An Investigation on the Lead Removal from Soil Contaminated by Mining and Industrial Wastes Using Soapnut in Batch Washing Process

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ABSTRACT

Eco-friendly saponin from soapnut was studied for the remediation of the soils contaminated by lead. This study applied a full factorial design of the experiment with 3-factors in 3-level (3×3 factors) to evaluate the effect and interactions of the washing parameters on the lead removal by soapnut in a batch experiment. The parameters studied include: soil-solution ratio, surfactant concentrations by mass, and pH of the washing solution. Two soil samples representing low lead concentration (C1) and high lead concentration (C2) were investigated. The findings indicate that the removal efficiency obtained, increases along with the soil-solution ratio and surfactant concentration, but decreases with an increase in the pH of washing solution. Polynomial models were developed to predict the experimental response and optimal conditions. The model predicted a maximum of 50.54% and 47.44% lead removal from the contaminated soil C1 and C2, respectively. Multiple washing was investigated using the higher values of the parameters; the responses obtained significantly increased the percentage of lead removed and achieved 79.98% removal for C1 and 77.49% removal for C2. The effective performance of the soil washing process demonstrates the potential usage of soapnut saponin in the remediation of contaminated soil. Saponin from soapnut is cheap and environment-friendly.

Keywords: soapnut; lead; saponin; contaminated soil; soil washing; surfactant

INTRODUCTION

The soil pollution by poisonous metals has been widely reported in agricultural soils (Järup, 2003, Sharma et al., 2007, Li et al., 2001, Manta et al., 2002, Fakayode and Olu-Owolabi, 2003, Gäbler and Schneider, 2000, Razo et al., 2004). Human activities, urbanization, and rapid industrialization were linked as the major cause of these pollutions (Wei and Yang, 2010, Cheng, 2003). The incidences of soil contamination around the world are rapidly increasing (Wang and Mulligan, 2004, Qixing, 2002). While the world population has expanded to an estimated figure of 9 billion, there is no corresponding increase in the size of available land. This has made the arable land and clean soil scarce and expensive, as only pristine land can be used for agriculture, property development, wildlife protection and recreational facilities (Hurni, 1996, Morf et al., 2013). Soil pollution also reduces the monetary value of land,

and makes it unsafe for inhabitation. About one-third of the world's agricultural soils is lost to soil contamination, making them unsuitable for crop production and grazing (Godfray et al., 2010). Therefore, there is an urgent need for efficient remediation technologies to decontaminate soils in order to address this threat. Soil remediation and restoration have also become crucial in achieving the basic human need for safe food and clean water.

Several technologies for the remediation of heavy metal contaminated soils have been developed over the years (Mulligan et al., 2001). These technologies are classified based on two major objectives. The first objective is to immobilize the heavy metals as well as reduce their bioavailability and migration. The second objective is to promote mobility, bioavailability and migration of the heavy metals into the liquid phase for solubilisation and desorption using surface active ingredients known as surfactants. The first technology is not a permanent solution because heavy metals are non-biodegradable, but they can easily transform by sorption, methylation, complexation and changes in the valence state (Hong et al., 2002). The second objective appears to be more promising, as it affords a permanent removal of the metals from soil into the liquid phase where it can be precipitated and recovered (Moon et al., 2015, Shin et al., 2006, Imani et al., 2011, Adeniji, 2004, Hong et al., 2002, Zhou et al., 2013).

The soil washing technologies utilize washing agents to aid in removing contaminants during the washing process. Surfactants are surface-active agents that can reduce the surface tension between two liquids or between a liquid and solid. This mechanism causes splitting up and desorption of the hydrophobic compounds and heavy metals using their hydrophobic and hydrophilic properties (Bustamante et al., 2012). The application of surfactants to the soil washing for soil remediation relies on its ability to produce micelles and reduce both the surface and interfacial tension. Surfactants can be produced from both chemical and biological means. The chemical surfactants are known as the synthetic surfactants while the surfactants obtained from plants, animals and microorganisms are called biosurfactants (Soll and Blanco, 2001, Soberón-Chávez and Maier, 2011).

Biosurfactants have been successfully used in soil remediation for both the organic and heavy metal contaminants. Mulligan (2009) reported that the rhamnolipids from pseudomonas aeruginosa have been extensively studied and are produced commercially by Jeneiel Biotech Inc. (Wisconsin). Biosurfactants are easily degradable, environment-friendly and non-toxic. Moreover, they have high specificity, biocompatibility, unique structures, excellent foaming characteristics, and high stability at extreme pH, salinity and temperature, which make them suitable for use in very difficult situationd. These properties have distinguished biosurfactants from the synthetic surfactants giving the former a wider application in industry and environmental remediation efforts (Kobayashi et al., 2012, Lin, 1996, Mulligan, 2009).

Lead is one of the hazardous metals commonly found in mining sites. The soils contaminated with lead can cause serious risk to the human health as well as damage to the environment. Remediation of contaminated soils is targeted at reducing the risk associated with the contaminants and improving the quality of the environment. Saponin, a plant-derived non-ionic biosurfactant is becoming increasingly effective for desorption of metals in the soil washing processes (Hong et al., 2002). Biodegradability, low toxicity, easy recovery and reuse, and potential to improve aqueous dispersion have been identified as the benefits of plant-based saponin (Hong et al., 2002, Kommalapati et al., 1998, Roy et al., 1997). It has also been effective in the solubility improvement of polycyclic aromatic hydrocarbon (PAHs), according to Zhou et al. (2011).

