Paddy Soils through Soil Leaching Combined with Biosorption

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Abstract. Soil contamination and associated pollution plays a detrimental role in the sustainable development of agriculture. In this paper, a novel approach, soil washing combined with biosorption, to remove heavy metal from paddy soil, which contaminated by high levels of Cd, Pb, Cu, Cr and Zn, was evaluated in laboratory-scale batch based on environmental and efficient analysis. The mixture of 3M HCl and 0.2M EDTA solution was used as the leaching agent. Collagen fiber modification persimmon tannin (PTCF) and chitosan functionalization persimmon tannin (PTCS) were used as the biosorbents. The beaker and enlarge experimental results showed that PTCF, PTCS, mixture of PTCF and PTCS can effectively remove five metal ions from leaching liquid of contaminated soil. For the prepared Grade III soil which is critical conditions for the growth of plants (Environmental Quality Standard for Soils/GB 15618-1995), the metal removal efficiency was achieved at 53.36%, 44.89%, 37.73%, 7.60% and 6.02% for Cd, Pb, Cu, Cr and Zn at 10% mixture PTCF and PTCS adsorbent (1:1), respectively. All the results proved that the feasibility of the soil washing combined with biosorption remediation has great potential in the treatment of heavy metal pollution.

1. Introduction
With the rapid development of global industry, soil contamination has become an increasingly important environmental issue in both developed and developing countries. Trace metal contamination of paddy soil and subsequent potential fouling of groundwater may potentially pose health risk to humans since the major route of metals exposure to humans is through soil-food crop pathway via dietary intake. Heavy metal ions such as Cd, Pb, Cu, Cr, Zn, Hg and Ni are non-biodegradable, toxic and carcinogenic even at very low concentrations.

To some extent, contamination of soils with heavy metals can be solved by the remediation of the contaminated soil. The remediation of metal-contaminated sites has been tested firstly by excavation of the contaminated soils, followed by the immobilization of metal contaminants by solidification/stabilization (S/S) technology prior to disposal of the materials treated. The soil remediation technologies based on S/S technology are no longer considered a permanent environmental solution because the metals are not removed from contaminated media and the long-term management of the solidified/stabilized materials, which is based on landfilling, requires soil caps to prevent erosion problems. Hence, there is a great need to promote effective soil treatment technologies to remove the heavy metals from the soils.

Remediation technologies for soils contaminated with heavy metals include physical, chemical, and biological remediation methods. Soil washing, which uses physical or chemical processes to remove the
metal contaminants from soils by ex situ techniques, is one of the few permanent treatment alternatives to separate the metals from soils. After soil washing, sequential removal of heavy metals in the washing solutions will be conducted. Precipitation, ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, and adsorption are the conventional methods for removal of heavy metal ions from aqueous solutions. Each of the current technologies has its own merits and demerits besides playing an important role in preventing widespread heavy metal toxicity in nature. Among them, adsorption is one of the powerful treatment processes for the removal of metal ions from water with high efficiency, low cost, and friendly operating conditions in various industries at large scales.

Tannins, natural biomass containing multiple adjacent hydroxyl groups and exhibiting specific affinity to metal ions, can be used as effective and efficient sorbents for the recovery of metal ions. However, tannins are water-soluble compounds, thus when they are used directly as an adsorbent from aqueous systems, they have the disadvantage of being leached by water. To overcome this disadvantage, attempts have been made to immobilize tannins onto various water-insoluble matrices and made good adsorption capacities for recovery of heavy metal ions from aqueous solutions such as Pb, Au, Ag, Cd, Pd.

Accordingly, in the paper, two kinds of biomass materials, collagen fiber modification persimmon tannins (PTCF) and chitosan functionalized persimmon tannins (PTCS), were prepared and used as the novel biosorbents. The mixture of 3M HCl and 0.2M EDTA solution was used as the leaching agent for soil washing to favour the dissolution of the heavy metals and their transportation out of the soil. The main aim of this work was to evaluate the feasibility of the soil washing combined with biosorption remediation to remove heavy metal from contaminated soil in laboratory-scale batch. The effects of PTCF and PTCS on the amelioration of heavy metal contaminated soil were investigated using both chemical and biological assessments.

2. Materials and methods

2.1. Reagents and instruments
Persimmon tannin and collagen fiber were purchased from Guangxi Huikun Company of agricultural products. Chitosan, glutaraldehyde, Cd (NO$_3$)$_2$·4H$_2$O, Pb(NO$_3$)$_2$, Cu(NO$_3$)$_2$·3H$_2$O, K$_2$Cr$_2$O$_7$ and Zn(NO$_3$)$_2$·6H$_2$O were obtained from Guangdong Xilong Chemical Co., Ltd. All other chemicals used were of analytical grade without further purification.

