Study on removal efficiencies and mechanism of heavy metal from sewage-irrigated soils by saponin compared with commonly used washing agents

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Abstract: In present study, batch washing experiment was performed to evaluate the removal feasibility of heavy metal by saponin, a kind of biosurfactant, in sewage-irrigated soil. The results showed that water alone only removed minimal amounts of Cu, Cd, Pb, and Zn (less than 5%), but the removal efficiency of Cu, Cd, Pb, and Zn were 43.87%, 95.11%, 83.54%, and 20.34% by 3.0% saponin solution, respectively. Desorption efficiencies of heavy metals in sewage-irrigated soil sample were changed significantly by addition of saponin in washing solution. The results also showed that the removal efficiency increased with increasing of concentration of saponin, and it decreased with increasing of pH value. It also indicated that ionic strength had a slightly negative influence or no influence on desorption of heavy metals, which demonstrated clearly that saponin, under certain conditions, could effectively increase desorption of heavy metal. Meanwhile, heavy metal from washing solutions could be recovery and the used saponin solution could recycle of used. Analysis the experimental results, saponin could effectively removed the heavy metal in sewage-irrigated soil as a clean agent.

Keywords: Saponin, Heavy metal, Desorption, Sewage-irrigated soil

1. Introduction

Soils have been contaminated with heavy metals as a result of numerous industrial activity and sewage irrigation. Copper, Cadmium, Lead and Zinc in the polluted soils are considered the most hazardous heavy metals, and they are persistent, cannot be biodegraded and can return to the environment by different pathway (Peters, 1999). They can not only adsorb onto the soil, runoff into the rivers or leach into groundwater, but also lead to accumulation in animals, plants and humans by drinking water and foods, which are more hazardous for human health.

There are two fundamental technologies to remediation heavy metal contaminated soils (Peters, 1999; Dermont et al., 2008). The first technology immobilizes heavy metals tightly bound solid matrix to minimize migration, another technology is to promote heavy metals

obility and migration to the liquid phase by desorption and solubilization in a washing solution (Peters, 1999; Khodadoust et al., 2005; Luo et al., 2005; Leštan et al., 2008; Giannis et al., 2009; Pathak et al., 2009; Zhang et al., 2010a). The latter usually employs wash solutions that contain acids (Wasay et al., 1998; Wen et al., 2009), chelating agents (Elliot and Brown, 1998; Zou et al., 2009; Zhang et al., 2010b), or other additives (Giannis et al., 2009; Guo et al., 2009; Arwidsson et al., 2010). In practice, acid washing and chelator washing are most prevalent heavy metals removal methods, and the most chelating agent studied in the literature is Ethylenediamineletracelic acid (EDTA) and [S,S]-ethvlenedia-mine -disuccinic acid (EDDs) because of its strong chelating nature (Tuin et al., 1990; Meers et al., 2005; Leštan et al., 2008), and it has been effectively studied to remove heavy metals from contaminated soils and sediments.

Recently years, surfactants have shown some potential for environmental remediation of pollutant from soils and sediments (Doong et al., 1998; Mulligan, 2005; Torres et al., 2011), surfactant can be added into washing solution to assist desorption of heavy metal. Cationic surfactants, especially, can be used to modify soil surface to promote displacement of metal ions from the solid to the liquid phase in some literature. It causes the transfer of the soil-bound metal to the liquid phase through ion exchange processes and other function of surfactants (Doong et al., 1998).

Recently, ethyl lactate has been recognized as a “green solvent” due to numerous attractive properties including its high solvency power, complete biodegradability, ease of recycling, non-destructive to soil characteristic, and relatively inexpensive (Herman et al., 1995; Mulligan et al., 1999, 2001). Biosurfactant, such as rhamnolipids, surfactin and sophorolipid, also are a kind of surfactant and of particular interest for using in remediation technologies for some reasons: they are naturally products and have biodegradability, excellent surface activity properties and have low toxicity. Meanwhile, they have unique metal binding capacities and selectivity in comparison to synthetic chelators or surfactants. The feasibility of using biosurfactant to remove heavy metals from contaminated soils and sediments is recently demonstrated by batches washing with rhamnolipids, surfactin and sophorolipid (Herman et al., 1995; Mulligan et al., 1999, 2001).