In this study, the efficiency of soapnut (*sapindus mukorossi*) for the remediation of the contaminated soil in mining areas was investigated. An intensive soil and sediment characterization were carried out in the mining district of Santa Maria del la Paz, located in the municipalities of Villa de la Paz Metehuala in the state of San Luis Potosi (Mexico) by Razo et al. (2004). The study recommended an efficient and environment-friendly remediation approach for the restoration of the contaminated soils and sediments. Various options available for soil remediation have been studied worldwide, but soil washing using biosurfactants seems to be the most effective, environment-friendly and a feasible solution for removing metals from the contaminated soil (Venkatesh and Vedaraman, 2012, Maity et al., 2013a).
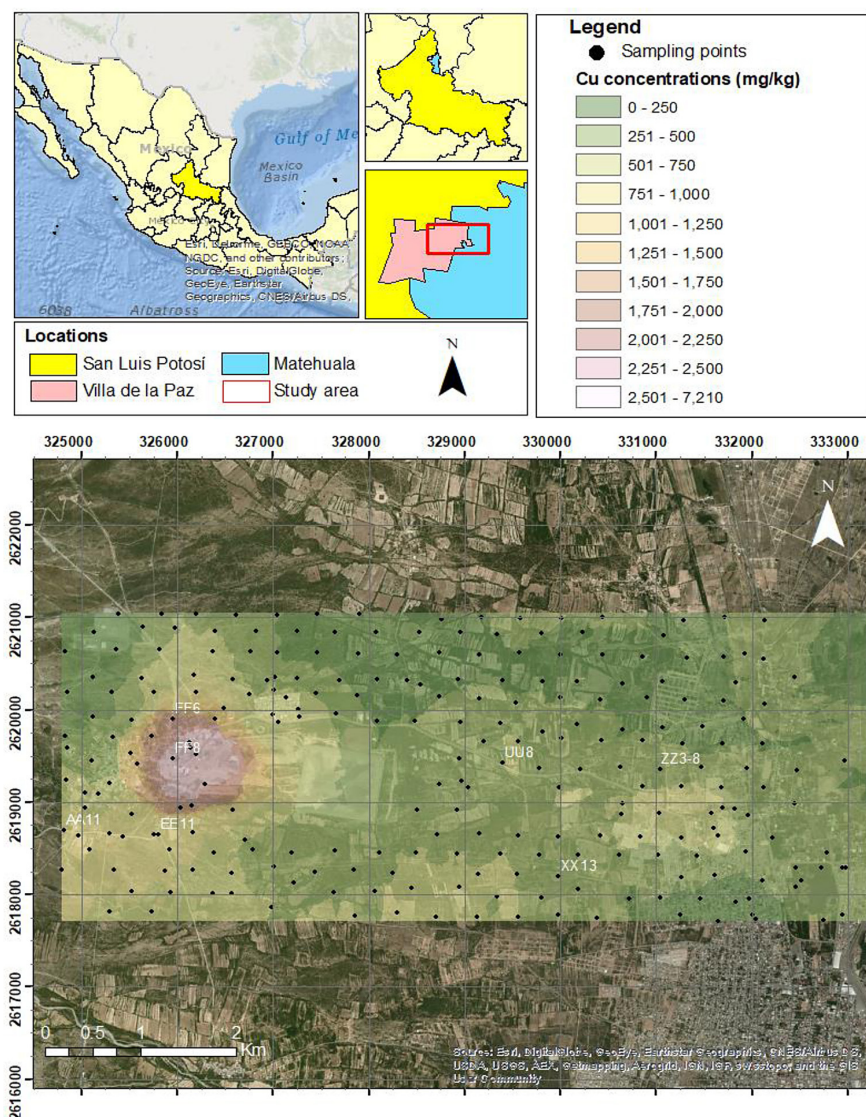
MATERIALS AND METHODS

Soil sample collection

The soil samples used in this study were contaminated as a result of historical and recent mining activities at various locations of Villa de la Paz-Matehuala, San Luis Potosi (Mexico). The sampling was designed to collect the real contaminated soil samples to remove the lead content using natural surfactants. Extensive sampling was carried out from a total of 105 km² study area to further select 8 sampling sites to represent a range of lead contamination. The sampling locations are shown in Figure 1. Two samples were selected to represent the high and low contaminated soils. The sampling points included urban areas, school playgrounds and agricultural land.

Soil physicochemical analysis

The collected samples were dried at room temperature (<35 °C) on plastic trays at a layer less than 2.5 cm thick. Subsequently, the air dried samples were homogenized and sieved through 2 mm screen (10 mesh). Soil characterization was done to determine various physical and chemical properties of the soil sample in-situ and in the laboratory. The soil moisture content was determined in-situ with HSM50 precision digital soil moisture meter. The data were recorded in triplicate, according to the values read from the LCD display of the meter. The organic matter content was determined by weight loss on ignition method (ASTM D 2974). The soil pH and electrical conductivity (EC) were measured with the slurry method according to Official Mexican Standard NOM-021-SEMARNAT-2000

Figure 1. The map showing corresponding to spatial distribution for Lead and sampling points used for the experiments

(DOF, 2002). Cation exchange capacity (CEC) was determined by sodium acetate following the method 9081 (Chapman, 1965). XRD analysis was performed to identify the mineralogical components of the soil using a Bruker D8 advance X-ray diffractometer fitter with a Cu Kα source. Total metal analysis was performed using X-ray fluorescence spectrometry (XRF) according to Environmental Protection Agency (EPA) Method 6200 (Hseu et al., 2016).These physicochemical properties are shown in Table 1 and Figure 2.

Preparation of plant based surfactant

The soapnut (*Sapindus mukorossi*) powder procured from Davis Finest production, Hampshire, UK was used in this study as surfactant. In order to prepare 10% stock solution of the washing fluid, 10 g of pure dry organic soapnut powder was added to 100 ml of distilled water. The solution was thoroughly mixed for about 3 hr at room temperature before being centrifuged at 3000 rpm for 25 min and then filtered before being diluted to the desired concentration following a modification of similar procedures (Zhang et al., 1998). The washing solutions were used freshly without storage.

Surfactant characterization

The surfactant used in this study was characterized in terms of the surface tension, molecular structure and pH. The surface tension and critical micelle concentrations (CMC) were measured by pendant drop experiment using Theta Lite contact angle goniometer. With a syringe, a sessile drop of the liquid was formed and placed at the film surface. Image recording started before the drop touched the surface by a camera coupled to the goniometer. The surface tension and CMC were calculated by the Young-Laplace equation using the OneAttension control software. Readings were repeated for ten times, the results were copied to Microsoft Excel, and the mean and standard deviation were calculated. The molecular structure of the surfactant was characterized before and after washing using Fourier transform infrared spectroscope (FTIR). This was meant to test if there was any chemical interaction between the soil and the surfactant and also to assess the process causing the removal of metals from the soil. The pH of the surfactant was determined for each concentration used. The results for surfactant characterization are shown in Table 2.

Experimental design and statistical analysis

Preliminary investigation was conducted to help screen out some factors, which were not necessary for the effective experiments. Essential factors were used to conduct the second phase of the experiments, which are kinetic and full factorial design. All experiments were conducted in triplicate and the average values were reported. The statistical analysis was carried out using

