

Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil

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Abstract

BACKGROUND: This study explores the possible application of a biodegradable plant based surfactant, obtained from *Sapindus mukorossi*, for washing low levels of arsenic (As) from an iron (Fe) rich soil. Natural association of As(V) with Fe(III) makes the process difficult. Soapnut solution was compared to anionic surfactant sodium dodecyl sulfate (SDS) in down-flow and a newly introduced suction mode for soil column washing.

RESULTS: It was observed that soapnut attained up to 86% efficiency with respect to SDS in removing As. Full factorial design of experiment revealed a very good fit of data. The suction mode generated up to 83 kPa pressure inside column whilst down-flow mode generated a much higher pressure of 214 kPa, thus making the suction mode more efficient. Micellar solubilisation was found to be responsible for As desorption from the soil and it followed 1st order kinetics. Desorption rate coefficient of suction mode was found to be in the range of 0.005 to 0.01, much higher than down-flow mode values. Analysis of the FT-IR data suggested that the soapnut solution did not interact chemically with As, offering an option for reusing the surfactant.

CONCLUSION: Soapnut can be considered as a soil washing agent for removing As even from soil with high Fe content.

Keywords: soil washing; soapnut; *Sapindus mukorossi*; arsenic; plant based surfactant

Abbreviations:

D: Down-flow mode; S: Suction mode; L: Low contaminated soil ; H: High contaminated soil
PV: Pore Volume; SDS: Sodium dodecyl sulphate; SN: Soapnut; As: Arsenic

Introduction

Accumulation of arsenic (As) in soil due to unsafe agricultural practices, mining, smelting, coal burning, wood preservation and illegal waste dumping activities continue to be a serious threat to human health and environment (Tokunaga and Hakuta, 2002). The non-biodegradability of As and its variable mobility under different geochemical processes and soil redox conditions ensure its transformation and continued presence in the soil matrix for a long period of time (Cheng et al., 2009; Craw, 2005). A number of methods have been reported for the treatment of As contaminated soils (Wang and Zhao, 2009). Soil washing by acids, alkaline reagents, phosphates and Bureau of Reference (BCR) three-step sequential extraction procedure are well researched (Alam et al., 2001; Jang et al., 2007; Jang et al., 2005; Ko et al., 2005; Yang et al., 2009). Biosurfactants synthesised by living cells for the removal of toxic metals from soil matrix is also currently being assessed (Chen et al., 2008; Mulligan and Wang, 2006; Polettini et al., 2009; Wang and Mulligan, 2009a). In this research work, a natural surfactant obtained from *Sapindus mukorossi* plant or soapnut has been used to wash low level of arsenic(V) from soil and its performance has been compared with sodium dodecyl sulphate (SDS), an inorganic anionic surfactant. The soil matrix used here has a high level of Fe rich mineral maghemite, which has a good affinity for As(V) (Chowdhury and Yanful, 2010; Yamaguchi et al., 2011). The pollutant removal becomes difficult at lower concentrations (Sundstrom et al., 1989).

Saponin for soil washing

The fruit pericarp of *Sapindus mukorossi* or soapnut is a source of saponin, an effective plant based surfactant (Chen et al., 2008; Song et al., 2008). Soapnut tree is common in Indo-Gangetic plains, Shivaliks and sub-Himalayan tracts. The soapnut fruit pericarp contains triterpenoidal saponin; a natural surfactant that has been used as an environment friendly detergent and medicine for many

decades (Suhagia et al., 2011). Previously, saponin was used for removal of Cd, Zn, Ni and a number of organic pollutants with success (Chen et al., 2008; Kommalapati et al., 1997; Poletini et al., 2009; Roy et al., 1997; Song et al., 2008). The mechanism for pollutant removal involved increase of wettability of the soil by surfactant solution, sorption of the surfactant molecules onto the soil surface, physical or chemical attachment with the pollutant, detachment of the pollutant particle or molecule from the soil into the surfactant solution, and subsequent association with surfactant micelles. However, saponin extracted from soapnut has never been used for removal of soil arsenic, which has entirely different chemical characteristics from the heavy metals. As(V) was used in this study as the pH and redox values in the sampling site as well as in the column favoured the presence of As(V) over As(III) (Dobran and Zagury, 2006; Smedley and Kinniburgh, 2002). Speciation was confirmed by a solvent extraction process. Moreover As(V) is more difficult to remove than As(III), from Fe(III) bearing minerals of soil components (Yamaguchi et al., 2011). The soil sample used in this work contains maghemite, which has a high affinity for As(V) (Chowdhury and Yanful, 2010). Arsenic polluted sites such as mine tailings and agricultural fields contain high level of iron. The intension of using high iron containing soil in this study is to test the efficiency of soapnut solution in such challenging conditions.