As one of biosurfactant, saponin is a natural product with high biodegradability, surface activity and low toxicity. It also has some carbonyl and hydroxyl with stronger capability of complexing with heavy metals. However, less information on removal efficiencies and mechanism of heavy metals by saponin are available. The objectives of the present study were: (1) to determine the feasibility of heavy metals removal, (2) to obtain detailed information on the influencing factors, and (3) to elucidate removal mechanism of heavy metals by saponin in sewage-irrigated soil.

2. Material and Method

2.1 Soils

Soil samples were collected from the farmland in BaiYin city of GanSu province; soil had been contaminated with heavy metals by wastewater irrigations for more than ten years. Then it was air dried and sieved by 1mm sieve and stored in a plastic container for experiments. The total contents of heavy metals in soil sample were determined by acid digestion (1 HNO_3+3 HCl) and perchloric acid at boiling temperature and analyzed by atomic adsorption spectrometry (WFX-310, Beijing second instrument com., Beijing, China). The total contents of copper, cadmium, lead and zinc are 182.7 mg kg^{-1}, 24.01 mg kg^{-1}, 179.3 mg kg^{-1} and 344.5 mg kg^{-1}. And the other chemical and physical characteristics of soil are presented in Table 1.

Table 1. The chemical and physical characteristics of heavy metal polluted soil

	Texture	pH-water	Water (%)	CEC ($cmol{\cdot}kg^{-1}$)	Organic matter (%)
Soil sample	Clay loam	7.36	8.74	5.74	1.26

2.2 Materials

Saponin selected in this study was from Quillaja bark, and was obtained from Sigma Chemical Company. All the glass apparatus were washed successively with $K_2Cr_2O_7$-H_2SO_4 solution, running water, deionized water. Reagent blank and method blank were used to correct the instrument readings. All reagents were analytical grade and used without further purification, and the deionized water used in all these experiments. The critical micelle concentration (CMC) of saponin was 0.1 %, and surface tension was 36 mNm^{-1} (Hong et al., 2000, 2002).

2.3 Procedure for washing studies

Washing study were performed by varying concentrations、pH values and ion strength in centrifuge tubes while maintaining a constant solution to soil ratios (25.0 ml/1.0g). Soil sample was taken after 12 hours shaking on a reciprocating shaker at 160 oscillations per min and static equilibrium 12 hours at room temperature, and then centrifuged 12 min at 3000 r/min. The supernatants were collected and analyzed for metal concentration by atomic adsorption spectrometry. The rates of metal removal were calculated based on total contents of heavy metals in soil sample. Sequential extraction procedure for the speciation of heavy metals was used as described in previous literature (Tessier et al., 1979). All experiments were performed in triplicate and the average of results was presented.

2.4 Recovery of heavy metal from washing solutions and recycle of used saponin

The mixture supernatants were reclaimed in procedure 2.3 and analyzed for metal concentration by atomic adsorption spectrometry, then heavy metals were precipitated by sodium sulphide from soil washing solutions in this experiments at high pH values and high concentration of sodium sulphide, then centrifuged, and, concentration of saponin in supernatants was analyzed by U-Vision Spectrometry (UV-2000, Shanghai Unico com., Shanghai China) at the wavelength 320nm, then this saponin solution diluted to 0.6% and reused to wash the 1.0g soil sample to evaluate the efficiency of used saponin. The washing procedure was same as procedure 2.3.