Table 1. Physiochemical properties of soils used for the experiments

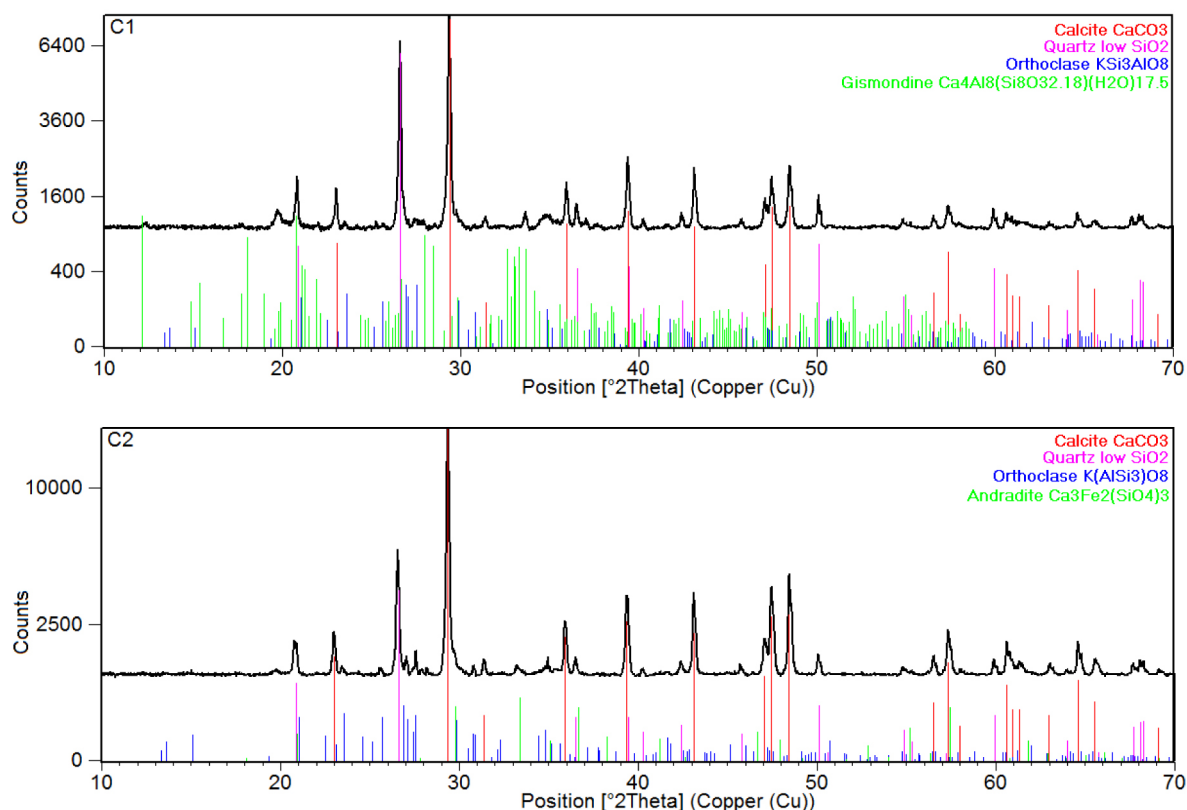| Soil properties	Values		Method
	C1	C2	
pH	7.45	7.30	NOM-021-SEMARNAT-2000
Electrical conductivity (dS/m)	0.18	0.12	
Soil moisture content (%)	7.1	12.0	
Soil CEC (meq)	2.15	1.50	Sodium acetate method 9081
Organic matter content	19.0	6.3	Ignition method (ASTM D 2974)
Particle size distribution	Sandy-loam	Loam	NOM-021-SEMARNAT-2000
Silt	40	46	
Sand	56.04	42.04	
Clay	3.96	11.96	
Lead (mg/kg)	1345	287	EPA Method 6200 (USEPA 2007)
Arsenic (mg/kg)	1050	519	
Copper (mg/kg)	400	1616	
Zinc (mg/kg)	2129	761	
Iron (mg/kg)	241200	21185	
Potassium (mg/kg)	12094	7327	
Calcium (mg/kg)	162617	276210	
Manganese (mg/kg)	1106.43	412	

Figure 2. XRD spectra showing various counts of minerals components of the soils used in the study C1 is the soil with high Pb contamination (1345 mg/kg), while C2 is the soil with low Pb contamination (287 mg/kg)

Table 2. Characterization of surfactant and deionized water used for soil washing experiments

Surfactant	Empirical formula	Mol. Wt	CMC	Conc. used	Surface tension	pH
Deionized water	H_2O	18			73.56± 0.95	5.74 ± 0.23
Soapnut	$C_{52}H_{84}O_{21}.2H_2O$	1,081.24	0.1%	1%	36.96± 0.89	4.33 ± 0.09
				2%	34.91± 0.57	4.29± 0.56
				3%	34.50 ± 0.37	4.25± 0.09
				4%	34.29± 0.51	4.23 ± 0.23

analysis of variance (ANOVA) followed by the T-test at 0.05 and 0.01, significance levels. The data summary and calculations were performed using Microsoft Excel and Minitab, and the graphs were drawn using Origin software.

Soil washing experiments

Batch extractions were conducted in laboratory scale to investigate the effect of surfactant concentrations, soil solution ratio and pH of the washing solution. The batch tests were conducted in 125 ml conical flask over a rotary shaker at about 200 rpm for a given contact time at room temperature (24°C). The pH of the surfactant solution was increased or reduced accordingly by the addition of hydrochloric acid or sodium hydroxide (Mulligan et al., 1999b). The supernatants were collected and filtered using a Whatman filter paper after centrifuging at 9000 g for 15 min (Luna et al., 2016). A drop of nitric acid was usually added to the samples for preservation and stored for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The response was usually recorded as percentage of lead removed and calculation was done by using a similar equation as that reported by (Wuana et al., 2010):

$$Percentage\ of\ lead\ removal = \frac{C_1 V_1}{C_S M_S} 100\% \quad (1)$$

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 (l); M_S is the dry mass of the soil (kg).

The pH of the solution was recorded before washing and after washing in supernatant. In order to ensure precision, all the experiments were performed in replicate and results were presented as averages of the replication values (Zou et al., 2009).

Multiple washing

Three series of batch washings were conducted using optimum conditions from the full factorial design. The optimum experimental conditions used were pH 4, soil-solution ratio 1:100 and surfactant concentrations of 6%. The procedures given in section 2.5 were followed for the batch experiment and, at each setup of multiple soil washing, fresh saponin solution was added to each poly-ethylene tube. The Pb removal was determined after every wash using Equation 1.

Kinetic study

Kinetic studies were conducted to test the rate of desorption of lead over time. According to (Zou et al., 2009), metal desorption from soil is a kinetic process, and, therefore, extraction time plays an important role in soil washing. A method similar to the one used by (Mukhopadhyay et al., 2015) was used to conduct the experiments. Five grams of contaminated soil were shaken with 100 ml of soapnut solution at a 5% concentration in a 250 ml conical flask. The pH of the surfactant solution was adjusted to 4, and the test was run at: 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 6.0, 8.0, 24.0, and 48.0 hours. The removal of lead from the soil was estimated at each time interval by collecting 5 ml samples, which were later filtered and preserved by adding 1 drop of nitric acid and stored for ICP-OES analysis.