Sodium dodecyl sulphate (SDS), an anionic inorganic surfactant has been used by various research groups for soil washing to remove heavy metals and organics (Hernández-Soriano et al., 2011; Torres et al., 2012; Zhang et al., 2007). In this study, SDS has been used to compare the efficiency of soapnut with respect to this widely used anionic surfactant.

The objectives of this research were to study; (i) the performance of the natural surfactant soapnut solution compared to commonly used SDS in washing arsenic from a soil column; (ii) the desorption kinetics and the mechanism of arsenic removal by soapnut solution; and (iii) the advantage of a newly introduced suction mode compared to traditional down-flow mode of column washing.

Materials and methods

Soil sample, surfactants and analytical methods

A composite soil sample was collected from the first layer aquifer in Hulu Langat area, Selangor, Malaysia. The soil was dried in an oven overnight at 105°C and then crushed and passed through a 2 mm sieve (Roy et al., 1997). All soil parameters are measured according to standard procedures as shown in Table 3. XRD analysis was performed by a Panalytical Empyrean diffractometer using Highscore Plus software. As(V) salt ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was used for spiking the soil matrix depending on the Eh and pH of the unspiked soils (Tokunaga and Hakuta, 2002). Although As(V) salt is soluble in water, it binds strongly with Fe(III) minerals and cannot be removed by water alone. The soil was spiked by 50 and 200 mgL^{-1} concentrations of sodium arsenate solution, at room temperature by mixing it for 7 days at a weight: volume ratio of 3:2. In order to increase field relevance and wash away the loosely bound water soluble arsenic, the spiked soil samples were leached with 2 pore volumes of artificial rainwater of pH 5.9 consisting of 5×10^{-4} M CaCl_2 , 5×10^{-4} M $\text{Ca}(\text{NO}_3)_2$, 5×10^{-4} M MgCl_2 , 10^{-4} M Na_2SO_4 , and 10^{-4} M KCl (Oorts et al., 2007). Pore volume for a 300 gm soil column was calculated to be approximately 80 mL which was evaluated by measuring the weight difference between dry and water saturated soil column (Dwarakanath et al., 1999). After this stage, the soils were allowed to drain overnight, then air dried at 25°C for 24 h and sieved through a 2 mm mesh. They were digested following USEPA method 3050B to measure metal contents by ICP-OES (Perkin -Elmer Optima 7000DV). All the samples were analyzed in triplicate and the results were reproducible within $\pm 3.5\%$. Based on some preliminary experiments, 20 mM of SDS, 0.5 and 1% (w/v) of soapnut extractions were selected for the study and were compared against a standard blank sample. All of the surfactant concentrations greatly exceeded the critical micelle concentration (CMC) of the respective surfactants.

The surfactant was extracted from the soapnut fruit pericarp by water (Roy et al., 1997). The CMC and surface tension of surfactants were measured by a ring type surface tensiometer (Fisher Scientific

Manual Model 20 Surface Tensiometer). The functional groups present in the soapnut extract and the effluent solution were characterized by FT-IR spectroscopy (PerkinElmer Spectrum 100 Series) collected in the range of 400–4000 wave numbers (cm^{-1}). Zetasizer Nano ZS series (Malvern Instruments Ltd, UK) was used to measure zeta potential of the soil particles in the presence of different surfactant solutions following the methods reported elsewhere (Mulligan et al., 2001).