3. Results and discussions

3.1 Washing efficiencies of different concentrations of saponin

Soil washing experiments were performed with different concentration of saponin at pH 5.0, and it was gradually changed from 0.003% to 3.0%. The metal removal efficiency was found to be dependent on saponin concentration, with the increasing of saponin concentration, the removal of Cu, Cd, Pb, and Zn were also increased, and abruptly increased with increasing of saponin concentration to 0.1%, and the critical micelle concentration (CMC) of saponin was 0.1 %, which suggested that above CMC, saponin can effectively remove the heavy metals in soil. It could informed that high desorption only took place at high surfactant concentration, and the removal efficiencies of Cu, Cd, Pb, and Zn were 43.87%, 95.11%, 83.54%, and 20.34% by 3.0% saponin washing solution, respectively. The ability of heavy metals desorption was Cd > Pb > Cu > Zn. The result was showed in Fig 1.

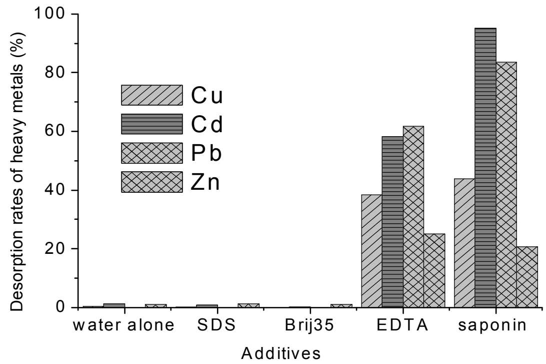

Fig. 1 The removal efficiencies of heavy metal by different additives of washing solution

3.2 The effect of pH on removal of heavy metals

The effect of pH on removal of heavy metals with 0.6% of saponin added was studied at the various pH values between 2 and 11 when 0.1M HNO_3 and NaOH were used for the adjustment. The results showed in Fig. 2, the adsorptions efficiencies of Cu, Cd, Pb, and Zn were decreased with an increase of pH, indicating a strong pH effect, but desorption efficiencies of copper were not affected by pH increasing. It might be caused by the stable of complexation between copper and saponin, at the same time, saponin could be adsorbed onto surface of soil and changed the character of soil surface which could be weaken the bound of the soil-heavy metal with the decrease of pH.

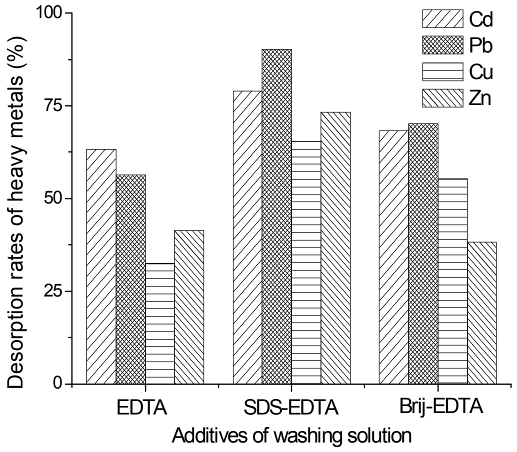

Fig. 2 The removal efficiencies of heavy metals by different mixed additives of washing solution

3.3 The effect of ionic strength on removal of heavy metals

As ionic strength in soil solution is one of the key factors for soil washing, the different concentrations of $NaNO_3$ were added into the washing solutions to investigate the influence of ionic strength. The results were shown in Fig. 3 in which the removal of Pb and Zn appeared to be less effective with the variation of ionic strength in the comparison with Cd and Cu meanwhile the removal of Cd and Cu reduced 25 % and 10 %, respectively, as the concentrations of $NaNO_3$ reached 0.1mol L^{-1}. The reason might be attributed to the competition adsorption between sodium ion and heavy metals for bonding with saponin, which could lead the formation of Na-saponin complex and weaken the bond of saponin formed with Cu and Cd, respectively (Hong et al., 2000, 2002). But the complexes of Pb-saponin and Zn-saponin were more stable than others, and less affected by changing ionic strength, and maybe the different effect of ionic strength was also due to the different electro negativity of heavy metals.