RESULTS AND DISCUSSIONS

Soil characterisation

The soils used in this study were predominantly calcite calcium carbonate ($CaCO_3$) with associating minerals (see Fig. 2). Soil with high Pb contamination (C1) has Calcite $CaCO_3$ (35%), Brushite $KaHPO_4(H_2O)_2$ (23%), Quartz low SiO_2 (30%), Cristobalite SiO_2 (1%) and Orthoclase $K_{0.94}Na_{0.06}(AlSi_3O_8)$ (11%). The soil with low Pb contamination (C2) has Calcite $CaCO_3$ (62%),

Quartz alfha SiO_2 (22%), Orthoclase $K(AlSi_3O_8)$ (9%), and Andradite $Ca_3Fe_2(SiO_4)_3$ (4%). The higher level of arsenic and heavy metals content in soil (C1) may be due to high organic matter content which has been reported to have great affinity for metal binding (Zeng et al., 2011, Micó et al., 2006, Maity et al., 2013a). Table 2 shows the results related to the physiochemical properties of the soils used in the experiments. The pH of the soil which is slightly neutral favours the existence of plants and living organisms, although at lower pH, the removal of metal from soil is enhanced. Electrical conductivity (EC) measures the level of salinity in the soil. High EC is known to have adverse effect on the survival of plant and microorganisms in the soil. The EC value of 0.18 is essential and 0.12 dS/m is within the non-saline range of soil. Soil C1, has high organic matter content which makes it rich for crop production and microbial activities. CEC measures the capacity of soil to allow for exchange of cations. The sources of CEC in the soils are clay and organic matter. The CEC obtained from the two soils are generally low. Generally, the low values of EC and CEC in the soils used for this experiments means that the soil was permeable and will enhance leachability of metals by soil washing (Wuana et al., 2010, Sarubbo et al., 2015).

Surfactant characterization

pH and surface tension of the washing solutions

Table 3 shows the results of the pH and the surface tension of the deionized water and soapnut used in this study. The deionized water has a low pH compare to pure water due to carbon dioxide dissolution from the atmosphere. The results of surface tension show that the natural surfactant used is capable of lowering the surface tension even at the lower concentration (1%). The pH of the surfactant at various concentrations indicates that the surfactant is a weak acid. According to (Kommalapati et al., 1998) the saponin has a critical micelles concentration of 1000 mg/l and 10% solution has an equivalent total organic carbon value of 41 g/l.
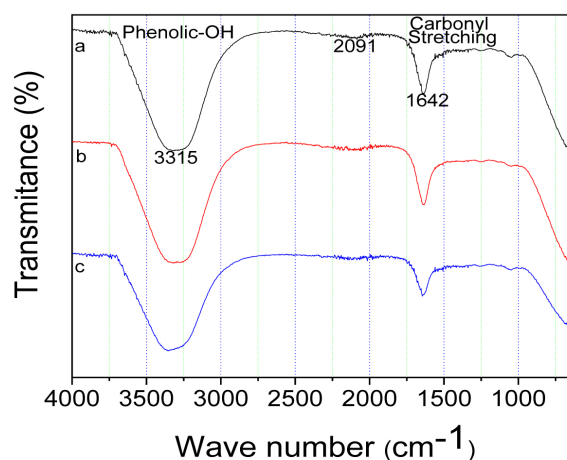
FT-IR spectral data of soapnut before and after to washing

FT-IR (Thermo Nicolet modlo 6700) spectra of aqueous soapnut are shown in Figure 3, where we can observe the differences between

Table 3. Full factorial design matrix with the experimental response and predicted values for the removal of Pb from contaminated soil C1 and C2

		Independent variables		(%) removal of Pb from soil (C1)			
S/N	pH	Soil-solution ratio (SSR)	Concentration (Conc.)	C1		C2	
				Observed	Predicted	Observed	Predicted
1	4	20	0	0.19	2.50	0.17	2.50
2	5	20	0	0.16	1.95	0.12	1.76
3	6	20	0	0.12	1.40	0.09	1.01
4	4	20	2	13.72	9.10	12.32	8.51
5	5	20	2	8.28	7.01	7.48	6.27
6	6	20	2	6.86	4.91	5.26	4.02
7	4	20	4	22.92	22.31	21.22	20.53
8	5	20	4	16.25	17.12	13.85	15.29
9	6	20	4	12.75	11.93	11.25	10.05
10	4	60	0	1.11	5.63	1.11	5.22
11	5	60	0	1.12	4.37	1.12	3.97
12	6	60	0	0.51	3.10	0.51	2.73
13	4	60	2	21.65	15.99	20.95	14.81
14	5	60	2	18.40	13.28	17.80	12.23
15	6	60	2	15.76	10.67	13.86	9.65
16	4	60	4	31.62	36.43	30.32	33.99
17	5	60	4	27.49	31.11	24.39	28.75
18	6	60	4	22.57	25.79	21.17	23.50
19	4	100	0	1.55	8.77	1.15	7.93
20	5	100	0	0.92	6.79	0.90	6.19
21	6	100	0	0.68	4.81	0.58	4.44
22	4	100	2	33.81	22.70	31.01	21.10
23	5	100	2	28.72	19.56	26.02	18.19
24	6	100	2	21.77	16.42	20.37	15.28
25	4	100	4	48.43	50.54	44.93	47.44
26	5	100	4	42.71	45.10	40.89	42.20
27	6	100	4	38.78	39.65	35.71	36.96

the transmittance spectra for soapnut solutions, together with the absorption range of different molecular vibrations, such as the phenolic-OH bond located at 3315 cm^{-1} and the C=C stretching located at 1638 cm^{-1} which indicate the presence of alkene groups. Similar observations were reported by Pradhan and Bhargava, (2008) in another study. In these results, it can be observed that there is no displacement of the peaks in the FT-IR spectrum between the soapnut solution before and after being used to wash contaminated soils C1 and C2. FTIR of the solutions collected after soil washing showed no apparent changes in the spectra, which would indicate that there was no chemical interaction between the saponin and soil throughout the washing process (Figure 3).

Figure 3. FTIR: a) soapnut before washing, (b) soapnut after washing soil C1, (c) soapnut after washing soil C2

Soil washing experiments

Screening experiments

The results from the screening experiment (Graeco-Latin square not shown) established that the surfactant concentration has the highest influence in lead removal efficiency, against time of reaction, contaminant concentration and pH of the surfactant concentration. The response was recorded for the removal efficiency in the batch washing test using Equation 1. The removal efficiency obtained from the full factorial design ranged from 0.08% to 1.5% for deionized water and 6.86% to 48.43% for soapnut saponin solution, as shown in Table 3. The highest removal efficiency was obtained at the surfactant concentration of 4%, pH of 4 and soil-solution ratio of 1:100. Low removal efficiency obtained at single washing generally depicts the strong binding of Pb to the soil, and the fact that metals are strongly adsorbed on contaminated soil, making them very difficult to remediate (Sarubbo et al., 2015). Generally, the Pb removal increases along with the saponin concentration and soil-solution ratio but decreases with an increase in the pH of washing solution. The same trend was reported by Zhou et al. (2013) in the study of enhanced soil washing of phenanthrene by a plant-derived natural surfactant. Furthermore, Maity et al. (2013a) reported an increase in the removal efficiency of nickel (Ni) and Manganese (Mn) when the surfactant concentration increased from 0.015 to 0.150 g/l. Hong et al. (2002) also reported a higher removal efficiency of saponin at the concentration of 3% and at pH of 3. In this study, the surfactant concentration and soil solution ratio were the main factors influencing the removal efficiency.

