Removal of cadmium from contaminated soil using soapnut, shikakai, rhamnolipids and EDTA

Ugwu Elijah Chibuzo, Adebayo Adeloye and Sengupta Bhaskar [*]
School of Energy, Geoscience, Infrastructure and Society,
Heriot-Watt University, Water Academy, William Arrol Building 2.02A,
EH14 4AS Scotland, UNITED KINGDOM
*b.sengupta@hw.ac.uk

Abstract

This study investigates the operating variables of washing experiments involving four washing agents [Sapindus mukorossi (soapnut), Acacia concinna (shikakai), rhamnolipids and Ethylenediaminetetraacetic acid (EDTA)] for removal of cadmium (Cd) from contaminated soil in laboratory scale batch and column experiments. The operating variables included: time (2, 3, 4, 6, 8, 12, 24, 48 and 72 hrs), soil-solution ratio (1:10, 1:20, 1:30, 1:40 and 1:50), surfactant concentrations (1, 2, 3, 4, 5 and 6% by mass) and the pH of the washing solution (3, 3.5, 4, 4.5, 5 and 5.5). Results show that the removal efficiency increases with increase in surfactant concentration, soil-solution ratio as well as washing time, but decreases as pH increases.

It was also observed that the maximum removal efficiencies of 84.9% for soapnut, 87.4% for shikakai and 68.9% were obtained when 0.01M EDTA was mixed with biosurfactants at different concentrations. In column experiments, the highest removal efficiencies of 74.05%, 73.08%, 69.07%, 63.08% and 12.78% were obtained for EDTA, soapnut, shikakai, rhamnolipids and distilled water. The overall performance of the washing process indicates that saponin utilization in soil washing is much more effective than rhamnolipid.

Keywords: Soil washing, Biosurfactants, Saponin, Spiked soil, remediation.

Introduction

Cadmium (Cd) is a lustrous, ductile and malleable metal usually found in the earth's crust in association with copper, lead and zinc ores. The source of Cd in soil, water and air can be attributed to (i) mining, smelting and refining of non-ferrous metals, (ii) production and application of phosphate fertilizers, (iii) disposal and incineration of industrial waste, (iv) production and combustion of fossil fuel, (v) disposal of wastewater from agriculture, industry and household and (vi) production of sludge and application in agriculture[1,2].

Several factors such as pH and availability of organic matter influence the mobility of Cd and its compounds through soil. When Cd accumulates on the surface of soil, it generally binds strongly to organic matter content of the soil. This strong affinity can lead to immobilization of Cd in the soil and possible uptake and assimilation by plant from where it eventually passes into the food chain[3]. The addition of Cd to the soil can be extremely unsafe, as it can cause its concentration to exceed the allowable threshold limit of 4 and 15 for agricultural and industrial soils respectively[4]. Cd mobilises in acidic soil and plant uptake increases when soils are acidic. This poses a great risk to grazing animals as well as humans who are exposed to Cd through the food chain.

Cd is classified by the US Environmental Protection Agency (EPA) as a priority pollutant and listed in carcinogen category I[5]. Cadmium is highly toxic and accumulates in the liver, kidneys, pancreas and thyroid gland. It has been widely reported that Cd causes lung, testicular and prostate cancer[5]. Cd exists as aerosol in the air[3]. It has been reported that large population may have been exposed significantly to Cd poisoning through inhalation and oral route in America[6].

A recent report has highlighted the importance of reducing Cd in soil in Europe[7]. The study reported that human activities were responsible for the unprecedented increase in heavy metals and metalloids in the soil. Cases of Cd contamination in Australia, China, Bangladesh, India and New Zealand have been widely reported in the literature[2,8,9]. The high concentration of Cd often found in rice and tobacco plants has raised serious concern for human health[2]. For instance, rice is the major source of Cd in Japan. About 9.5% of Japanese paddy soil has been reported to be polluted by Cd while about 4,816 ha of paddy soil has been identified by the Japanese ministry of the environment (Agricultural Land Soil Pollution Prevention) as contaminated field[10].

Concentrations of Cd and other heavy metals in soil are rapidly increasing around the world and becoming more difficult to clean-up[11,12]. Remediation of heavy metal contaminated soil is a difficult task because of their non-biodegradable nature.

Soil remediation is necessary to reduce various health risks associated with soil pollutants. Several studies have focused on the ways by which Cd could be reduced, removed or immobilized in the environment[1,2,8,13-16]. Soil washing is among new technologies available for cleaning contaminated soil. According to Chmielewska et al[17], soil washing is an effective treatment for various organic and

inorganic contaminants in the soil such as heavy metals and PCBs. 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.

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 metal contaminated soils. Many reported works have focussed on the production and use of saponin from different species of plants as cleaning agents[18,19]. *Sapindus mukorossi* was applied for the removal of arsenic from iron rich soils, cadmium and phenanthrene[20] as well as Cu, Pb and Zn.[19]

Saponin from Acacia concinna, known as shikakai, has long been used for traditional hair treatment in India and other parts of the world but has not been used for soil remediation. Rhamnolipids, a class of microbial cleaning agents have been studied widely and applied in soil remediation[21]. As for chemical reagent, EDTA is a soluble chemical having many commercial applications including soil remediation[22].

This study has attempted to show a detailed comparison in the use of these washing agents for cleaning Cd contaminated soil. The scope of combining both synthetic and natural surfactants was also explored. Therefore, the objectives of this work are: 1. To determine the removal efficiency of four washing agents on soil spiked with Cd. 2. To assess how some factors such as contact time, pH of the washing solution, soil-solution ratio, concentration of the washing solution and combination of surfactant and EDTA could influence the removal efficiency in batch experiments and 3. To assess the removal efficiency of the four cleaning agents in soil column washing experiments using optimum factors.