Speciation of Arsenic in spiked soil by solvent extraction

Arsenic in the soil spiked with sodium arsenate was speciated by the solvent extraction process (Chappell et al., 1995). This extraction was performed in three steps; first, total As was extracted following Method 3050B, secondly, any trivalent As was extracted from an aliquot of this total As extract in CHCl_3 in a separating funnel and again back extracted into aqueous layer, and thirdly, total inorganic As was determined by adding 50% w/v KI solution with the As extract and then extracting inorganic As by CHCl_3 in a separating funnel. The concentration of As for each solution was determined by ICP-OES.

Design of experiments by full factorial design

A number of factors influencing the soil column washing process have been investigated; viz. the type of surfactant and its concentration, level of As contamination in the soil and the washing mode. A full factorial design was followed to include all possible combinations of the levels across all of these control factors. Design Expert 7.0.0 was used to plan the experiments and to analyze the results. The full factorial design reveals the effect of each factor on the response variable, as well as the interactions between factors on the response variable. In total, 96 experiments were conducted in duplicate in three identical experimental setups. The levels and ranges of the studied process parameters are given in Table 1, and the experimental design is presented in the appendix in Table A1.

Response is recorded in terms of percentage of As removal from the column in each pore volume, defined by the Equation 1.

$$A_{\text{rem}} (\%) \text{ in } N \text{ h P} = \frac{[A]_{\text{effluent}} - [A]_{\text{column}}}{[A]_{\text{column}}} \times 100 \quad (1)$$

where $[As]_{\text{effluent}}$ is the concentration of As in the effluent (mg L^{-1}), As_{column} is the total amount of As in the 300 gm of soil inside the column initially (mg).

Table 1. Control factors and their levels for the experimental design

Control Factors	Coded symbol	No of Levels	Levels					
			1	2	3	4	5	6
Wash solution	A	4	Water	SDS 20 mM	Soapnut 0.5%	Soapnut 1%		
Washing mode	B	2	Down-flow	Suction				
Soil Contamination	C	2	High	Low				
Pore Volume	D	6	PV1	PV2	PV3	PV4	PV5	PV6

Statistical Analysis: ANOVA for As removal in each PV

Analysis of variance (ANOVA) is a general statistical method used for testing the hypothesis that the means among two or more groups are equal. It was used for analysing the data to obtain the interaction among different control factors. After the data was gathered from the experiments, a square root transformation was applied to the data which was then fitted into the 2FI model. Square root transformation was applied on the data because without any transformation, the Coefficient of Variance (CV) came up to be very large, which is unacceptable. Some of the important factors in the ANOVA method are sum of squares (SS), R^2 , adjusted R^2 , P-value and adequate precision (AP). The SS of each control factor quantifies its importance in the process. As the value of the SS increases, the significance of the corresponding factor in the undergoing process also increases. A high R^2 value, close to 1, is desirable to ensure a satisfactory adjustment of the mathematical model to the experimental data. A reasonable agreement of R^2 value with adjusted R^2 value is also necessary (Nordin et al., 2004). Model terms were evaluated by the P-value (P values <0.05 are potentially significant) with 95% confidence level. AP is a type of signal to noise ratio and compares the range of the predicted values at the design points to the average prediction error. AP value greater than 4 indicate adequate model discrimination (Mason et al., 2003).

Column washing procedure

The contaminated soil was packed in a 10 cm long plexiglass column having 5.5 cm internal diameter (Roy et al., 1997). Approximately 300 gm of soil was packed in each column. Circular plexiglass discs with perforations were inserted at 3 cm intervals to distribute the liquid flow and to avoid preferential flow. Arsenic extraction was induced by pumping 6 pore volumes (PV) of flush solution. The packed column was flooded with water from the bottom at the rate of 5 mL min⁻¹ to remove air spaces. Then flushing solution was pumped into the saturated soil column from top to provide wash in a down-flow mode. In the suction mode, flush solution was introduced from the top of the saturated column while a peristaltic pump was attached at the outlet to suck the wash liquid out of the column. The effluent were collected for each PV and As concentrations were measured by ICP-OES. The cumulative As removal was measured after each pore volume by the Equation 2. The pressure drop across the soil column was monitored in both cases. The experimental setup is shown in Fig. 1.