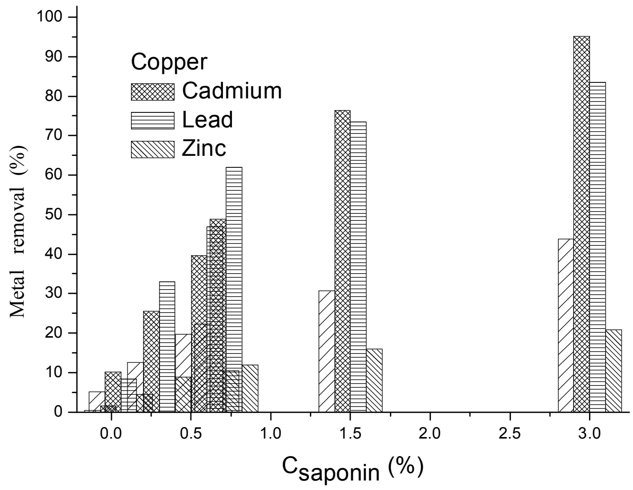

Fig. 3 The removal efficiencies of heavy metals with different concentration of saponin

3.4 The species transformation of heavy metals before and after washing by saponin

As showed in Figure 4, the contents of the soluble and exchangeable, and carbonate bound Cd are 39.73% and 24.16%, respectively, followed by oxides-bound before desorbing by saponin. After desorption, the levels of the soluble and exchangeable and carbonate bound of Cd dramatically decreased to below detection limits, the contents of the oxides- and organic combination decreased more than 80%; Pb are mainly in residue in soil, followed by soluble and exchangeable, the contents are 65.43% and 18.59%, respectively, after the removal efficiencies of Pb except soluble and exchangeable increased more than 90%, the residual of Pb in soil was also reduced to 9.64%; Cu, before desorbing, the contents of soluble and residue are higher, after desorption, the soluble and exchangeable and carbonate bound of Cu are reduced to about 50%, but the residual of Cu changes little; The soluble and exchangeable and carbonate bound of Zn decrease more than other morphological changes.

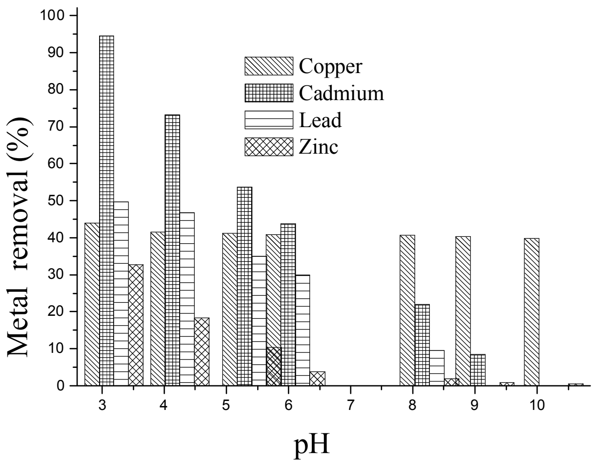

Fig. 4 The effect of different pH on removal efficiencies of heavy metals with saponin washing solutions

It is said that the soluble and exchangeable state is the most susceptible to transfer from soils to plants; the carbonate combined form is relatively easy effected by pH and released back into the aqueous phase, and it is also absorbed by organism (Wang, 2004). The concentrations of soluble and exchangeable, carbonate-bound of heavy metals are sharply reduced by saponin in washing solution, in particular, even the residual of Pb also can be transferred to the washing liquid, thereby reducing the bioavailability and toxicity of the heavy metals in sewage irrigated soil.

3.4 Recovery of heavy metal from washing solutions and recycle of used saponin

The mixture supernatant were precipitated by 1M sodium sulphide solution from soil washing solutions at pH 10, then centrifuged and analyzed for metal concentration in supernatant, and it was found that heavy metals could not detected. Meanwhile, the supernatant was adjusted the pH 5.0, the concentration of saponin in this supernatant was 1.17%, then this solution was diluted to 0.6% and reused to wash the 1.0g soil sample to compare the efficiency of used saponin. The result(in Figure 5) showed that the removal efficiency dropped not more than 10% by this saponin washing solution. As a result, recycle of used saponin was considered to be effective for the application.