Material and Methods

Soil samples and characterization: Fine sand and garden topsoil were procured from a garden centre in Edinburgh. The soil samples were air dried and screened through 2mm sieve to remove coarse sand and other aggregates. The soil was then homogenized by thoroughly mixing together 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 method (Table 1). The readings were taken and were then multiplied by a relevant conversion factor for each soil type following a method suggested elsewhere[23]. The bulk density and porosity of

each soil type were determined using Gravimetric method and methods used by Urum[24]. The standard oven drying method was used to determine its moisture content. The organic matter content of each sample was analysed by a standard method i.e. loss of weight by ignition. The results of the initial soil characteristics are shown in Table 1.

Soil contamination procedure: Method used in this work was adopted from previous reports on similar studies[25,26]. The soil spiking was carried out to increase the concentration of Cd. About 4 kg of dry soil was contaminated with 3 litres of distilled water containing dissolved cadmium nitrate $Cd(NO_3)_2.4H_2O$. The chemical was supplied by Fisher Scientific Chemicals Ltd., UK. The solution was thoroughly mixed with the soil into a 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 for Cd.

The soil analysis using inductively coupled plasma optical emission spectroscopy (ICP OES) revealed that the value of Cd in the soil was approximately 700 mg/kg. This value is far above the threshold values of 4 and 15 for agricultural and industrial soils respectively[4]. Therefore, batch and column washing were conducted on the contaminated soil to remove Cd. While the batch washing experiments mimic ex-situ soil washing, the column experiments represent in-situ washing.

Preparation of washing solutions: Certified pure dry organic soapnut and shikakai powder were supplied by Davis Finest, Hampshire, UK while EDTA and Rhamnolipids were supplied by Fisher Scientific Chemicals Ltd., UK which were used as cleaning agents. A stock solution of 10% concentration of each of the agents was prepared by weighing 10 g powder and adding to 100 ml of distilled water. The solution was stirred for 3 hr at room temperature and then filtered after centrifuging at 3000 rpm for 25 min following a modification of procedures used by Zhang et al[27]. The filtrate was diluted to the desired concentration for soil washing. The solutions were prepared when needed and used freshly without storage after diluting to required concentrations.

Procedure for batch soil washing studies: Washing studies were conducted in batches to investigate the effect of biosurfactant and EDTA concentration, soil solution ratio, pH as well as washing time on the removal of Cd from contaminated soil. Series of batch tests were conducted in 125 ml conical flask over rotary shaker at 200 rpm for a given contact time at room temperature (24°C) and then aliquots were collected and centrifuged at 9000 g for 15min[28]. The initial pH of the surfactant solution was modified either by addition of hydrochloric acid or sodium

hydroxide[29]. The supernatants were collected after filtration using Whatman filter paper.

The samples were preserved with 1 drop of nitric acid and stored for ICP-OES analysis. The details of the experimental conditions and variables are shown in Table 1. Deionized water was used as washing solution. The response was recorded as percentage of copper removed from the washing experiment and calculated using a similar equation as reported by Wuana et al.[26]

$$\text{Percentage Cd removal (\%)} = \frac{C_1 V_1}{C_s M_s} \text{X } 100 \qquad (1)$$

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 M_S is the dry mass of the soil (kg). The pH of the solutions before washing and supernatants after washing was recorded. To ensure precision, all the experiments were performed in replicate and results were presented as averages of the replication values[30]. Details of experimental standards and variables are given in Table 2.

Procedure for column soil washing studies: The advantages of in-situ remediation of contaminated soil by using soil washing techniques cannot be over emphasized[31]. In this study, column washing was setup to represent an in-situ washing techniques. This technology has been piloted successfully in field remediation of paddy rice as well as in the laboratory condition[21,32]. The column washing was performed in the laboratory using the setup (Fig. 1). Distilled water as well as the optimal concentrations of the four different surfactants were used as washing fluids (Table 1). About 200 g of dried contaminated soil was packed into plastic columns. The soil bulk density of 0.8 g/cm³ was maintained for this work.

The column height was 17.5cm with the internal diameter of 5 cm. The porosity of the soil column was 68% and the pore volume (PV) was 146.8 cm³. Washing fluids were introduced into the soil column at the rate of 5 ml/min. 10 pore volumes of the surfactant solution were used for the column washings. A down-flow mode washing was established by pumping washing solution from the beaker into the soil (Fig. 1). After each pore volume, the effluent is collected and stored for heavy metal analysis. Heavy metal analysis was performed as described earlier.

Results and Discussion

Physicochemical analysis of soil: Table 2 shows the results of the physico-chemical properties of the virgin soil. The clean soil used in this study is the combination of fine sand and topsoil. The topsoil is made up of loam soil and organic matter used as soil amendment for both garden and other agricultural needs. The soil combination is an example of a typical soil used for cultivation of crop and can be classified as loamy sand. Sandy soils have been identified with low retention capacity for both water and heavy metals while the topsoil retains heavy metals due to its organic content[26].

It may be noted that neutral pH generally favours the growth of plants, a lower soil pH is necessary for heavy metal desorption from soil. Electrical conductivity (EC) is the measure of salinity of the soil. High EC is not good for the survival of plants as well as microorganisms in the soil. The EC value of 1.2 dS/m is within normal range for agricultural soil. The soil has low organic matter due to the greater percentage of sand; organic matter is known to have great binding strength with copper and other metals. CEC is the capacity of soil to retain a particular group of nutrients called cations. It is known that CEC comes from clay and organic matter present in the soil.