$$C_1 \quad A \quad r \epsilon \quad i \quad N \quad h \quad P \quad (\%) =$$

$$A \quad r \epsilon \quad (\%) i \quad (N - 1) t h \quad P + A \quad r \epsilon \quad (\%) i \quad N \quad h \quad P$$

(2)

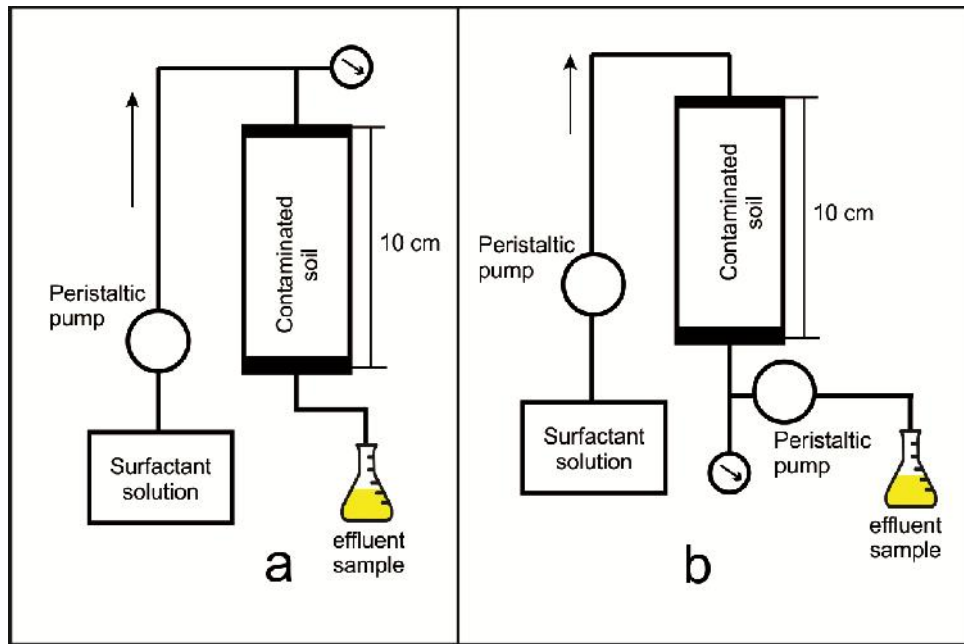


Fig. 1. Schematic diagram of the column washing experiment (a) down-flow mode (b) suction mode

Desorption kinetics

The cumulative concentration of As remaining in the soil column (mg As kg^{-1} soil) was used to plot the kinetics (Sparks et al., 1980). Desorption of As varied with variation in the flow rate of the surfactant. Column washing was performed in continuous mode by 6 pore volumes of wash liquid and effluent samples were collected at different times. The time intervals were noted down accordingly and has been shown in Appendix (Table A2). The time taken for different modes vary due to development of pressure inside the column. The apparent desorption rate coefficient (k'_d) and the order of the processes was determined using Equation 3 (Sivasubramaniam and Talibudeen, 1972).

$$\ln (A_s/A_{s_0}) = - k'_d (t) \quad [3]$$

$$\text{which can also be written as } A_s = A_{s_0} \exp (- k'_d t) \quad [4]$$

Where, A_s is the quantity of As on soil exchange sites at time t of desorption or amount of As in soil column at time t , A_{s_0} is the quantity of As on exchange sites at zero time of desorption or the amount of As in soil column at initial stage before column washing was initiated, and t is time in minutes. The $\ln(A_s/A_{s_0})$ vs. t relationship is linear if the rate of release of As follows first-order kinetics.

