Removal of Cu, Cd, Pb and Zn from Contaminated Soil by Using Plant-Based Surfactants, *Sapindus mukorossi L* (Soapnut) and *Acacia Concinna* (Shikakai)

Elijah Cbibuzo Ugwu, Bhaskar Sen Gupta, Adeloye Adebayo and Nadia Mart ńez-Villegas

***Abstract*—The performance of two plant-based surfactants in the removal of heavy metals (Cu, Cd, Pb and Zn) from soil was studied ex-situ. Experimental parameters were: six soil-solution ratios (1:10, 1:20, 1:30, 1:40, 1:50 and 1:60), six surfactant concentrations (0, 1, 2, 3, 4, 5 and 6% by mass), seven washing times (2, 3, 4, 6, 8, 24, and 48 hr) and four pH values of the washing solution (3, 4, 5 and 6). In general, removal efficiency increased with an increase in surfactant concentration, time and soil-solution ratio but decreased with increase in the pH of washing solution. The removal of heavy metals was in the following range: Cu, Cd, Zn and Pb for both surfactants reaching up to 90%, 80%, 53% and 52% respectively. The overall performance of the batch washing process indicates that both surfactants were very effective in soil washing. The effectiveness of these surfactants is due to their ability to form micelles and subsequent removal of heavy metals from the soil surface by reducing the interfacial tension. Both surfactants have the advantages of being environment-friendly and cost effective.**

***Index Terms*—Soil washing, heavy metals, soapnut, shikakai.**

I. Introduction

Soil contamination resulting from activities such as mining, automobile manufacturing, battery production, agriculture, smelting as well as other forms of waste pollution on environment and public health have been widely reported [1]-[3]. The commonly found heavy metals in soil include lead, nickel, mercury, arsenic, chromium, cadmium, zinc, and copper. Most of these heavy metals exist as cationic (lead, zinc and copper) and anionic (arsenic and chromium) in soil that are moderately contaminated [4].

In contaminated soil, these heavy metals might coexist in their different oxidation states and interact with other minerals or organic compounds, which undergo either oxidation or reduction under the influence of soil moisture environment [5]. Soil washing may be carried out in-situ or ex-situ by means of water and steam, often aided by acids, surfactants as well as various chelating or cleaning agents.

The application of several chemical reagents and biological extracts have been studied for their effectiveness in removing heavy metals and organic contaminants from soil. Saponin, a plant-based surfactant with distinctive foaming characteristics is gaining attention due to its potential in remediation of both organic and heavy metals contaminated soils. Many reported works have focused on the production and use of saponin from different species of plants and their comparison with other cleaning agents [6]. *Sapindus mukorossi* was applied for the removal of arsenic from iron rich soil [7], removal of cadmium and phenanthrene simultaneously [8], and removal of Cu, Pb and Zn by foam fractionation [9]. Purum and triterpene glycoside from quillaja bark have been used to remove Cu, Cd and Zn [1]. Saponin from *Acacia concinna*, known as shikakai, has long been used for traditional hair treatment in India but has not been used for soil remediation. Therefore, this new low-cost and plant-based surfactant offers an attractive alternative to cleaning agents based on synthetic chemicals.

The objective of this study was to compare the efficiencies of saponin derived from soapnut (SN) and shikakai (SH) for the remediation of Cu, Cd, Pb and Zn contaminated soil. Selection of best available saponin, which is effective and economical, will provide cheap and alternative means of soil cleaning.