Therefore, low value of CEC was due to low organic matter. Thus, the low values of EC, CEC, organic matter and moderate porosity obtained from the physiochemical analysis of the soil mean that the soil was permeable and will enhance leachability of heavy metals and the possibilities of remediation by soil washing[24,26]. Soil analysis also revealed very low levels of heavy metal concentration and thus the spiking with a quaternary mixture was required to increase the level of heavy metal concentration.
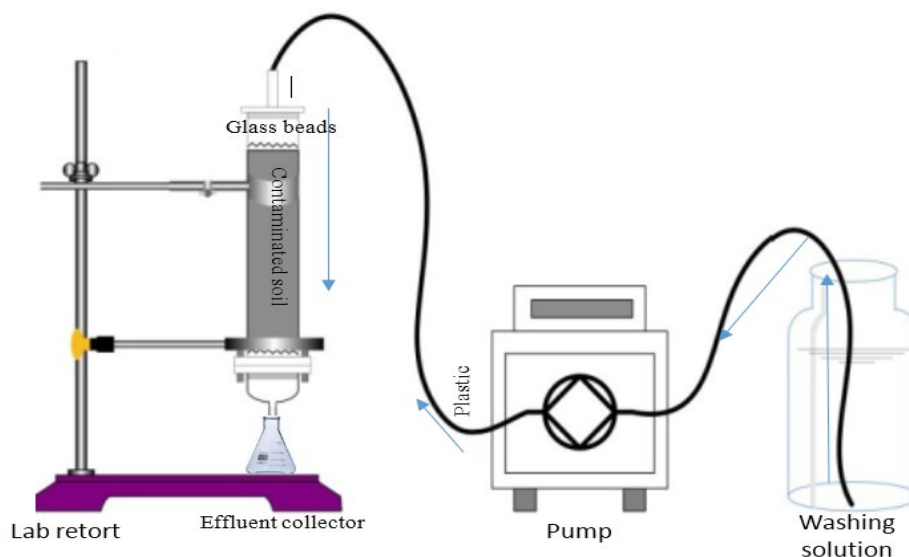
Figure 1: Diagram of soil column washing experimental setup

Table 1
Essential physicochemical properties of the original soils

Soil properties	Values	Units	Methods
pH	7.21		US EPA method 9045D
Electrical conductivity	1.2	EC dS/m	Violante and Adamo method [23]
Soil moisture content	9.2	%	ASTM D2216
CEC	8.3	meq 100g^{-1}	Ammonium acetate method
Bulk density	1.43	g/cm^3	Gravimetric method
Porosity	49		[24]
Organic matter content	2.4	%	Loss of weight by ignition
Sand	80	%	USDA classification
Topsoil	20	%	
Heavy Metal content			
Lead	1.17	mg/L	Digestion USEPA 3050B and measured by ICP-OES
Copper	14.65	mg/L	
Zinc	34.21	mg/L	
Cadmium	2.09	mg/L	

Table 2
Experimental conditions and variables for the batch and column washing

Factors	Conditions	Variables
Effect of surfactant concentrations	Standard conditions	Soil/Solution ratio: wt:vol = 1:40 (1 g soil:40 ml solution)
		Temperature = ±25 °C
		Shaking time 24 hrs
		pH 3
	Variable conditions	Biosurfactant (Rhamnolipids, soapnut and shikakai) =1%, 2 %, 3 %, 4 %, 5%, 6%
		EDTA = 1%, 2 %, 3 %, 4 %, 5%, 6%
Mixture of EDTA and biosurfactant	Standard conditions	Temperature = ±25 °C
		Shaking time = 24 hrs
		Unadjusted pH
		0.01M of EDTA
	Variable conditions	Biosurfactant = 1%, 2 %, 3 %, 4 %, 5%, 6%)
Effect of pH	Standard conditions	Soil/Solution ratio: wt:vol = 1:40
		Temperature = ±25 °C
		Shaking time = 24 hrs
		Biosurfactant = 3%

		3% EDTA
	Variable conditions	pH = 3, 3.5, 4, 4.5, 5, 5.5
Effect of soil: solution ratio		Temperature = ±25 °C
		Biosurfactant = 3%
	Standard conditions	EDTA = 3%
		Shaking time =24 hrs
		pH = 3
	Variable conditions	S/S ratios: w/v = (1:10, 1:20, 1:30, 1:40 and 1:50)
Effect of washing time		Temperature = ±25 °C
		Biosurfactant = 3%
	Standard conditions	EDTA = 3%
		pH = 3
	Variable conditions	Washing time = (2, 3, 4, 6, 8, 12, 24, 48, 72) hrs
Column		Temperature = ±25 °C
		Biosurfactant = 5%
	Standard conditions	EDTA = 5%
		pH = 3

Batch soil washing experiments: Series of batch soil washings were performed on Cd contaminated soil in the laboratory. The Cd removal efficiency by the four washing solutions (soapnut, shikakai, rhamnolipids and EDTA) was investigated at different levels of factors. The effect of surfactant concentration, pH of washing solution, soil-solution ratio and washing time were considered as the main factors of interest in Cd removal by soil washing.

Effect of concentration of washing solutions: The spiked soils were washed with soapnut, shikakai, rhamnolipids and EDTA at concentrations 0 (distilled water), 1, 2, 3, 4, 5 and 6 (%) by mass. The experiments were conducted at pH 3 and soil-solution ratio of 40 following results from preliminary studies. The effects of concentration of different washing solutions (Fig. 2) were expressed in terms of percentage (%) with respect to the initial concentration of Cd in the spiked soil using eq. 1. The Cd removal increased rapidly when the contaminated soil was washed with 1% to 3% concentration of biosurfactant (soapnut, shikakai and rhamnolipids) and as the concentrations were further increased from 3% to 6%, there was proportional increase. The increase in Cd removal may have resulted from reduction in the surface tension of the solutions and increase in micelle formation when surfactants are introduced into the solution according to Mukhopadhyay et al.[33]

EDTA on the other hand maintained a steady increase in Cd removal efficiency from 1 to 6% strength, achieving the highest removal efficiency of above 77%. Soapnut, shikakai and rhamnolipids achieved the removal efficiency of 73.6%, 75.4% and 53.1 respectively. Distilled water removed 3.01% of Cd, which was perhaps weakly bound to the soil particles. In general, the removal efficiency was found to be dependent on the concentration of the washing solutions. This observation is in agreement with the previous studies[15,19,30,34]. The results show that the plant-based surfactants can compete favourably with EDTA for soil washing.[4]

Effect of soil solution ratio: The influence of soil-solution ratio was studied in batch extraction process to investigate the quantity of washing solution and soil ratio that will be appropriate to remove Cd from spiked soil. Series of soil washings were performed by varying the ratio between soils and washing solution quantities. The concentration and pH of the washing solutions were kept constant at 3% and 3 respectively (Table 1). Effects of soil-solution ratio studied were at ratios: 1:10, 1:20, 1:30, 1:40 and 1:50. The result of the experiment (Fig. 3) show soil-solution ratios had a positive effect on the removal efficiency of Cd. The removal efficiency increased with increase in ratio of mass of contaminated soil to the washing solution with respective to surfactant and EDTA.