Results and discussion

Soil and surfactant characterization

The soil was classified as sandy soil according to USDA soil classification (Table 2). XRD analysis of both spiked and unspiked soils revealed that the soil samples contained Silicon Dioxide as quartz (SiO_2 , XRD displacement 0.158), Magnesium Aluminium Silicate Hydroxide as mica ($(\text{Mg}, \text{Al})_6 (\text{Si}, \text{Al})_4 \text{O}_{10} (\text{OH})_8$, XRD displacement 0.119), Sylvine, sodian ($\text{Cl}_1 \text{K}_{0.9} \text{Na}_{0.1}$, XRD displacement -0.171), Maghemite Q (Isometric $\text{Fe}_{21.333} \text{O}_{32}$, XRD displacement 0.001), feldspar Albite ($\text{Al Na O}_8 \text{Si}_3$, XRD displacement -0.053). The XRD spectrum of the spiked soil is shown in Fig. 2. Arsenic was not

detected in the mineral phase as expected in such low levels as 52.5 mg Kg^{-1} . Table 2 and 3 summarize the characteristics of the soil and surfactants respectively.

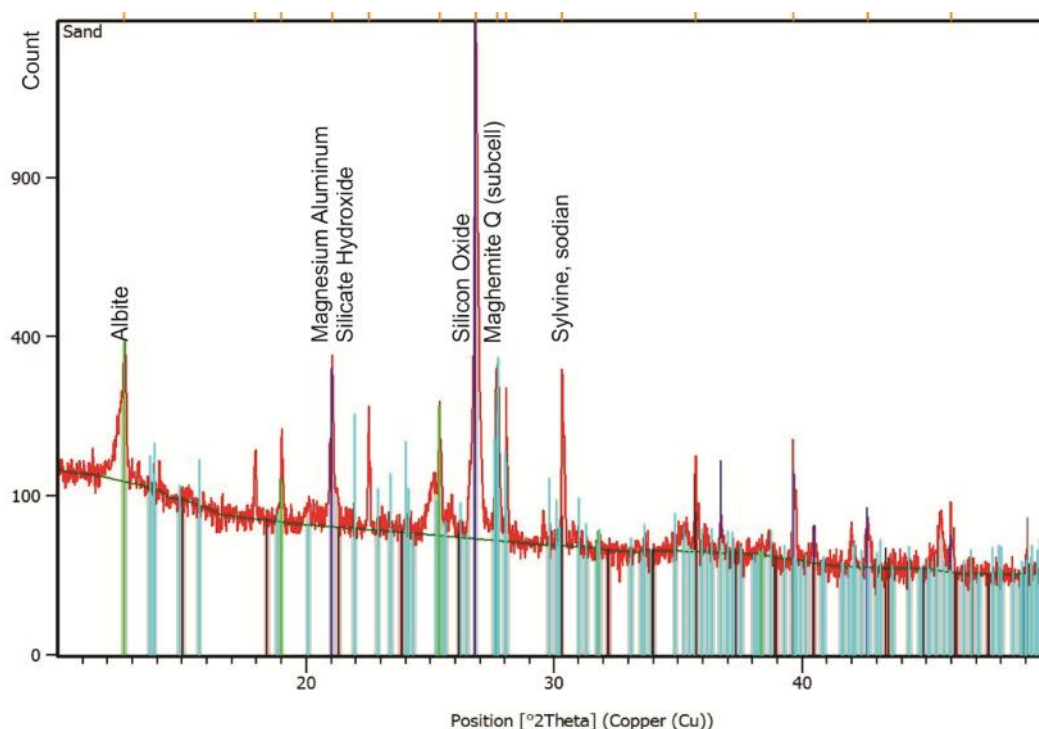


Fig. 2. XRD spectra of the As spiked soil sample (52.5 mg Kg^{-1})

Table 2. Characterization of unspiked and spiked soil

a. Characterization of natural soil sample		
Soil properties	Value	Method
pH	4.5	USEPA SW-846 Method 9045D
Specific Gravity	2.64	ASTM D 854 - Water Pycnometer method
CEC (meq+/100g)	5	Ammonium acetate method for acidic soil (Chapman, 1965)
Organic matter content	0.14 %	Loss of weight on ignition (Storer, 1984)
Bulk Density (gm cc ⁻¹)	2.348	
Total arsenic (mg kg ⁻¹)	3	
Total iron (mg kg ⁻¹)	3719	
Total silicon (mg kg ⁻¹)	~390,00	
Aluminium (mg kg ⁻¹)	0	USEPA 3050B
Total manganese (mg kg ⁻¹)	2400	
Magnesium (mg kg ⁻¹)	185	
Lead (mg kg ⁻¹)	635	
Zinc (mg kg ⁻¹)	11	
	18	
Soil particle size distribution		
Sand (< 50 μm)	92.66 %	Sandy soil according to USDA Soil Classification
Silt (50-2 μm)	5.2 %	
Clay (> 2 μm)	2 %	

