

# REMEDIATION OF CONTAMINATED SOIL (BY HEAVY METAL IONS) USING SAPONIN OBTAINED FROM SAPINDUS MUKOROSI: A REVIEW

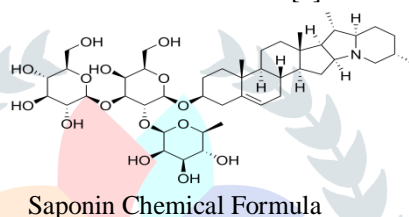
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**Abstract :** Increasing industrial activity around the world has left behind large number of contaminants such as heavy metals which can easily get into food chain and bio-cumulate in tissues of living organism with detrimental effect. Requirement of today 's era is to remove these contaminants (heavy metals) from the soil as they results in nausea, vomiting, epigastric pain, lethargy, and fatigue(particularly zinc)[1]. tumour in some cases. This study explores the possible application of a biodegradable plant-based surfactant saponin obtained from *Sapindus mukorossi* or soapnut, for washing zinc[4], arsenic[3], phenanthrene[3], cadmium from contaminated soil. . It was observed that soapnut was more efficient than SDS due to its lower pH. Soapnut solution removed more than 73% zinc while SDS solution could only wash out up to 31% of the total zinc from the soil under similar experimental conditions[4]. Analysis of the FT-IR data suggested that saponin did not interact chemically with zinc, offering an option for reusing the surfactant after precipitating the zinc by using NaOH at pH of 10.3. Damage to the soil was found to be negligible. Soapnut CGAs removed more than 70% arsenic[2]. saponin has a removal rate of 87.7% and 76.2% of cadmium and phenanthrene, respectively, from the combined contaminated soil.[3]



**Keywords:** Soil washing; Soapnut; Sapindus mukorossi; Zinc; Plant based surfactant

## I. INTRODUCTION

Soil is one of the most essential and non-renewable resources available to human beings. A number of metal ions in the form of contaminants getting added into the soil during different processes such as industrialization, cultivation(use of fertilizers, pesticides). Presence of these metallic ions above tolerance limit causes various diseases which are of huge concern. Permissible limits of these metal ions may vary for different aspects like natural concentration of Zn in soils varies between 30 to 150 mg kg<sup>-1</sup>. A European Union Council Directive has limited the values of zinc in arable soil to 300 mg kg<sup>-1</sup> for Zn [5]. Recently there has been increasing anxieties concerning arsenic related problems. Occurrence of arsenic contamination has been reported worldwide. In Canada, the main natural arsenic sources are weathering and erosion of arsenic-containing rocks and soil, while tailings from historic and recent gold mine operations and wood preservative facilities are the principal anthropogenic sources.[6] Arsenic (As) is known to be a very toxic element and carcinogen to humans.[6] In nature, As is released in the environment through weathering and volcanism[9] anthropogenic activities, such as mining.[10] Lead is also of main concern because in the study of superfund sites in USA, lead was the second most contaminant and it is second on the list of top 20 hazardous substances. It has been observed that lead in soil is threat for groundwater. [7] Mercury (Hg) in soils has increased by a factor of 3 to 10 in recent times mainly due to combustion of fossil fuels combined with long-range atmospheric transport processes, chlor-alkali plants, gold mining. [8].

**II. METHODOLOGY:** Different metal ions are removed from soil by different methods.

**2.1 Lead removal using Phosphate:** Removal of lead from soil by phosphate treatment: Two samples(one from rifle range and the other was an industrial waste of lead contaminated material) were tested. The soils were treated with varying doses of phosphate, using sodium phosphate solutions of varying concentration at Ph 7. Lead reacts with phosphate to form a series of low solubility compounds including lead phosphate pyromorphite, chloropyromorphite and many more.[7]