Development of regression model equation using full factorial design

A full factorial design with 3-factor and 3-level was applied to evaluate the mutual effects of three independent variables, including pH, Soil-solution ratio (SSR), and surfactant concentration (Conc.), on the lead removal efficiencies of soapnut from the contaminated soil C1 and C2. The second-order polynomial regression equations were generated by the Minitab 18 software to describe the lead removal efficiencies. The equations are expressed in uncoded forms, as shown in Eqns. 2 and 3:

$$\begin{aligned}
\text{\% Pb removed by } SN\,(C_2) ={}& 3.1 - 0.49\,\text{pH} + 0.118\,\text{SSR} \\
&+ 5.29\,\text{Conc.} - 0.0124\,\text{pH·SSR} \\
&- 0.792\,\text{pH·Conc.} + 0.0365\,\text{SSR·Conc.} \\
&+ 0.0021\,\text{pH·SSR·Conc.}
\end{aligned} \quad (2)$$

$$\begin{aligned}
\text{\% Pb removed by } SN\,(C_1) ={}& 1.7 - 0.19\,\text{pH} + 0.150\,\text{SSR} \\
&+ 5.68\,\text{Conc.} - 0.0179\,\text{pH·SSR} - \\
&0.82\,\text{pH·Conc.} + 0.0359\,\text{SSR·Conc.} \\
&+ 0.0025\,\text{pH·SSR·Conc.}
\end{aligned} \quad (3)$$

The experimental design and details along with the response values as well as predicted values are shown in Table 3. The relationships between the predicted values and experimental responses (Fig. 4) show that the developed quadratic models demonstrate proper fitting to the lead removal efficiency for the experimental data. The model predicted a maximum removal of 50.54% as against 48.43% observed response for the contaminated soil C1. Similarly, the model predicted 47.44% Pb removal from the contaminated soil C2 as against 44.93% observed from the experiment. The normal probability plot of residual values and the Pareto plots are not shown.

ANOVA analysis for lead removal from contaminated soils (C1 and C2) using soapnut

The results of experiments were analysed in Minitab and presented in ANOVA Tables 4 and 5. The model terms of the ANOVA for all the experiments were significant ($P<0.05$). The ANOVA tables indicate that there were strong interaction between the surfactant concentration and the soil-solution ratio, and the pH of the washing solution. The surfactant concentration and soil-solution ratio were significant in all the experiments. This was similar to the findings of the preliminary experiments, which showed that the surfactant concentration was a major controlling factor.

The squared regression R-sq and adjusted R-sq are strong indication of a reliable fit of the model to the experimental data and its usefulness in predicting the responses. In this study, high values of R-sq were recorded in the range of 89.96% to 90.37%. The range for adj R-sq was from 86.26.71% to 86.82%. The predicted R-sq values were in the range of 80.74% to 81.05%. The S values were between 4.98 to 5.42. The low value of S and high values of R-sq, adjusted R-sq and predicted R-sq suggested a good fit of the model to the experimental data. In general, there is strong evidence that the model is adequate to fit the data and predict the response (Venkatesh and Vedaraman, 2012).
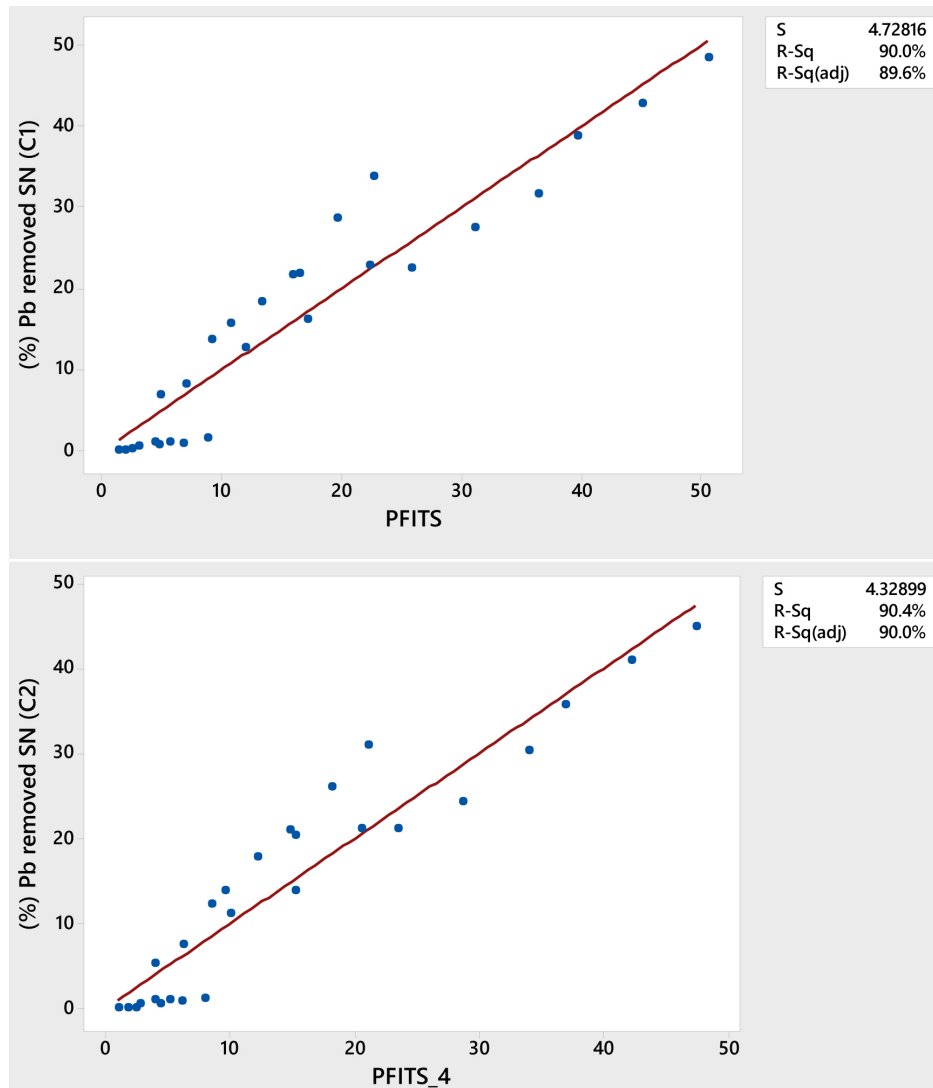
Figure 4. Predicted values of percentage Pb removal from contaminated
soil C1 versus actual values (PFITS is the predicted values)

Table 4. Analysis of variance for Pb removal by soapnut from contaminated soil (C1)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	5006.49	715.21	24.31	0.000
Linear	3	4719.53	1573.18	53.48	0.000
pH	1	191.61	191.61	6.51	0.019
SSR	1	1190.47	1190.47	40.47	0.000
Conc.	1	3337.45	3337.45	113.46	0.000
2-Way Interactions	3	469.29	156.43	5.32	0.008
pH*SSR	1	2.10	2.10	0.07	0.792
pH*Conc.	1	51.03	51.03	1.73	0.203
SSR*Conc.	1	416.16	416.16	14.15	0.001
3-Way Interactions	1	0.72	0.72	0.02	0.878
pH*SSR*Conc.	1	0.72	0.72	0.02	0.878
Error	19	558.89	29.42		
Total	26	5565.38			
Model Summary					
S		5.42			
R-sq		89.96%			
R-sq(adj)		86.26%			
R-sq(pred)		80.74%			

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Table 4 illustrates the ANOVA of Pb removed by soapnut from the contaminated soil C1. It can be observed from the Table 4 that the model term, the pH, soil-solution ratio, and surfactant concentration are all significant (P<0.05). The 2-way interactions of the model are significant; the 2-way interactions of soil-solution ratio and surfactant concentration are also significant. The 2-way interactions between the pH and surfactant concentrations as well as pH and soil-solution ratio were not significant. Moreover, the 3-way interactions of the model and parameters were not significant. The model summary shows that the values of S, R-sq, R-sq (adj) and R-sq (pred) are 5.42%, 89.96%, 86.26.765% and 80.74% respectively.