A rapid increase in removal efficiency of Cd was observed when there was increase from ratio 10 to 40 for both surfactant and EDTA which did not happen when the ratio increases from 40 to 50. Although, highest removal efficiencies were obtained at ratio 50 (soapnut 72.9%, shikakai 74.2%, Rhamnolipids 50.1% and EDTA 75.7%), there was no significant difference between what was obtained at ratio 40 (soapnut 70.6%, shikakai 72.2%, Rhamnolipids 48.7% and EDTA 74.0%).
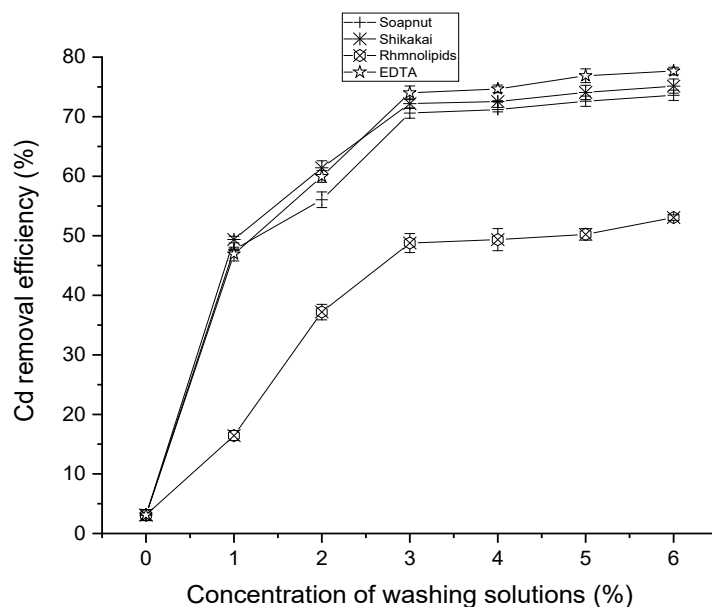
**Figure 2: Removal efficiency of different concentrations of washing solutions
(washing time =24 hr, pH=3 soil-solution ratio=40)**

Previous studies of Zou et al30 and Mukhopadhyay et al35 reported similar increase within soil-solution ratios. Zou et al30 suggested that washing of soil could be better done with higher soil-solution ratios with lower concentrations of surfactant than higher concentration of surfactant with lower soil-solution ratios. This could be useful in preventing clogging of soil during leaching.

Effect of pH of washing solution on the removal efficiency of Cd: Soil-surfactant pH as well as EDTA are very important factors that should normally be considered in metal desorption; this is because pH of washing solution determines the amount of metal sorption onto soil and influences the extent of metal desorption from the

soil30,34,36. Fig. 4 shows the removal efficiencies of Cd from soil by washing it with 3% of biosurfactants and 3% of EDTA at variable pH (3, 3.5,4, 4.5, 5.5 and 6). The result indicates that pH of the washing solution has great effect on the removal efficiency. The removal efficiency decreases with increase in pH of the washing solution.

At pH 3, all the washing solutions attain the highest removal efficiency (soapnut = 70.6%, shikakai = 72.2, rhamnolipids = 48.7 and EDTA = 74.0%). It was also observed that there was gradual decrease in the removal of Cd by EDTA and rhamnolipids as well as soapnut and shikakai from pH 3 to 6. These results are in agreement with previous studies[19,30,34].
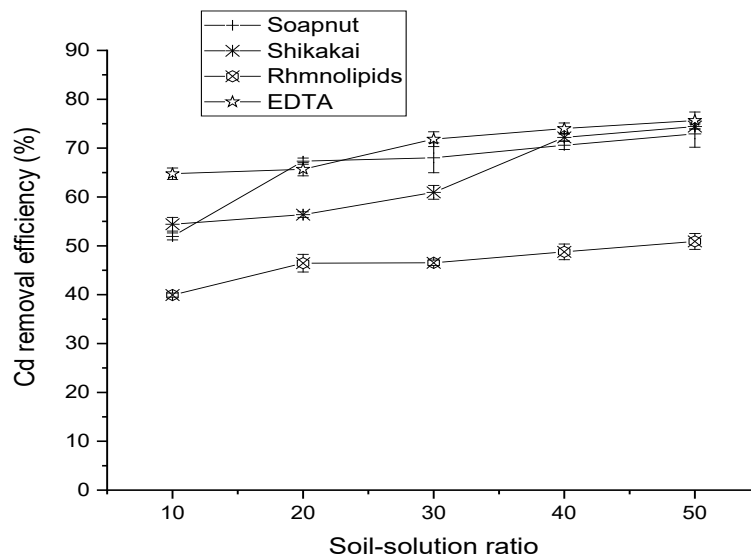
Figure 3: Removal efficiency of different soil-solution ratios
(washing time =24 hr, pH=3 biosurfactant concentration 3%, EDTA 3%)
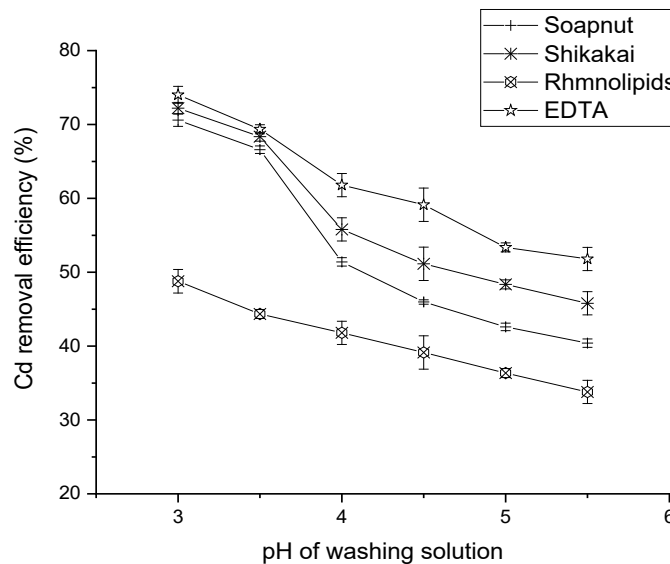