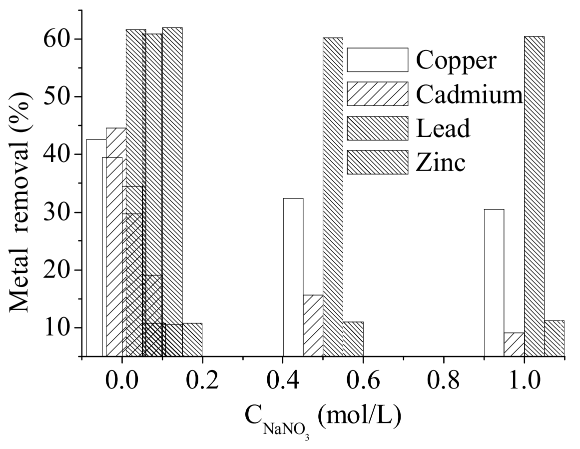

Fig. 5 The effect of different ionic strength on the removal efficiencies of heavy metals with saponin washing solutions

3.5 The mechanism of heavy metal removal by saponin

Since metal removal by surfactants has not been extensively investigated previously, the mechanisms by which surfactants may remove metals are not understood clearly. The experiment results showed that water could removed the heavy metals less than 5% in soil sample, and previous studies also showed that surfactants could only removed less contents of heavy metals in soil, but saponin could removed heavy metals effectively, which could be informed that desorption mechanism by saponin was not mainly because of ion exchange or micelle function. It was also demonstrated that heavy metal, such as Cu, Cd, Pb, and Zn, were retained due to some form of complexation with carboxyl in saponin and thus a stronger bond between the metals and saponin must be responsible for metal desorption from the soil sample (Mulligan et al., 1999; Hong et al., 2000).

The saponin therefore was formed complexation through contact with the adsorbed metal contaminants and then the saponin itself adsorbed on soil surface and reduced the surface properties through lowering of the interfacial tension. The lowering of the interfacial tension reduced the work of adhesion between metal and the soil surface, which weaken the bond and enables the lifting of metal from the soil surface. However, at the low saponin concentration, although the stable complexation was formed between saponin and metal, but the complexation about single saponin monomer bond metal might re-adsorbed on soil surface, so that the metal removal was less effectively at low surfactant concentration.

The adsorption between the metal and the soil surface might be fairly stable at low saponin concentration, but as the concentration of saponin increased, the number of micelles also increased, and more collisions occurred between the micelles and the metal association with the micelles becomes less stable. However, since there seemed to be some affinity of the metals with the organic portion, it was possibly that structure of micelles it was not a perfect sphere but has bent surfactant monomers (Mulligan et al., 1999), this type of structure could enabled metal ion entrapment which can prevent the metal from re-adsorbing onto the soil surface. Thus, heavy metals were removed numerous at high concentration of saponin.

4. Conclusion

In conclusion, water alone only removed minimal amounts of Cu, Cd, Pb, Zn, but the removal efficiency of Cu, Cd, Pb, Zn were higher by saponin washing solution. Desorption efficiencies of heavy metals in sewage irrigated soil sample were changed significantly by addition of saponin in washing solution. The high removal of heavy metals by saponin only took place in the week acidic environment, it also indicated ionic strength had a slightly negative influence or no influence on desorption of heavy metals. Comparing the species transformation of heavy metals before and after washing by saponin solution, it was evident that soluble and carbonate fraction of metals absorbed on soil surface were mostly washed away. As a result, the toxicity and bioavailability of heavy metals in soil sample significantly decreased.

The heavy metals desorption mechanism by saponin washing might occur complex between heavy metals and carboxyl in saponin, at the same time, complexation must be entrapped in micelles at high surfactant concentration which prevent metal ion from re-adsorbing on soil surface, thereby heavy metals were removed numerous at high concentration of saponin. Compared with synthetic surfactant, the saponin has stronger complexing capability with heavy metals, and the toxicity and bioavailability of heavy metal are dramatically reduced in wastewater irrigated soil, so saponin is an effective washing agent for the heavy metals contaminated by wastewater irrigation.

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