**2.2 Zn Removal using Soapnut and SDS (Sodium dodecyl sulfate):**

Figure 1(a) shows the removal of Zn from the soil by washing it with water, 20 mM SDS and 1% soapnut solutions at unadjusted pH. SDS has an alkaline pH in the range of 9-10, soapnut has acidic pH of 4.5 and water has neutral pH of 7 (Table 2). Water removed only 6% of the Zn, indicating that it bound strongly with the soil. Although SDS is anionic and soapnut is non-ionic, the efficiency of soapnut solution is higher than anionic SDS indicating that reduction of surface tension between soil particles and wash liquid interface, micellar solubilisation and lower pH played a more significant role than ionic interactions. The mobility of Zn depends largely upon pH, much higher in the range 4-6, decreasing significantly above 6 [11]. While soapnut solution of 1% concentration removed 68.33% Zn, 20 mM of SDS solution could remove only 30.11% of the Zn from soil. Figure 1b) shows Zn removal by SDS and soapnut at different concentrations and at fixed soil solution ratio of 1:20. It was observed that the Zn extraction increased with increasing surfactant concentrations. Soapnut at 0.5% concentration removed 66.43% zinc and the removal increased to 73.54% at 2.5% concentration. However, 1% concentration of soapnut removed 72.33% of zinc and 2.5% concentration did not improve the performance much. SDS removed less zinc than soapnut. At 10 mM, SDS removed 22.66%

zinc and 30 mM removed 31.45% of zinc. At higher concentration of surfactants, the solution contains more micelle and has lower surface tension that helps in solubilising the contaminant more effectively. pH is one of the most important factors. In removing heavy metals since it has a strong bearing on the solubility of metals in aqueous media. At lower pH, higher concentrations of H<sup>+</sup> ions compete with the contaminants for the adsorption sites. In order to determine the effect of pH on the desorption efficiencies of Zn(II) ions, pH was varied between 4 to 7 using HNO<sub>3</sub> and NaOH. It was observed earlier that soapnut did not undergo any structural change with change in pH [12]. Also, it is not feasible to remove metals at pH higher than 7 due to reduced solubility.