Figure 4: Removal efficiencies of surfactants and EDTA at different pH of washing solutions
(Soil-solution ratio = 40, washing time =24 hr, biosurfactant concentration 3%, EDTA 3%)

At pH 3, Hong et al34 obtained a removal of 90-100% of Cd from soil treated with saponin while 50-75% was obtained when the pH increase to 6. It also known that pH affects the capacity of surfactant in forming complexes and keeping the desorbed metal in suspension36.

Effect of washing time on the removal efficiency of Cd:
Reaction time has been found to be an important factor in soil washing since metals and metalloids desorption is a kinetic process[30]. To understand this and select the optimum washing time for Cd removal, a kinetic study was conducted following method adopted by Zou et al.30 Detailed description of experimental conditions and variables are

shown in Table 1. Results of the kinetic experiments (Fig. 5) indicate that the Cd removal followed a two-step desorption process. This implies that there was rapid increase in desorption of Cd within the first few hours of the experiment followed by steady and gradual increase in desorption, precisely after 12 hours.

There seems to be uniform behaviour of all the washing solutions (Fig. 5) with soapnut, shikakai, rhamnolipids and EDTA attaining the highest removal efficiency of 71.5%, 72.9%, 53.8% and 76.2% at 72 hr. From the result obtained by this kinetic experiment, 24 hr was chosen as the extraction time for proceeding further to reduce the effect of

corrosion of the washing solution on soil and maintain maximum extraction efficiency.[33]

Effect of 0.01 M of EDTA on the removal by surfactants: To understand the effect of mixing biosurfactant with EDTA for desorption of Cd from soil, 0.01 M EDTA was added to biosurfactant at various concentrations (1%, 2%, 3%, 4%, 5% and 6%). The experimental details are shown in Table 1. The results from this experiment (Fig. 6) generally show positive relationship between the addition of 0.01M EDTA and the removal efficiency obtained by the biosurfactant especially for rhamnolipids. It was observed that the removal of Cd increased with an increase in the biosurfactant concentration.

Addition of 0.01M of EDTA to the biosurfactant increased the previous results obtained without EDTA. High volume of surfactant was observed to increase desorption of metals[35]. In this study, 84.9% removal efficiency was obtained when soapnut was mixed with 0.01M of EDTA against 63.6% obtained at the same condition. Also, the addition of 0.01M of EDTA to shikakai increased the removal efficiency from 65.4% to 87.4% and that of rhamnolipids from 53.1% to 68.9%. The mixture of biosurfactant and EDTA could be a promising step in soil washing technology.

Column washing experiments: The purpose of conducting column washing experiments on the Cd contaminated soil was to further assess the performance of soapnut, shikakai, rhamnolipids and EDTA solutions. Column experimental setup simulates in-situ washing of heap-leaching process[15]. In this study, details of procedures used for conducting column experiments are shown and the experimental conditions are shown in Table 1. Cumulative removal efficiency of Cd by distilled water, biosurfactants and EDTA are shown in Fig. 7. The result (Fig. 7) shows that the removal efficiencies obtained in the column experiments are in agreement with that of the batch experiments.
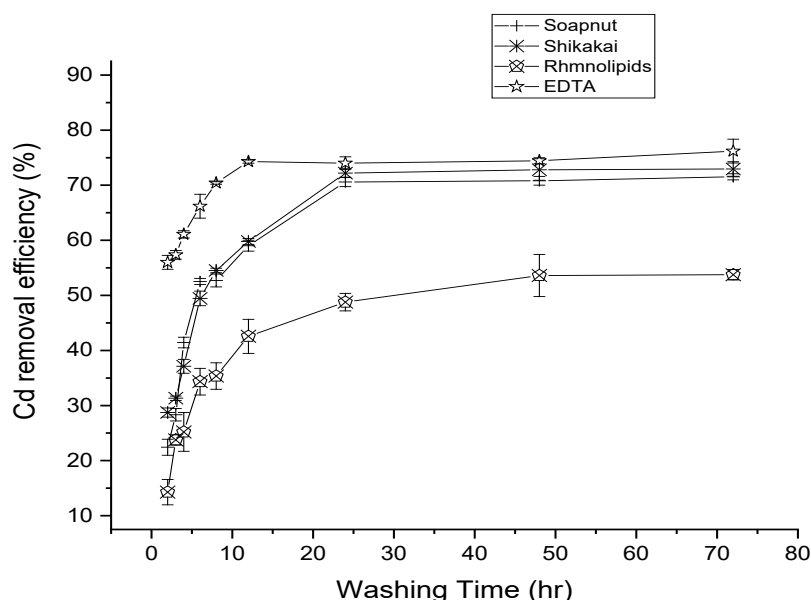

Figure 5: Removal efficiencies of biosurfactants and EDTA at different washing time (Soil-solution ratio = 40, pH= 3 surfactant concentration 3%, EDTA 3%)

There was a gradual increase in the cumulative removal of Cd by all the washing solutions used. After 10 pore volumes, EDTA recorded the highest removal efficiency of 74.05% followed by shikakai (73.08%), soapnut (69.07%), rhamnolipids (63.08%) and distilled water (12.78%). Distilled water accounts for the removal Cd that is weakly bound to the soil particles and readily available for mobilization[15]. Wang and Mulligan[37] reported successful removal of arsenic and heavy metals (Pb, Cu and Zn) from mine tailings.