The pH of all solutions was measured on a Sartorius Scientific Instruments model PB-10 pH meter. The adsorption experiments were studied by a batch technique using a model TS-100C thermostated shaker (Shanghai, China). Metal ion concentrations were measured using flame atomic absorption spectrophotometry (AAS, Zeenit 700P, and Germany).

2.2. Preparation PTCF adsorbent by collagen fiber modified with persimmon tannins
PTCF adsorbent was prepared by collagen fiber modified with persimmon tannins through glutaraldehyde crosslinking reaction according to our previous study with minor modification. Briefly, 30 g of persimmon tannin was dissolved in 1000 mL of deionized water and mixed with 20 g of collagen fiber. The mixture was stirred at room temperature for 20 h. Then the suspended matter was filtered and washed with distilled water. Afterwards, 100 mL of glutaraldehyde (25wt %) was added into the suspended matter. The mixture was first stirred at 298K for 4h and then stirred at 313K for 4 h. Finally, the product was washed with distilled water and filtered. The filter cake was dried in vacuum at 323K for 24h. Then the biosorbent was crushed and sieved to 100 meshes prior to use.

2.3. Preparation PTCS adsorbent through chitosan functionalized persimmon tannins
PTCS adsorbent was prepared through chitosan functionalized persimmon tannins according to our previous study. In brief, 10 g persimmon tannin was dissolved in 300 mL of deionized water and mixed with 5 g chitosan at pH 7.0. The mixture was stirred at room temperature for 6h. Then the suspended matter was filtered and washed with distilled water. Afterwards, 300 mL of glutaraldehyde (25 wt%) was added into the suspended matter. The mixture was first stirred at 298K for 1h and then stirred at 323K for 5h. Then, the pale yellow product was washed with distilled water and filtered. The filter cake
was dried in vacuum at 323K for 20h. Finally, the dried product was crushed and sieved into uniform particles of up to 200 nm in diameter.

2.4. Pretreated of the test soil
The soil used in this study was sampled from the excavation material of a construction site in Dongtian Village paddy field in Guilin city, Guangxi province, China. The soil specimen was taken from the sub-soil in the layer between 10 cm and 40 cm below the surface. Stones, sticks and big roots (>1 cm) were manually removed. The soil was passed through a 10 mesh after air-dried and ground. Then the soil was thoroughly mixed to ensure uniformity and stored in a plastic barrel at room temperature for subsequent use in experiments. Soil characteristics were reported in Table 1. Firstly, five soil samples were digested for determining total initial heavy metal concentration using HCl-HNO3-HF-HClO4 digestion system method (GB/T17138-1997). Then, the soil was spiked in the lab with five heavy metals: Cd, Pb, Cu, Cr and Zn. About 1 kg of oven dry soil was thoroughly mixed with 1 L of deionized water containing dissolved salts of cadmium nitrate (Cd(NO₃)₂·4H₂O), lead nitrate (Pb(NO₃)₂), copper nitrate (Cu(NO₃)₂·3H₂O), potassium dichromate (K₂Cr₂O₇) and zinc nitrate (Zn(NO₃)₂·6H₂O). The concentrations of those salts reached the standard of Grade III soil (Environmental Quality Standard for Soils/GB 15618-1995) based on the initial soil. After the spiking process, the soil was stored in a plastic box in darkness for a period of about six months with frequent thorough mixing to ensure the aging of the contaminants. The aim of this process was to ensure that the contaminated soil behaved in a similar way to real contaminated soil. The soil specimen was analyzed in triplicate for total metal content by AAS. The heavy metal concentrations in the soil before the experiments were (mg/kg dry soil): 1.0 for Cd, 400 for Cr, 500 for Pb, 400 for Cu and 500 for Zn.

| Property                          | Value       |
|----------------------------------|-------------|
| Soil pH                          | 6.9±0.3     |
| Background concentrations of the original soil |            |
| Cd                               | 0.1±0.02mg/kg |
| Pb                               | 11±2mg/kg   |
| Cu                               | 8±2mg/kg    |
| Cr                               | 11±2mg/kg   |
| Zn                               | 28±4mg/kg   |
| Metal concentrations of the test soil |          |
| Cd                               | 1±0.2mg/kg |
| Pb                               | 482±56mg/kg |
| Cu                               | 415±10mg/kg |
| Cr                               | 387±42mg/kg |
| Zn                               | 490±23mg/kg |

2.5 Leaching test and experimental procedure
Three washing reagents, dilute hydrochloric acid (HCl) solution, ethylene diamine tetraacetic acid (EDTA) and disodium salt of EDTA (Na₂EDTA), were selected for their capacity to solubilize and extract heavy metals from the soil, and the results were compared with the extraction with DI water. The tests were accomplished by placing certain amounts of soil in 100 mL plastic beakers followed by addition of varying volumes of the washing solution. The samples were placed on a shaker for 2 h at 150 rpm and room temperature. Then, the samples were allowed to settle for 15 min and filtered through a 0.45 μm membrane filter to remove all the particles in suspension. The pH of the washing solution before contact with the soil and the pH of the filtrate were measured and recorded. The supernatant was stored at 4°C before it was analyzed for metal concentration by AAS. Removal efficiency (R %) were determined by dividing the heavy metal release quantities by the initial quantity in the soil as equation (1).
Where \( C_0 \) and \( C_e \) were the initial mass and equilibrium concentration of metal ions (mg).