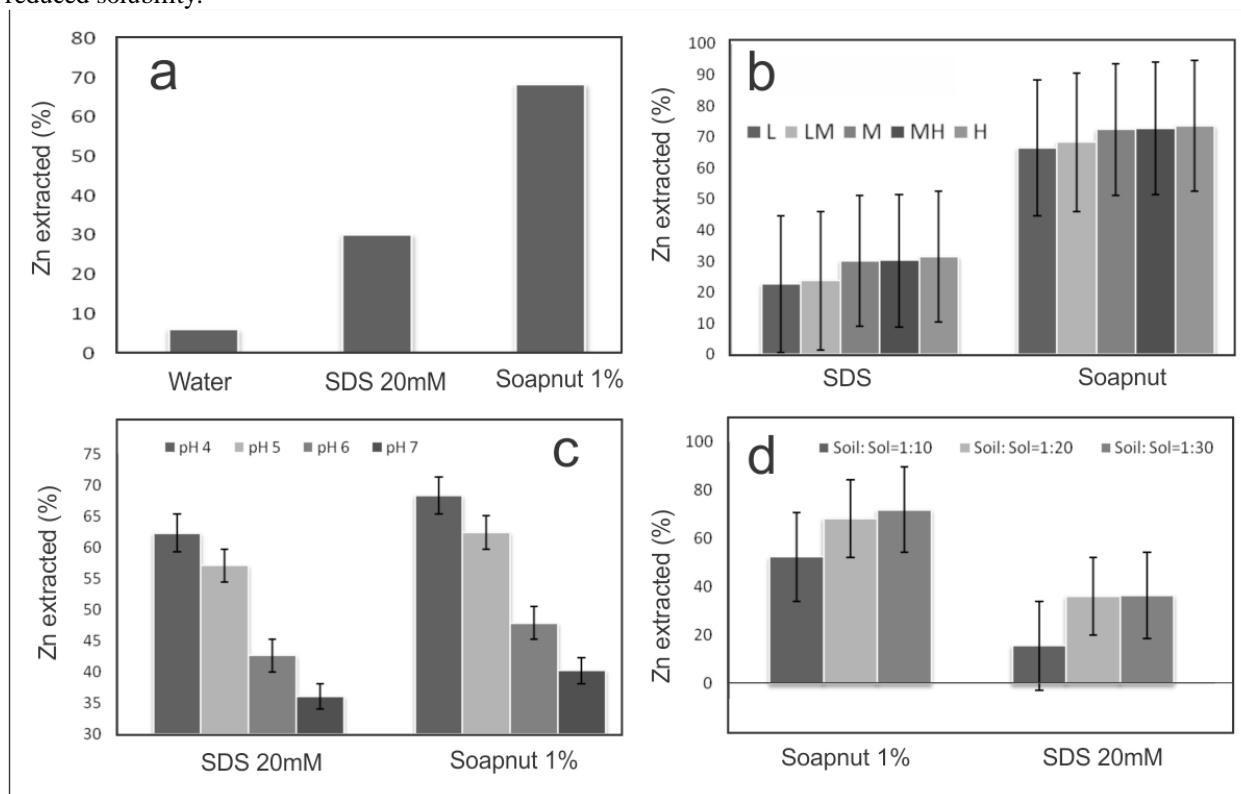


Fig. 1: (a) Zinc extraction with water, 20 mM SDS and 1% soapnut solutions at unadjusted pH; (b) Effect of surfactant concentration on Zn removal at soil: solution ratio of 1:20 (SDS: L=10 mM, LM=15 mM, M=20 mM, MH=25 mM, H=30 mM; Soapnut: L=0.5%, LM=1%, M=1.5%, MH=2%, H=2.5%); (c) Zn removal by SDS and soapnut at different pH values at soil: solution ratio of 1:20; (d) Effect of soil: solution ratio on Zn removal at pH 5

Table 1

Extractants	Empirical Formula/ Chemical name	Concentrations used	pH	Amount of Zn removed
Soapnut(SN)	C <sub>52</sub> H <sub>84</sub> O <sub>21</sub> .2H <sub>2</sub> O	0.5	4.6	66.4
		1.0	4.4	68.3
		1.5	4.3	
SDS (Sodium dodecyl sulfate)	NaC <sub>12</sub> H <sub>25</sub> SO <sub>4</sub>	10Mm	9.6	22.6
		20Mm	10.0	30.1
		30mM	10.2	31.4

**2.3 As removal from soil:**

A weighed sample (0.25 g or as otherwise stated) was transferred to a clean extraction chamber together with a magnetic bar. A glass microfiber filter was then placed on the outlet followed by a rubber gasket and the chamber cover was securely clamped in position. The chamber was connected to the extractant reservoir and the collector vial using silicone tubing and placed on a magnetic stirrer as shown in Fig. 2. The magnetic stirrer and peristaltic pump were switched on to start the extraction. Extracts from the continuous-flow extraction chamber were collected in plastic vials at 20-mL volume intervals. When the As concentration decreased approximately to the baseline, the next extractant was passed through and the collection of fractions was repeated until all leaching steps were completed. For most soils examined, it was found that 4, 8, 8, and 6 subfractions were sufficient to leach the As completely for Steps 1, 2, 3, and 4, respectively. The extractants used for the four steps and the nominal forms of arsenic extracted were:

- Step 1:** ultrapure water (water-soluble As)
- Step 2:** 0.5 M NaHCO<sub>3</sub> (surface-adsorbed As)
- Step 3:** 0.1 M NaOH (Fe- and Al-associated As)
- Step 4:** 1 M HCl (carbonate-bound As)

For the final step the residue was removed from the chamber and transferred to a digestion vessel (UNI- SEAL Co., Haifa, Israel) of 20 mL capacity, and 5 mL HNO<sub>3</sub> and 5 mL HF were added. The vessels were then tightly sealed and heated in an oven at

150degrees celcius for 16 h. After cooling, the digested clear solutions were made up to volume in a 50-mL volumetric flask. Total As in separate samples (0.25 g) determined using the same digestion procedure. [16]

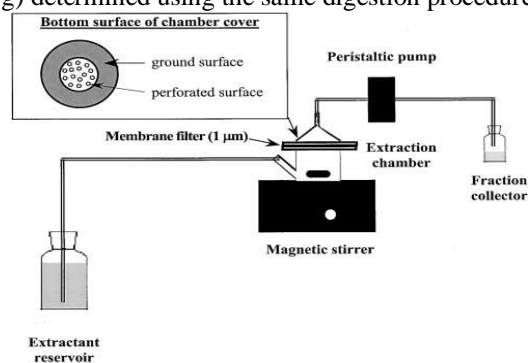


Fig. 2 The continuous-Flow Extraction system

### Step 1 (Water Soluble–Extractable Arsenic)

A sample of soil (1.00 g) was suspended in 30 mL of deionized water in a Nalgene polypropylene centrifuge tube (NalgeNunc International, Rochester, NY) and shaken for 16 h. The soil suspension was centrifuged using a Hettich-Zentrifugen (Tuttlingen, Germany) Model D 7200 centrifuge at 3000 rpm/15 min and the supernatant solution filtered through Whatman No. 40 filter paper.