Wang and Mulligan [37] removed 73.2 % of Cd and 68.1% of Ni using biosurfactant foam and 61.7% Cd and 51.0% Ni with liquid biosurfactant solution; however, distilled water removed only 18% of both Cd and Ni.

This result demonstrates that in-situ soil remediation of Cd can be effective using biological surfactant as well as EDTA. While EDTA and rhamnolipids are expensive, soapnut and shikakai are relatively cheap. However, the in-situ process obviates the need for the usual excavation of contaminated soil and washing it outside the site.
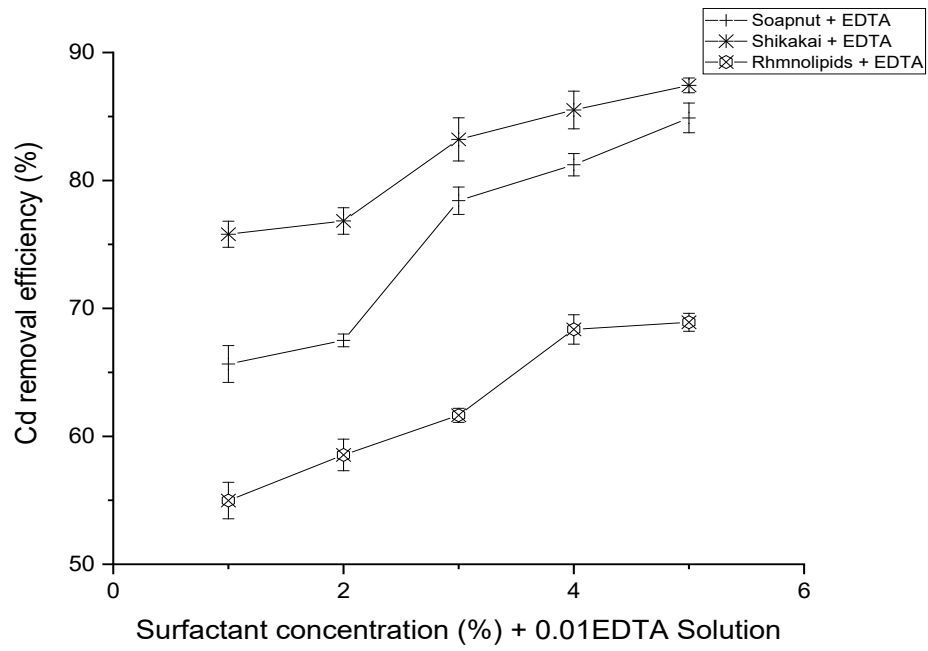
8

Figure 6: Removal efficiencies of biosurfactants and 0.01M EDTA at different concentrations (Soil-solution ratio = 40, pH= 3)
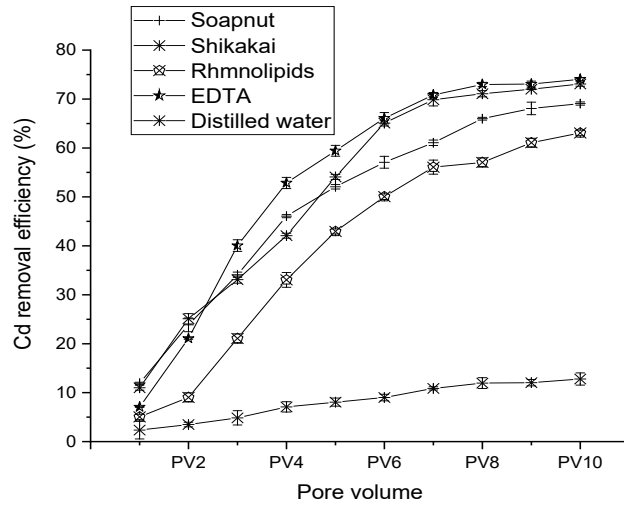

Figure 7: Removal efficiencies of biosurfactants and 0.01M EDTA at different concentrations (Soil-solution ratio = 40, pH= 3)
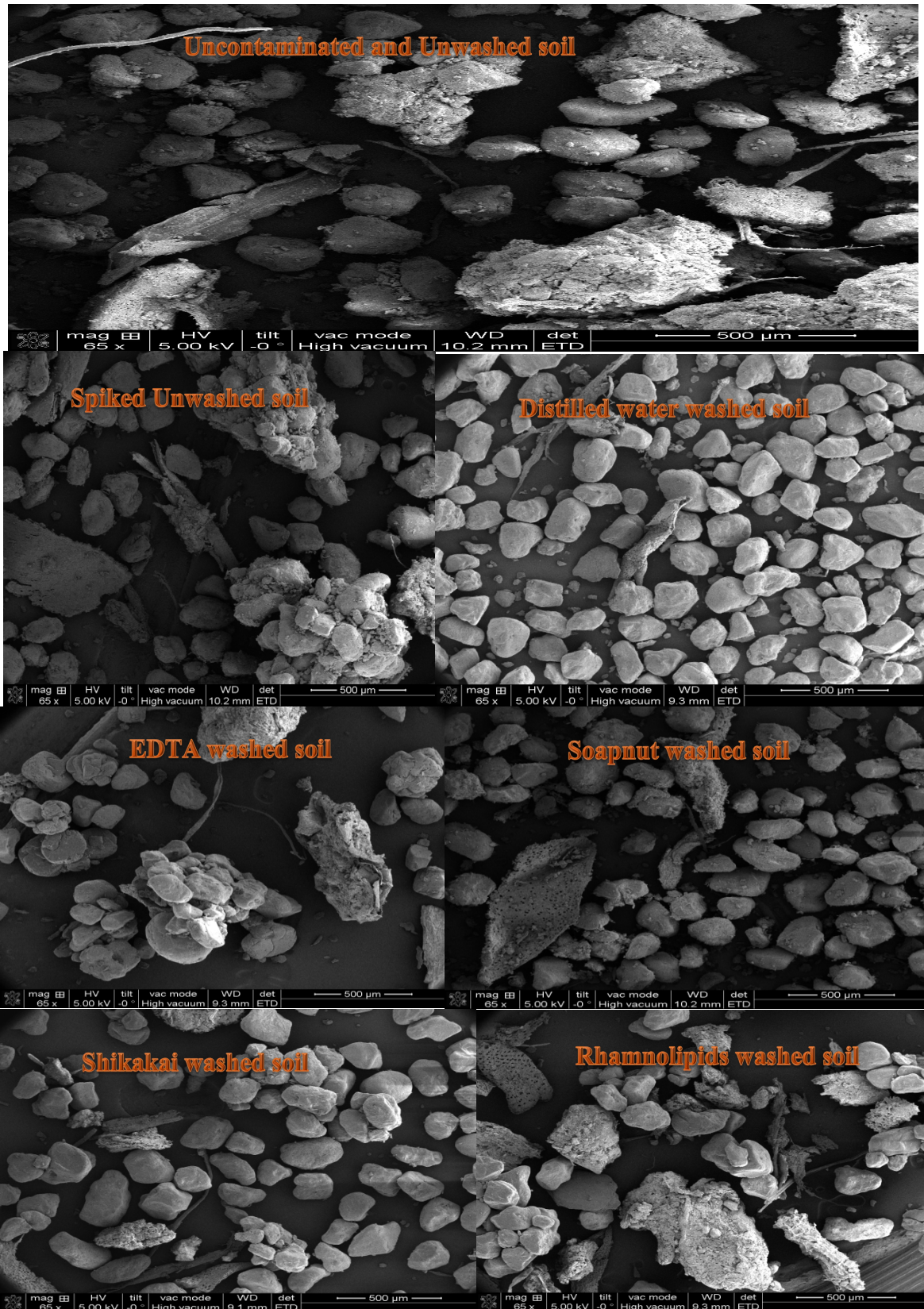
Figure 8: Figure 8 SEM images of original soil, contaminated soils and soil washed with distilled water, biosurfactants and EDTA