II. Materials and Methods

A. Soil Samples and Characterisation

Clean and uncontaminated fine sand and garden topsoil were procured from a garden centre in Edinburgh. The soil samples were air dried and sieved through 2mm sieve to remove coarse sand and other aggregates. The soil was then homogenized and stored in plastic bags for subsequent use. A range of relevant soil parameters, such as pH, electrical conductivity, bulk density, porosity, particle size distribution, cation exchange capacity (CEC), organic matter and moisture content were determined. The pH values were measured using pH/ ORP-999 probe. 20g of soil was added to 50ml of distilled water before being shaken and left for 1 hour prior to taking measurements with the probe following the standard EPA method (9045C). The results were then multiplied by a relevant conversion factor for each soil type following a method suggested elsewhere [10]. The bulk density and porosity of each soil type was calculated using a standard method [11]. The standard oven drying method was used to

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determine moisture content (method AS1289 B1.1). The organic matter content of each sample was analysed by a standard method of acid digestion (EPA 3050B); the difference in mass was measured before and after to quantify the organic matter content. The initial soil characteristics are shown in Table II.

B. Soil Contamination Procedure

The soil spiking with heavy metals was carried out to increase the contents of Pb, Cu, Cd and Zn. About 4 kg of dry soil were contaminated with 3 litres of distilled water containing dissolved cadmium nitrate, ($Cd(NO_3)_2.4H_2O$, copper sulphate $Cu(SO_4)_2$, Zinc nitrate, $Zn(NO_3)_2$. $6H_2O$ and lead nitrate, $Pb(NO_3)_2$. These chemicals were supplied by Fisher Scientific Chemicals Ltd, UK. The solution was thoroughly mixed into slurry, before being left to age and cure for about 6 months with frequent mixing. After the period of curing, the slurry was air dried to a constant mass. The virgin soils and spiked soils were digested using a standard method (EPA 3050B); the liquid was filtered out and diluted to required volume and the filtrate was analysed using flame atomic absorption spectrophotometer (FAAS, Perkin Elmer Analyst 200, Shelton, CT, USA). Methods used were adopted from previous report on similar studies [12].

C. Saponin Preparation

A 20% stock solution of saponin was made up using 40g of certified pure dried organic soapnut powder *(Sapindusmukorossi)*, produced by Davis Finest UK, and adding 200ml of distilled water. The solution was gently stirred for 3 hours at room temperature and then centrifuged at 7000 rpm for 15 minutes before being filtered using a method reported elsewhere [13]. Solutions such as 1%, 3% and 5% (w/v) were made by diluting the stock solution appropriately with distilled water. All solutions were freshly prepared on the day of use.

III. Results and Discussions

Washing studies were conducted in batches to investigate the effect of surfactant concentration, soil solution ratio and pH on the removal of heavy metals from contaminated soil samples. Details of the experimental conditions are given in Table 1. Series of batch tests were conducted in 125 ml conical flask over rotary shaker at about 200-rpm for a known contact time at room temperature (24^0C); then samples were collected and centrifuged at 7000g for 15min [14]. The initial pH of the surfactant solution was modified either by addition of hydrochloric acid or sodium hydroxide. The supernatants were collected after filtration using Whatman 41 filter paper. The samples were preserved with drops of nitric acid and stored for inductively coupled plasma optical emission spectrometry (ICP OES) analysis. Distilled water was used for washing as control. The response was recorded as percentage of copper removed from the washing experiment and calculated using a similar equation as reported elsewhere [15].

$$\text{Percentage copper removal (\%)} = \frac{C_1 V_1}{C_S M_S} \text{X } 100 \qquad (1)$$

where C_1 (mg/l) and C_S (mg/kg), are the concentrations of metal in supernatant and soil respectively; V_1 is the volume of supernatant (litres) and *MS* is the dry mass of the soil (kg). The pH values of the solutions before washing and that of supernatants after washing were recorded. To ensure precision, all the experiments were performed in three replicates and results were presented as averages.