b. As speciation in spiked soil

Low Contaminated soil

Total As (mg kg^{-1})	22.6	Solvent extraction (Chappell et al., 1995)
As(III) (mg kg^{-1})	1.7	
As (V) (mg kg^{-1})	20.9	

High Contaminated soil

Total As (mg kg^{-1})	52.5	Solvent extraction (Chappell et al., 1995)
As(III) (mg kg^{-1})	3.4	
As (V) (mg kg^{-1})	49.1	

Table 3: Characterization of extractant

Extractants	Empirical Formula	Molecular Wt	CMC at 25°C	Concentration	Surface Tension (mN m^{-1})	pH	Viscosity (at 25°C) cP
Water	H ₂ O	18	-	-	71.2	7	0.89 cP
Soapnut	C ₅₂ H ₈₄ O ₂₁ ·2H ₂ O	1081.24	0.1%	0.5%	41	4.33	1.1 cP
				1%	40	4.26	1.2 cP
SDS	NaC ₁₂ H ₂₅ SO ₄	288.38	8.2 mM	20 mM	34	7.5	1.4 cP

Arsenic sorption in soil

The soil spiked with 50 mg L^{-1} As solution is found to retain 22.6 mg kg^{-1} of As after washing with artificial rain water of pH 5.9, whilst soil spiked with 200 mg L^{-1} As solution retains 52.5 mg kg^{-1} As. The former is hereby referred to as "low contaminated soil" and the later is referred to as "high contaminated soil". Arsenic is retained in the soil matrix mostly by hydrous oxides of Fe(III) and Al(III) (Jacobs et al., 1970). Arsenic adsorption by soil organic matter and silica are negligible (Wasay et al., 1996; Weng et al., 1997).

The unspiked soil has a pH value of 4.5 and Eh value of 260 mV. According to the revised Eh–pH diagrams for the As–O–H system at 25°C and 1 bar (Lu and Zhu, 2011), arsenic is expected to exist in +5 state under these conditions in aqueous matrices. Hence, aqueous solution of Na₂HAsO₄·7H₂O was used to spike the soil. After spiking and washing the soil, the pH and Eh values of soil were found to be 5.2 and 210 mV respectively. In Fig. 3, the Eh–pH diagram illustrates this scenario; highlighting the initial and final Eh and pH values of both the unspiked and spiked soil samples. A

slight decrease in Eh value in the spiked soil was accompanied by an increase in soil pH value. The As speciation in high and low contaminated soils by solvent extraction confirmed the presence of As(V) species (up to 94% of total As), as shown in Table 2.