This has enormous disadvantages of cross-contamination and high cost. Therefore, even a more expensive cleaning agent may offset the overall cost of treatment as no excavation and material handling would be required.

Study of soil structure before and after washing: SEM analysis was carried out in order to understand the structural changes that occurred in the soil after washing with water, biosurfactants and EDTA in column experiment. The results in Fig. 8 indicate clearly that changes occurred after the soil was spiked and also when it was washed with distilled water, biosurfactants and EDTA. However, the extent of structural changes and corrosion that occurred was different and depended on the cleaning agents used. For instance, there were mild changes and corrosion observed on the soil surface after it was washed with soapnut and rhamnolipids compared with washing with EDTA and shikakai.

Although, distilled water removed little percentages of the heavy metal, it was observed through the SEM to have structural changes on the soil. Even the spiked soil looked very different from the original soil because of changes that occurred during the soil contamination.

Mukhopadhyay et al35 reported that dissolution of mineral components such as Ca, Mg, Al, Si and Fe did not occur when the soil was washed with soapnut and phosphate to remove arsenic. In this study, some of the organic matter of the soil seems to have been washed away or distorted by EDTA and Shikakai. Lower pH of the EDTA and Soapnut might have been the reason behind this observation. Soapnut and Rhamnolipids are best washing agents in terms soil structural changes.

Conclusion
Laboratory batch and column experiments have been conducted to study the removal of Cd from contaminated soil using soapnut, shikakai, rhamnolipids, EDTA and distilled water. Experimental factors such as the effect of concentration of washing solutions, pH of washing solution, soil-solution ratio and washing time were studied in the batch process. The results indicate that the Cd removal obtained with soapnut, shikakai and EDTA solutions was almost similar while the mixture of EDTA and biosurfactant yielded higher removal efficiencies.

The removal efficiencies obtained using rhamnolipids were generally lower than other washing agents. It was also observed that removal efficiencies obtained were influenced by the concentration of the washing solution, pH, soil-solution ratio and washing time. While the increase in the concentration of the washing solutions, soil-solution ratio and washing time increases the removal efficiency, increase in pH of the washing solution decreases the removal efficiency.

The effectiveness of saponin is due to its ability to form micelles and the solubilisation of Cd from the soil surface as well as reducing the interfacial tension existing in the solution. EDTA can break the bonds between the soil organic matters and can enhance the mobilization of heavy metals. Saponin usage in soil remediation has the advantages of being environment-friendly and cost effective. EDTA is expensive and can leave residual in the soil. Structural changes were also observed through SEM on the contaminated soil and the washed soil. The changes were attributed to the distortion of the original soil as they occurred irrespective of the washing solution used.

References
1. Giannis A. and Gidarakos E., Washing enhanced electrokinetic remediation for removal cadmium from real contaminated soil, *J of Hazardous Materials*, **123(1-3)**, 165-75 **(2005)**

2. Kirkham M., Cadmium in plants on polluted soils: effects of soil factors, hyperaccumulation and amendments, *Geoderma*, **137(1-2)**, 19-32 **(2006)**

3. Bruckmann P., Ambient air pollution by As, Cd and Ni compounds, NRW **(2001)**

4. Gusiatin Z., Bułkowska K. and Pokój T., Tannic acid as a cost-effective substitute for saponin in soil remediation, *Environmental Biotechnology*, **10(2)**, 66-72 **(2014)**

5. Jancic S.A. and Stosic B.Z., Cadmium effects on the thyroid gland, Vitamins and Hormones, Elsevier, 391-425 **(2014)**

6. Friberg L., Cadmium in the Environment: 0, CRC Press **(2017)**

7. Tóth G., Hermann T., Da Silva M. and Montanarella L., Heavy metals in agricultural soils of the European Union with implications for food safety, *Environment International*, **88**, 299-309 **(2016)**

8. Mahar A., Ping W., Ronghua L. and Zhang Z., Immobilization of lead and cadmium in contaminated soil using amendments, a review, *Pedosphere*, **25(4)**, 555-68 **(2015)**