TABLE I: Experimental Conditions and Variables for the Washing Rrocesses

Factors	**Symbol**	**Levels**						
pH	P	3	4	5	6			
Soil-solution ratio	R	1:20	1:30	1:40	1:50	1:60		
Surfactant concentration (%)	C	0%	1%	2%	3%	4%	5%	
Shaking Time (hr)	T	2hr	3hr	4hr	6hr	8hr	24hr	48hr

TABLE II: Soil Properties

Properties	**Values**	**Units**
Soil moisture content	23.1	%
Soil porosity	68	%
Soil pH in water	7.22	
Soil bulk density	0.8	g/cm
Soil organic matter content	8	%
Soil particle size	2	mm

Heavy metal removal by batch experiments

A. Effect of Surfactant Concentration

For this work, removal efficiency was calculated from Eqn 1. The removal efficiency for Cu increased with increase in surfactant concentration for both surfactants used (Fig. 1). The highest removal efficiency of 82.84% was obtained for 3% soapnut concentration while the highest removal for shikakai was 73.61% at the same concentration. SN removed more Cu than SH while SH removed more Cd than soapnut. It was also observed that as the concentration of the surfactant increased from 3% to 5%, for both SN and SH, removal efficiency decreased. Therefore, it is recommended to use 3% (w/v) as the optimum surfactant concentration for both SN and SH for washing of similar soil types. In general, Cu and Cd had the higher removal than Zn and Pb. Similar trend was observed by other researchers [16].

B. Effect of pH

The effect of pH of the washing solution on the removal efficiency of heavy metals was studied in the range of 3- 6 (Fig. 2). It shows that heavy metal extraction is pH dependent. When the pH increases for SH, the removal efficiency gradually decreases in most of the heavy metals studied. However, SN showed a different trend as the removal efficiency abruptly increased when the pH was increased from 3 to 4 but decreased with increase in pH from 5 and 6. The maximum removal of Cu was obtained at pH 3 for SH and pH 4 for SN. SH showed the highest removal efficiency of 68.96% while SN recorded the highest removal efficiency of 55.66%. As shown in Fig. 2, the removal efficiency for both surfactants decreased at pH 5 and 6. The two surfactants were more effective in removing Cu and Cd than Pb and Zn. This may be due to lower mobility of Pb and Zn in relation to Cu and Cd (1).

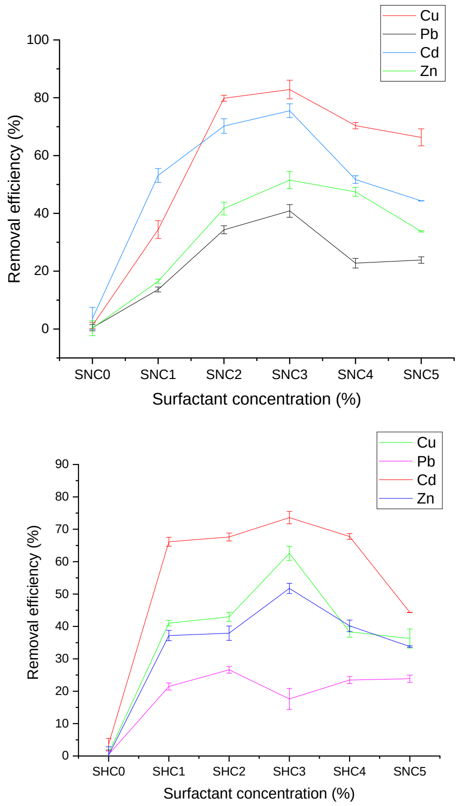
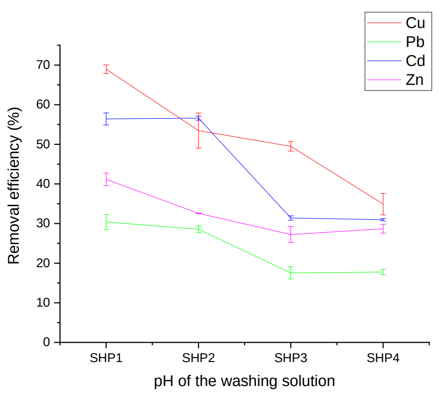


Fig 1. Effect of SN and SH concentration on the removal of heavy metals from soils (Soil-solution ratio = 40, time is 6 hr). Each point is the average of triplicate samples. Soapnut concentration (w/v) - SNC0 = 0%; SNC1 = 1%; SNC2 = 2%; SNC3 = 3%; SNC4 = 4%; SNC5= 5% w/v; Shikakai concentration (w/v) - SHC0 = 0%; SHC1 = 1%; SHC2 = 2%; SHC3 = 3%; SHC4 = 4%; SHC5= 5%.