All tests were carried out in triplicate and the variance among the triples was reported as standard deviation by means of error bars.

2.6 Beaker experiments in a laboratory scale
Soil samples were divided into three groups according to the adsorption of treatment. 100g soil put in 250 mL plastic beaker and added the most suitable washing solution based on above results of leaching test. One of the group used PTCF as adsorbent, the other used PTCS and the last one was the 1:1 mixture of PTCF and PTCS adsorbent. Each group include five treatments: using 1%, 3%, 5%, 7% and 10% of adsorbent (mass adsorbent), respectively. The adsorbent was mixed evenly with sample soil and shaken in 200r/min at room temperature for 5 days. The effectiveness of the additives on adsorption of metals was evaluated by Removal efficiency using equation (1).

3. Results and discussion

3.1 leaching test
As known, when metal-containing compounds are dissolved in water, the metallic component exists normally as free ions in solution. At a given pH value, metal precipitates will intermingle and become an integral part of the soil matrix while the concentrations of these metals exceed the solubility of their corresponding hydroxide or carbonate phase. For soil washing, a variety of washing agents, such as inorganic acids, organic acids, chelating agents and natural bio-surfactants, have been tested and showed substantial capacity for dissolve heavy metals. In this study, DI water, HCl solution, EDTA solution and Na\(_2\)EDTA solution were selected as the washing reagents for the decontamination studies. The removal efficiency using different solution was summarized in Table 2.

| Washing solution | Solution pH | Filtrate pH | Removal efficiency(%) | Cd | Cr | Pb | Cu | Zn |
|------------------|-------------|-------------|----------------------|----|----|----|----|----|
| DI water         | 6.9         | 7.2         | 26                   | 11 | 21 | 19 | 20 |
| 1M HCl           | 1.5         | 3.5         | 57                   | 31 | 39 | 89 | 71 |
| 2M HCl           | 0.9         | 2.7         | 63                   | 37 | 52 | 91 | 79 |
| 3M HCl           | 0.7         | 1.9         | 77                   | 42 | 55 | 95 | 85 |
| 0.01M EDTA       | 6.2         | 5.8         | 63                   | 27 | 34 | 56 | 35 |
| 0.1M EDTA        | 5.6         | 5.1         | 84                   | 49 | 48 | 63 | 54 |
| 0.2M EDTA        | 5.1         | 4.7         | 92                   | 53 | 52 | 71 | 59 |
| 0.01M Na\(_2\)EDTA| 6.5        | 6.5         | 75                   | 15 | 25 | 19 | 21 |
| 0.1M Na\(_2\)EDTA| 5.7        | 5.9         | 81                   | 19 | 27 | 35 | 26 |
| 0.2M Na\(_2\)EDTA| 5.1        | 5.7         | 91                   | 22 | 30 | 37 | 28 |

The objective of the leaching tests was to evaluate the capability of each chemical to dissolve heavy metals from soil. As shown in Table 2, HCl was the most effective chemical in dissolving heavy metals from soil, followed by EDTA, Na\(_2\)EDTA and DI water. HCl was very effective because of the very low pH of the extracting solution, which dissolved the heavy metals by the direct attack of the H\(^+\) ions on the soil matrix. The extraction of the heavy metals with EDTA or Na\(_2\)EDTA was due to a combination of the extracting solution pH and the complexing chelating capability of each organic acid. Each heavy metal showed a very different response to the leaching tests. Pb, Cu and Zn were better extracted under 3M HCl effect (55%, 95% and 85%). In the case of Cd and Cr, 0.2 M EDTA was more effective (92%, 53%).
Cd was the only metal presenting the highest extraction under Na₂EDTA effect, with approximately 91% of its mass from the artificial contamination removed by 0.2 M Na₂EDTA.

The importance of washing with DI water is to reveal the metal fraction that is weakly bound to the soil particles or absorbed at easily coordinated sites in the outer surfaces of soil particles. In Table 2, soil solubility in DI water was below 50 g·kg⁻¹ and below 30% for all tested metals. Conclusively, the bulk of the metals under investigation is very tightly bound and probably belongs to one or more of the following fractions: ion exchangeable, adsorbed, precipitated, organically bound or trapped in an insoluble form in the soil matrix. Thus, 3M HCl and 0.2 M EDTA were used as the soil eluents in the subsequent series of experiments. The soil samples before and after leaching were shown in Scheme 1.