9. Loganathan P., Hedley M.J. and Grace N.D., Pasture soils contaminated with fertilizer-derived cadmium and fluorine: livestock effects, *Reviews of Environmental Contamination and Toxicology*, **192**, 29-66 **(2008)**

10. Asami T., Pollution of soils by cadmium, Changing metal cycles and human health, Springer, 95-111 **(1984)**

11. Wang S. and Mulligan C.N., An evaluation of surfactant foam technology in remediation of contaminated soil, *Chemosphere*, **57(9)**, 1079-89 **(2004)**

12. Qixing Z., Technological reforger and prospect of contaminated soil remediation, *Techniques and Equipment for Env. Pol. Cont.*, **8**, 009 **(2002)**

13. Bolan N. et al, Remediation of heavy metal (loid)s contaminated soils–to mobilize or to immobilize?, *Journal of Hazardous Materials*, **266**, 141-66 **(2014)**

14. Herman D.C., Artiola J.F. and Miller R.M., Removal of cadmium, lead and zinc from soil by a rhamnolipid biosurfactant, *Env Sc and Tech.*, **29(9)**, 2280-5 **(1995)**

15. Abumaizar R.J. and Smith E.H., Heavy metal contaminants removal by soil washing, *Journal of Hazardous Materials*, **70(1)**, 71-86 **(1999)**

16. Juwarkar A.A., Nair A., Dubey K.V., Singh S. and Devotta S., Biosurfactant technology for remediation of cadmium and lead contaminated soils, *Chemosphere*, **68(10)**, 1996-2002 **(2007)**

17. Chmielewska E., Nussbaum M. and Szytenchelm R., An attempt to implement soil washing for central-Europe cleanup activities, *Chemické Listy*, **91(6)**, 438-43 **(1997)**

18. Mukhopadhyay S., Hashim M.A., Sahu J.N., Yusoff and Gupta B.S., Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil, *J. of Env. Sc.*, **25**, 2247-56 **(2013)**

19. Maity J.P. et al, Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from contaminated soils in Hai-Pu, Taiwan, *J. of Env. Sci.*, **25**, 1180-5 **(2013)**

20. Song S., Zhu L. and Zhou W., Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant, *Env. Pollution*, **156(3)**, 1368-70 **(2008)**

21. Mulligan C.N. and Wang S., Remediation of a heavy metal-contaminated soil by a rhamnolipid foam, *Eng. Geo.*, **85(1-2)**, 75-81 **(2006)**

22. Abumaizar R. and Khan L.I., Laboratory investigation of heavy metal removal by soil washing, *J. of The Air and Waste Mgt. Asso.*, **46(8)**, 765-8 **(1996)**

23. Race M. et al, Copper and zinc removal from contaminated soils through soil washing process using ethylenediaminedisuccinic acid as a chelating agent: A modelling investigation, *J. of Env. Chem. Eng.*, **4(3)**, 2878-91 **(2016)**

24. Urum K., Biosurfactant enhanced treatment of petroleum oil contaminated soils, Ph.D. thesis, Heriot-Watt University **(2004)**

25. Gusiatin Z.M. and Klimiuk E., Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin, *Chemosphere*, **86**, 383-91 **(2012)**

26. Wuana R., Okieimen F. and Imborvungu J., Removal of heavy metals from a contaminated soil using organic chelating acids, *International Journal of Environmental Science and Technology*, **7(3)**, 485-96 **(2010)**

27. Zhang C., Valsaraj K.T., Constant W.D. and Roy D., Surfactant screening for soil washing: Comparison of foamability and biodegradability of a plant-based surfactant with commercial surfactants, *J. of Env. Sci and Health, Part A*, **33(7)**, 1249-73 **(1998)**

28. Luna J.M., Rufino R.D. and Sarubbo L.A., Biosurfactant from Candida sphaerica UCP0995 exhibiting heavy metal remediation properties, *Process Safety and Environmental Protection*, **6**, 32-39 **(2016)**

29. Mulligan C.N., Yong R.N. and Gibbs B.F., On the use of biosurfactants for the removal of heavy metals from oil-contaminated soil, *Environmental Progress*, **18(1)**, 50-4 **(1999)**

30. Zou Z. et al, The study of operating variables in soil washing with EDTA, *Environmental Pollution*, **157(1)**, 229-36 **(2009)**

31. Wilson D.J., Kayano S., Mutch Jr. R.D. and Clarke A.N., Groundwater cleanup by in-situ sparging, I, Mathematical modelling, *Separation Science and Technology*, **27(8-9)**, 1023-41 **(1992)**

32. Makino T. et al, A practical soil washing method for use in a Cd-contaminated paddy field, with simple on-site wastewater treatment, *Geoderma*, **270**, 3-9 **(2016)**

33. Mukhopadhyay S., Mukherjee Sumona, Hashim M.A., Sahu J.N., Nadia Martinez Villegas and Gupta B.S., Zinc Removal from Soil by Washing with Saponin Obtained from Sapindus mukorossi, *Journal of Environmental Analytical Chemistry and Ecology*, **5**, 2380-2391 **(2018)**

34. Hong K.J., Tokunaga S. and Kajiuchi T., Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils, *Chemosphere*, **49(4)**, 379-87 **(2002)**

35. Mukhopadhyay S., Hashim M., Allen M. and Gupta B.S., Arsenic removal from soil with high iron content using a natural surfactant and phosphate, *International J. of Env. Sci. and Tech.*, **12(2)**, 617-32 **(2015)**

36. Açıkel Y.S., Use of biosurfactants in the removal of heavy metal ions from soils, Biomanagement of metal-contaminated soils, Springer, 183-223 **(2011)**

37. Wang S. and Mulligan C.N., Rhamnolipid biosurfactant-enhanced soil flushing for the removal of arsenic and heavy metals from mine tailings, *Process Biochemistry*, **44(3)**, 296-301 **(2009)**.