C. *Effect of Soil-Solution Ratio*

Soil-solution ratio is used to determine the amount of soils that can be effectively washed by a given quantity of surfactant solution. This is important in calculating the cost of remediating a given portion of land. In this study, six ratios were considered, and the results shown in Fig. 3. Again, SN and SH showed different trend in the removal efficiency obtained at different ratios. Increase in soil-solution favours SN from 10 to 40 (SNR1-SNR4) while there was general decrease from 50 to 60 (SNR5-SNR6). On the other hand, it was observed in SH that increase in soil-solution ratio causes the removal efficiency to decrease. The highest removal efficiency for SN was at SNR4 while that of SH was at SHR1 (Fig. 2). The removal of Cu and Cd were generally higher for both surfactants while Zn and Pb removal was the least for SH and SN respectively.



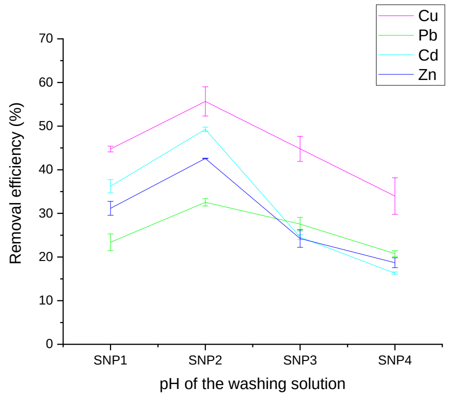


Fig 2. Effect of SN and SH pH on the removal of heavy metals from soils (Soil-solution ratio = 40, time is 6 hr concentration = 3). Each point is the average of triplicate samples. SNP1 = 3; SNP2 = 4; SNP3 = 5; SNP4 = 6; SHP1 = 3; SHP2 = 4; SHP3 = 5; SHP4 = 6.

D. *Effect of Time*

The effect of time on extraction of heavy metals with SN and SH was studied in batch experiments from 2 to 48 hr. The results of this study are shown in Fig. 4. Removal efficiency of heavy metals was seen to increase with increase in time from 2 hr to 24 hr with both surfactants, but further increase from 24 hr to 48 hr caused continuous rise in removal efficiency with SN; however, it decreased the removal efficiency for SH. It could be observed from the results that 24 hr is the optimum time for washing with SH while 48 hr showed higher removal efficiency for the SN. Again, removal of Cu and Cd were higher than Zn and Pb for both surfactants.