Table 5 illustrates the ANOVA of Pb removed by soapnut from the contaminated soil C2. It can be observed from the Table 5 that the model term, the pH, soil-solution ratio, and surfactant concentration are all significant (P<0.05). The 2-way interactions of the model are significant; the 2-way interactions of soil-solution ratio and surfactant concentration are also significant. The 2-way interactions between the pH and surfactant concentrations as well as pH and the soil-solution ratio were not significant. Moreover, the 3-way interactions of the model and that of the 3 parameters were not significant. The model summary shows that the values of S, R-sq, R-sq (adj) and R-sq (pred) are 4.97%, 90.37%, 86.82% and 81.05% respectively.

Effect of surfactant concentration

The effect of soapnut concentration on the removal of lead from the contaminated soil is expressed as the removal efficiency in percentage. In this study, the soapnut concentrations were investigated in 3x3 full factorial experiments. Three values of the concentration were tested, which include deionized water (0% surfactant) and 2%, and 4% of the soapnut saponin solution. Figs. 5 and 6, show the effects of surfactant concentration on the removal efficiencies observed for soapnut for the contaminated soils, C1 and C2. The results of the batch experiments show that the removal efficiency increases along with the concentration of surfactant.

This was shown by the ANOVA results that the surfactant concentrations were significant. Deionized water can only obtain a maximum removal efficiency of 1.5% showing that these metals are strongly bonded to the soil. Again, it shows that unlike saponin, which can reduce the surface tension of liquid and form micelles, deionized water cannot form micelles or complexes with metals that could hold the lead under suspension. Therefore deionized water is not as effective as in soil washing (Mukhopadhyay et al., 2015). The importance of washing with deionized water is to show the evidence of fractions of metals that is weakly bound to the contaminated soil and can be

Table 5. Analysis of variance for Pb removed by soapnut from contaminated soil (C2)

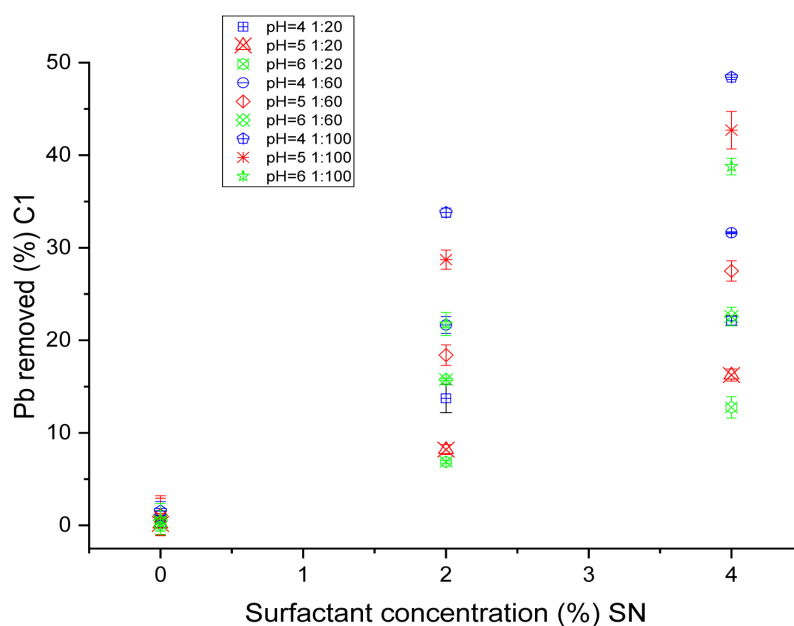| Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	4416.09	630.87	25.47	0.000
Linear	3	4143.14	1381.05	55.75	0.000
pH	1	185.57	185.57	7.49	0.013
SSR	1	1085.73	1085.73	43.83	0.000
Conc.	1	2871.84	2871.84	115.93	0.000
2-Way Interactions	3	443.74	147.91	5.97	0.005
pH*SSR	1	0.73	0.73	0.03	0.865
pH*Conc.	1	49.98	49.98	2.02	0.172
SSR*Conc.	1	393.03	393.03	15.87	0.001
3-Way Interactions	1	0.51	0.51	0.02	0.887
pH*SSR*Conc.	1	0.51	0.51	0.02	0.887
Error	19	470.65	24.77		
Total	26	4886.74			
Model Summary					
S		4.98			
R-sq		90.37%			
R-sq(adj)		86.82%			
R-sq(pred)		81.05%			

Figure 5. Effect of soapnut concentration on the removal Pb from contaminated soil (C1)
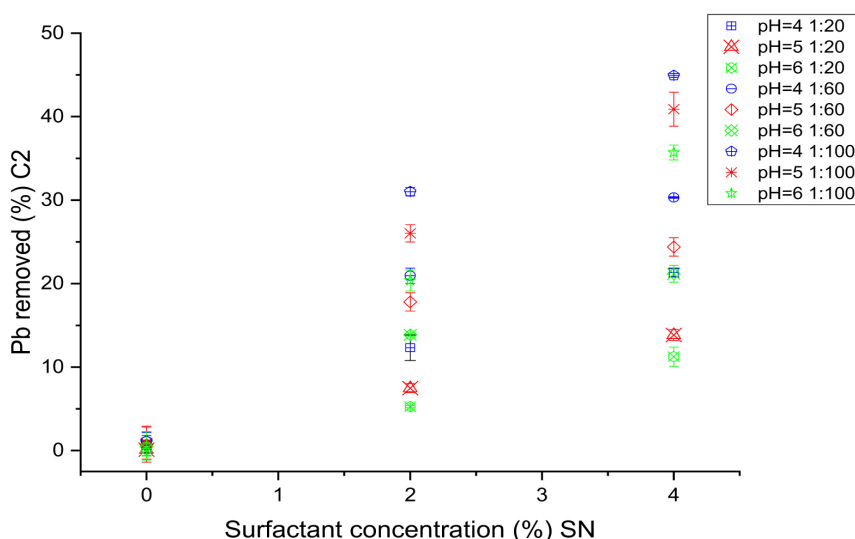

Figure 6. Effect of soapnut concentration on the removal Pb from contaminated soil (C2)

easily mobilized (Abumaizar and Smith, 1999). In this study, the poor performance of deionized water shown in the cumulative removal efficiency is an evidence of strong bond existing between the contaminated soil and the lead contaminant. Moreover, real soils from the contaminated sites are very difficult to remediate, especially if they have been contaminated for a long period of time (Chang et al., 2010). The lowest surfactant concentration of 2% produced the lowest lead removal, which could indicate that higher surfactant concentrations are more effective for lead removal, as reported in previous studies (Maity et al., 2013a, Mukhopadhyay et al., 2015).