### Step 2 (Sodium Bicarbonate–Extractable Arsenic)

The soil residue from Step 1 was washed with 30 mL of water and centrifuged, and the washing discarded by decantation. The residue was resuspended in 30 mL of NaHCO<sub>3</sub> (0.5 M) and shaken for 16 h. The soil was then centrifuged as in Step 1 and the supernatant solution filtered through Whatman No. 40 filter paper.

### Step 3 (Sodium Hydroxide–Extractable Arsenic)

The soil residue from Step 3 was washed with 30 mL of water and centrifuged, and the washing discarded by decantation. The residue was resuspended in 30 mL of NaOH (0.1 M) and shaken for 16 h. The soil was then centrifuged as in Step 1 and the supernatant solution filtered through Whatman No. 40 filter paper.

**Step 4 (Hydrochloric Acid–Extractable Arsenic):** The residue was resuspended in 30 mL of HCl (1 M) and shaken for 16 h. The soil was then centrifuged as in Step 1 and the supernatant solution filtered through Whatman No. 40 filter paper. The soil residue was oven-dried at 60 degrees celcius for 48 h and then finely ground in an agate mortar.

**Step 5 (Residual Arsenic):** Arsenic in the dried residue from Step 4 was determined using the HNO<sub>3</sub>–HF digestion procedure as described above.[16]

**2.4 Removal of Mercury with acidic potassium iodide:** A highly contaminated soil (max. 47.1 mg Hg/g) was used as a model sample. Evaluation was made on the effects of aqua regia, HCl, NaOH, Na-EDTA and KI solutions to extract mercury from polluted soil in a batch process. A mixture of 100 mM KI + 50 mM HCl (pH = 1.5) was found to be most effective. The acidic KI solution was passed through a column packed with 9.8 g polluted soil at a flow rate of 25 ml/h. After 15 fraction volumes, the mercury content decreased from 113.5 to 26.2 mg. The leachate from the column test containing Hg was treated with granular activated carbon.[17]

**2.5 Removal of Cadmium from soil using FeCl<sub>3</sub>:** In the present study, three concentrations of FeCl<sub>3</sub> were applied to the Cd-contaminated soils at two solid-to-solution ratios, and 1–3 washes were applied. The Cd removal percentages increased with the number of washes. An optimal treatment for removing Cd from the soil was a solid-to-solution ratio of 1/2 using 45 mM FeCl<sub>3</sub> and three washes. However, the application of FeCl<sub>3</sub> decreased the soil pH values, increased the soil electrical conductivity, and also changed the exchangeable concentrations of cations. These changes negatively influenced the germination percentage of pak choi (*Brassica campestris* L. ssp. *chinensis*) compared with control soils.[18]

**III. RESULTS AND DISCUSSION:** Dissolution of soil mineral components such as Ca, Mg, Al, Si and many more on washing with soapnut and SDS solution was evaluated. In this case, no considerable degradation was found in the soil structure. Both extractants dissolve very low percentage of these metals except Zn indicating negligible chemical weathering. High amount of Mg, Ca and Fe were present in the soil as observed from the XRD spectra. Therefore, their percentage in the extractants was higher than Al and Si which were bound more strongly as a part of the mineral structure of the soil. The extractants were not strong enough to dissolve Al and Si. It may be concluded that the soil washing by soapnut is safe for soil environment [4]. That's why we need separate methodologies to remove other harmful metal ions from soil, which involve the use of harmful chemicals as discussed above.

## IV. CONCLUSION:

A wide variety of toxic metal ions are present in the soil, which are removed by specific techniques. Each metal ion requires a separate methodology for its extraction from soil. This review involves the study of various metal ions present in soil and their removal. Each extraction process involves the use of harsh chemicals which actually destroys the properties of soil, many beneficial minerals are destroyed or getting converted to useless chemical composition. Out of studied techniques Zn removal process is better as it involves the use of natural product Saponin Obtained from *Sapindus mukorossi*. It can be recycled to use again and again as its chemical composition and structure remains same even after the extraction. The research of remediation technologies is still in individual and experimental stage. The development strategy of future remediation technologies is researching green, environmental-friendly biological remediation, combining remediation, in-situ remediation, based on equipped completely quick remediation, and supplying technical supporting for agricultural soil contamination, mining sites, etc.

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