**Scheme 1.** The soil samples of leaching before and after by 3M HCl and 0.2M EDTA

### 3.2 Beaker experiment

Fig. 1 showed the PTCF adsorbent removal efficiency of every heavy metal from contaminated soil using PTCF adsorbent through combined soil washing with 3M HCl and 0.2 M EDTA. Seen from Fig. 1, the removal efficiency increased with the PTCF dosage increasing from 1% to 10%, and the removal efficiency of variety ions was Cd > Pb > Cu > Cr > Zn. When the addition dosage of PTCF was 10%, the removal efficiency reached 36.57%, 28.53%, 25.50%, 18.72% and 15.02% for Cd, Pb, Cu, Cr and Zn in the contaminated soil, respectively. Evidently, the PTCF adsorbent had an effective effect of repairing contaminated soil for Cd, Pb and Cu.

**Figure 1.** The removal efficiency of heavy metals in the contaminated soil by PTCF bioadsorbent

**Figure 2.** The removal efficiency of heavy metals in the contaminated soil by PTCS bioadsorbent

Fig. 2 represented the results of PTCS adsorbent to remove heavy metals through combined soil washing with 3M HCl and 0.2 M EDTA. The removal efficiency of all heavy metals increased with the PTCS dosage increasing. The maximum removal efficiency was 21.50%, 33.49%, 24.80%, 12.30% and 8.10% for Cd, Pb, Cu, Cr and Zn when PTCS adsorbent was 10%. The PTCS adsorbent had an effective effect of repairing contaminated soil for Pb, Cu and Cd while a little effect of repairing contaminated soil for Cr and Zn.
Compared to the results of Fig. 1 and Fig. 2, PTCF and PTCS had different adsorption quantity for the same metal. The ability to remove various metal ions of PTCF was better than PTCS except for removal Pb. PTCF had higher removal efficiency for Pb than PTCF. For the contaminated soil, they both presented good removal efficiency for Cd, Pb and Cu. While for Cr and Zn, their removal efficiency was relatively poor.

Fig. 3 showed the removal efficiency of every heavy metal ions from contaminated soil using the mixture 1:1 of PTCF and PTCS adsorbent. Surprisingly, the removal efficiency greatly improved which were 39.16%, 34.53%, 26.31%, 19.63% and 16.02% for Cd, Pb, Cu, Cr and Zn when the mixture adsorbent was 10%. The content of the Cd and Pb have reached the standard of Grade II soil which is the critical to ensure farming security.

Fig. 4 showed the removal efficiency of every heavy metal ions from contaminated soil when the above three adsorbents were 10%. Seen from Fig.4, the order of the removal efficiency of Cd was Mixture > PTCF > PTCS. For Pb, the order was PTCS > Mixture > PTCF. For Cr, the order was PTCS > PTCF > Mixture. For Cu and Zn, there was the same order with PTCF > Mixture > PTCS. Through different persimmon tannin based-adsorbent had different removal efficiency of every heavy metal ions, they all could effectively fix the free metal ions in the soil and reduce the soil available metal content. This is because persimmon extract contains multiple adjacent phenolic groups (named as persimmon tannin) and is able to chelate with metal ion. The biosorption capacity of binary and ternary mixture of heavy metal solution onto the surface of PTCF and PTCS was found to be competitive where the biosorption capacity of the metals were lowered (5%–40%) with those of single metal ions.

4. Conclusions
In this work, the remediation of paddy soil contaminated with Cd, Pb, Cu, Cr and Zn was carried out by soil washing combined with biosorption in laboratory-scale batch. 3M HCl and 0.2M EDTA had the best effect on the leaching of metal elements in the contaminated soil. The maximum leaching efficiency of Cd, Pb, Cu, Cr, and Zn in soil were 92%, 53%, 55%, 95% and 85%, respectively. When the addition amount of PTCF biosorbent was 10%, the removal efficiency reached 36.57%, 28.53%, 25.50%, 18.72% and 15.02% for Cd, Pb, Cu, Cr and Zn in the contaminated soil, respectively. For PTCS, they were 21.50%, 33.49%, 24.80%, 12.30% and 8.10%, respectively. The adsorption capacity reached saturation after 15 days when the mixture PTCF and PTCS adsorbent was added into the contaminated soil being leached by 3M HCl and 0.2M EDTA. The removal efficiency of Cd, Pb, Cu, Cr and Zn reached 53.36%, 44.89%, 37.73%, 7.60% and 6.02%, respectively. All this results proved that the feasibility of the treatment scheme and the modification persimmon tannin biosorbent have great potential in the treatment of heavy metal pollution.

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6. References

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