Effect of pH

Electrostatic attraction between saponin and the soil surface determines the amount of saponin sorbed onto soils, and this amount increases with a decrease in pH (Açıkel, 2011, Hong et al., 2002). The pH is an essential factor that determines the extent of metal desorption. The pH of washing solution influences the amount of saponin adsorbed onto the soil that influences the extent of metal desorption from soil. It is also important in the formation of complexes and keeping the desorbed metals in suspension (Zou et al., 2009, Açıkel, 2011, Hong et al., 2002).

Effect of pH was tested in this study by performing experiments at pH 4, 5 and 6. In general, higher desorption of lead was obtained at pH 4, as shown in Figs. 7 and 8. The removal efficiency increased with a decrease in the pH of the washing solution and decreased with an increase in the pH. At pH 4, the lead removal efficiency reached its highest values with other parameters, namely, 4% surfactant concentration and 1:100 soil-solution ratio. This result is in agreement with the report of Hong et al. (2002) and Maity et al. (2013b) in which the highest removal efficiencies were obtained at lower pH. It is worth noting that the pH of the surfactant solution was the least significant factor among the three factors considered in this study. Although pH

played great role in metal desorption, other factors such as: contaminant nature, surfactant concentration, soil-solution ratio and time of reaction can exert greater influence in soil washing.

Effect of soil-solution ratio

The effect of soil-solution ratio on the removal of Pb was investigated in this study by varying the volume of saponin solution and the mass of the contaminated soils at three different ratios: 1:20, 1:60 and 1:100. From the results of the experiments shown in Figs. 9 and 10, it can be seen that there was a positive effect on the Pb removal efficiency as the increase in the
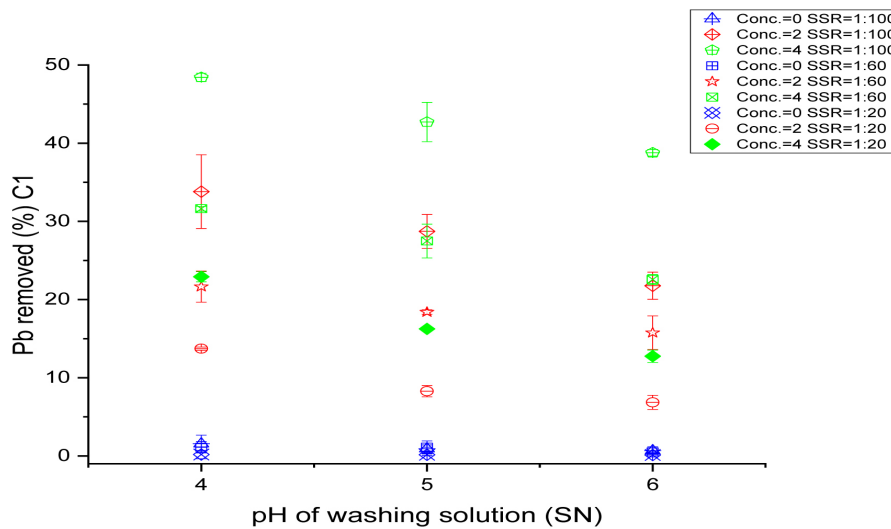

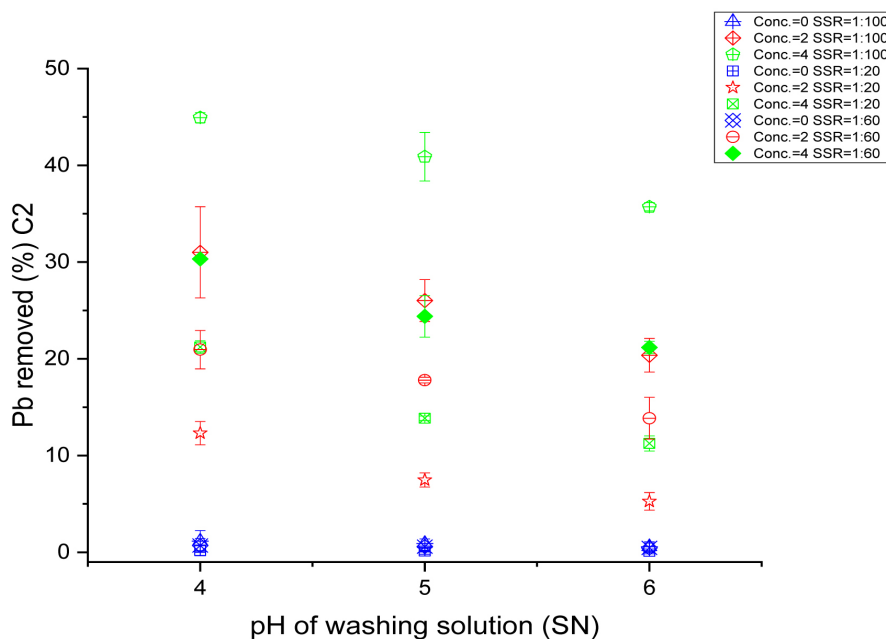**Figure 7.** Effect of soapnut pH on the removal of Pb from contaminated soil (C1)

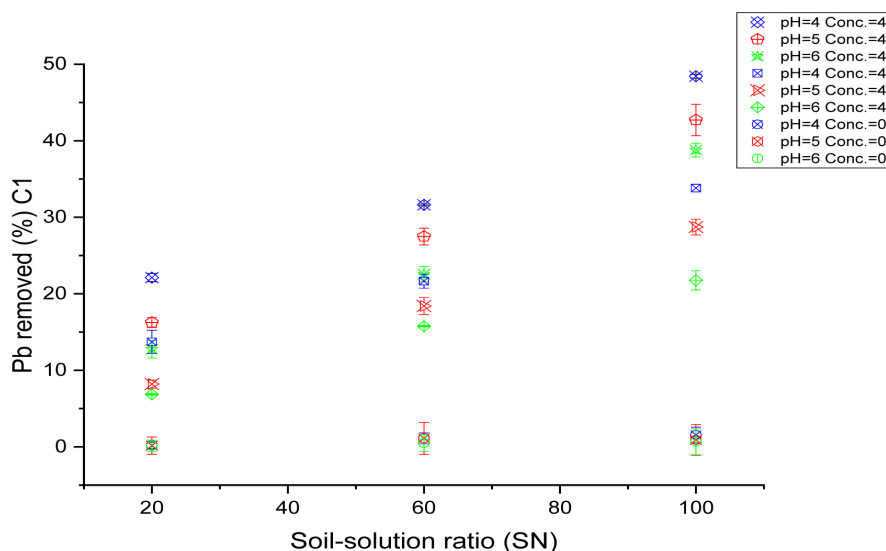**Figure 8.** Effect of soapnut pH on the removal of Pb from contaminated soil (C2)