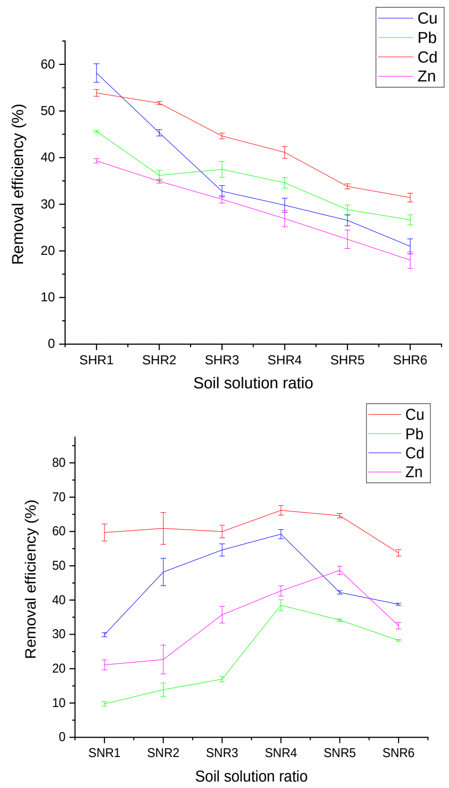


Fig. 3. Effect of soil-solution ratio of SN and SH on the removal of heavy metals from soils (time = 6 hr concentration = 3). Each point is the average of triplicate samples. Soil: shikakai solution (w/v) - SHR1= 1.2%; SHR2= 1.3%; SHR3= 1.4%; SHR4= 1.5%; SHR6= 1.6%; Soil : soapnut solution (w/v) - SNR1= 1.2%; SNR2= 1.3%; SNR3= 1.4%; SNR4= 1.5%; SNR6= 1.6%.

IV. Conclusions

The operating variables in soil washing with SN and SH for the removal of heavy metals for highly contaminated soil were studied in laboratory batch processes. Removal efficiencies recorded in this study showed that the surfactants used were effective in removing Cu, Cd, Zn, and Pb from the spiked soil. In general, removal efficiency obtained using the two surfactants increased with increase in surfactant concentration, time and soil-solution ratio but decreased with increase in the pH of washing solution. The optimum concentration of the surfactants was 3%. The highest removal efficiency was observed when the pH of washing solution was 4, soil-solution ratio was 40 and washing time was 48 hr for SN. However, highest removal efficiency was obtained when the pH of washing solution was 3, soil-solution ratio was 10 and the washing time was 24 hr for SH. The removal efficiencies of heavy metals were: Cu > C>, Zn> Pb for both surfactants. Utilization of both surfactants showed great potential for heavy metals remediation of contaminated soil.

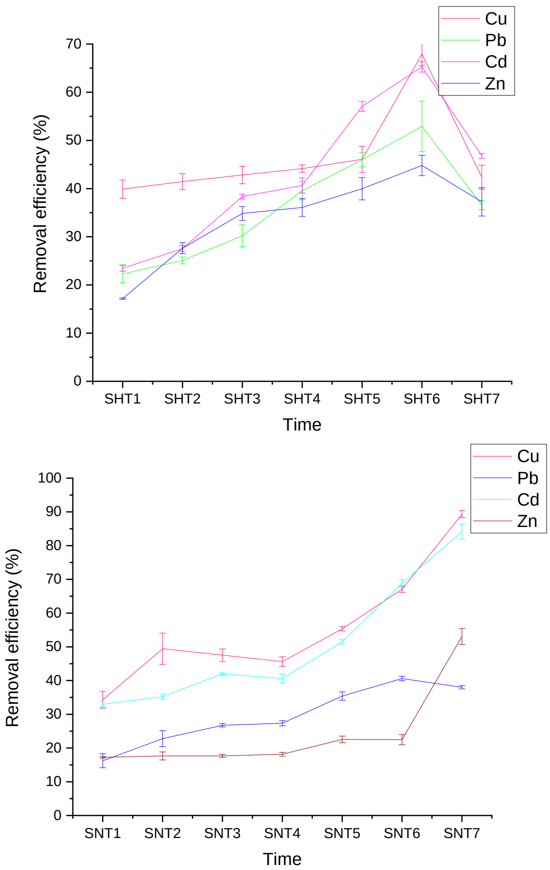


Fig. 4. Effect of time SN and SH on the removal of heavy metals from soils (Soil-solution ratio = 40, concentration = 3). Each point is the average of triplicate samples. Soapnut (hr) – SNT1 = 2; SNT2 = 3; SNT3 = 4; SNT4 = 6; SNT5 = 8; SNT6= 24; SNT7=48; Shikakai concentration (hr) - SHT1 = 2; SHT2 = 3; SHT3 = 4; SHT4 = 6; SHT5 = 8; SHT6= 24; SHT7=48.

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