Figure 9. Effect of soapnut soil-solution ratio on the removal of Pb from contaminated soil (C1)
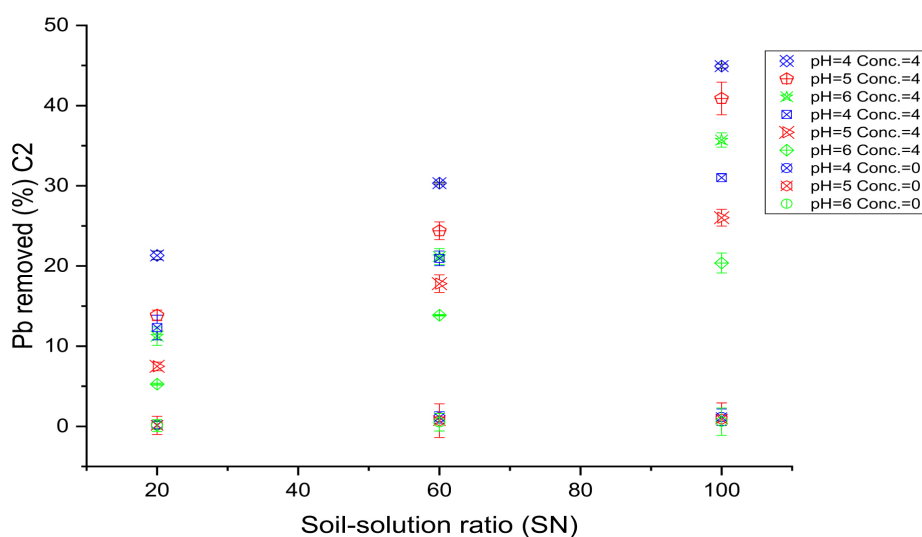

Figure 10. Effect of soapnut soil-solution ratio on the removal of Pb from contaminated soil (C2)

soil-solution ratio resulted in an increase in the amount of Pb removed. At a ratio of 1:100, high removal efficiencies were obtained for all the experiments carried out. Previous studies (Zou et al., 2009, Mukhopadhyay et al., 2015), reported similar increase with higher soil-solution ratios. Zou et al. (2009) suggested using a higher soil-solution ratio, rather than increasing the concentration of the washing solution.

With an increase in the soil-solution ratio, more saponin molecules will be added to the washing solution and more micelles will be formed. This would facilitate the saponin complex formation with metals promoting remediation of soils (Franzetti et al., 2014). In this study, the soil-solution ratio was statistically significant in all the ANOVA for the experiments. There was a significant difference between the Pb removed at

ratio 1:20, 1:60 and 1:100. Previous studies (Zou et al., 2009, Mukhopadhyay et al., 2015), reported similar results. The major reason for studying the influence of the soil-solution ratio is to determine the right amount of the washing solution that will be sufficient to remove the toxic metals from a known quantity of contaminated soil. This is essential for the adequate planning and determination of the operational cost for remediation. In the laboratory scale, this study can help in the modelling and determining the optimum values of the operating variables for satisfactory remediation of a known quantity of contaminated soil.

Influence of multiple washing

Although single extraction could remove Pb from the contaminated soil, the removal
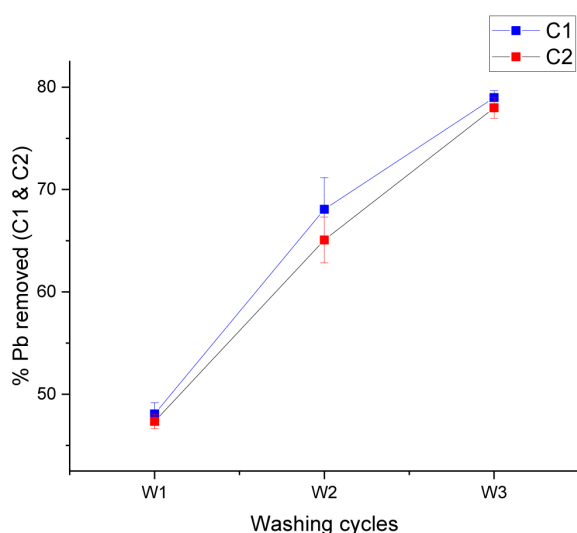
Figure 11. The cumulative percentage of Pb removed from contaminated soils C1 and C2 after triple washings

efficiency by one washing may not be enough to clean-up the contaminated soil. Multiple washing may be more suitable for complete remediation of the contaminated soil (Zou et al., 2009). Mulligan et al. (1999a) performed a series of washings in a bid to clean-up heavy metals from the oil-contaminated soil using biosurfactants. Gusiatin and Klimiuk (2012) studied the removal of copper, cadmium and zinc using multiple washing and stabilization with the help of saponin. Multiple washing was performed in this study to increase the removal efficiency obtained during a single washing. Three series of batch washings were conducted using selected values. These values are pH 4, soil-solution ratio 1:100 and saponin concentration of 4%. After each wash, fresh saponin solution of the same concentration was added to each poly-ethylene tube.

Figure 11 shows the cumulative removal efficiency obtained after three washings of C1 and C2 contaminated soil. It indicates that soapnut saponin removed a cumulative of 79.98% of Pb from the contaminated soil C1 while the cumulative of 77.48% was removed from the contaminated soil C2 after triple washing cycles.

CONCLUSION

The feasibility of using eco-friendly biodegradable saponin to remove the mining and industrial polluted soil was studied. Saponin from soapnut, a plant-based surfactant was investigated for its effectiveness as cleaning agent. The washing parameters studied include: soil-solution ratio, surfactant concentration and pH of the washing solution. The response was measured as the removal efficiency. There was a significant level of influence of the factors studied on the removal efficiency. An increase in the concentration of surfactant and soil-solution ratio resulted in an increase in the removal efficiency, while a decrease in pH of washing solution brought an increase in the Pb removed from the soil.

A single wash of the contaminated soil with soapnut solution could remove up to 48% of lead from the contaminated soil. The performance of multiple washing significantly increased the amount of Pb removed and higher removal efficiencies were recorded. The general performance of the washing liquid indicates that the soapnut utilization in soil washing can be effective and can compete favourably with commonly used chemical reagent. Moreover, the overall performance of the soil washing process demonstrates the potential usage of soapnut saponin in soil remediation of the contaminated soil. Saponin from soapnut is relatively cheap and environment-friendly, compared with the chemical washing agents.

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