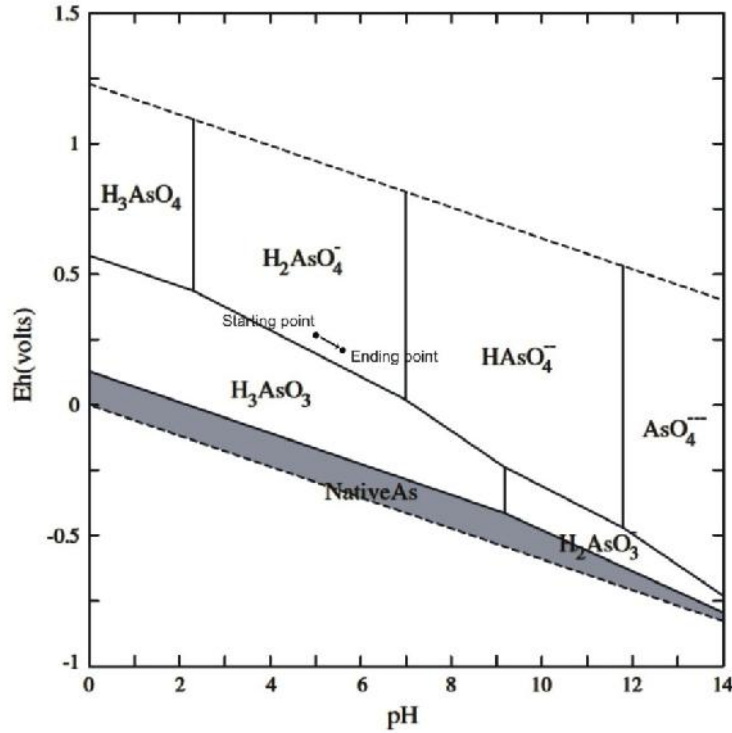


Fig. 3. Initial and final pH and Eh values of contaminated soil during column washing experiment reported in the Eh-pH diagram for the system As-O-H at 25°C and 1 bar with activities of soluble As species = $10^{-6}M$. The revised Eh-pH diagram is taken from Lu and Zhu.(Lu and Zhu, 2011) Gray shaded areas denote solid phases.

Cumulative As removal in down-flow mode and suction mode

The data for cumulative As removal from both low and high contaminated soil columns are provided in Fig 4. The cumulative As removal efficiency was the highest in the presence of 20 mM SDS solution in all four scenarios. SDS 20 mM solution was succeeded by 1% soapnut solution. Conversely, the As removal by 0.5% soapnut solution was considerably low. To account for the water soluble As in the column, it was washed with water which removed a maximum of 6.4% of As in the

low contaminated soil in 6 PVs. Therefore, it is evident that very little water-soluble loosely bound As was present in the soil column, perhaps in As(III) state as indicated by the speciation study. The column washing performances are graphically represented in Figs. 4a-4d. From low contaminated soil in down-flow mode, 20 mM SDS, 1 and 0.5% soapnut solution removed 8.8, 7.2 and 3.8 times more As respectively than that recovered with water. The corresponding values for high contaminated soil in down-flow mode are a factor of 9.8, 7.7 and 4.8 times greater than that recovered with water. The trend was similar in suction modes as well. For the low contaminated soil washed in suction mode with 20 mM SDS, 1 and 0.5% soapnut solution, the respective As removal was 8.7, 7.3 and 4 times more than that recovered with water. The corresponding values for high contaminated soil are a factor of 9.7, 8 and 5.2 times greater than that recovered with water.

Arsenic removal increased significantly when the concentration of soapnut was increased from 0.5 to 1%. For low contaminated soil in down-flow mode, after 6 PVs using 0.5% solution, approximately 1.66 mg of As was recovered compared to 3.1 mg using a 1% solution and 3.6 mg using 20 mM SDS solution. In contrast, the water flood recovered only 0.44 mg As under similar conditions. For high contaminated soil in down-flow mode, 0.5% and 1% soapnut, 20 mM SDS and water flood removed 3.4, 5.36, 6.85 and 0.70 mg of As from the column respectively. From the low spiked soil in suction mode, SDS removed 3.78 mg As, 1% soapnut solution removed 3.17 mg As whilst 0.5% soapnut solution recovered 1.8 mg of As compared to a 0.44 mg with water flood. In the case of the highly spiked soil in suction mode, the corresponding values are 6.74, 5.65, 3.6 and 0.7 mg respectively.

It is clear that with an increase in the concentration of natural surfactant, there is a significant increase in the removal of As from the soil column. This can be explained by the increased solubility of As in the surfactant micelles. Other studies observed that, with an increase in surfactant concentration above CMC, the number of micelles usually increase, resulting in enhanced solubilisation of pollutants, which are easily mobilized and washed from the soil matrix (Mulligan, 2005; Mulligan et al., 1999).

The square root of the percentage of arsenic removal in each pore volume for both down-flow and suction modes has been shown in Fig. A1. The As concentration in the effluent was highest during the initial PVs and continued to decrease in the subsequent washings. Roy et al. (1995) also observed high initial removal of residual transmission fluid from the soil column. This was attributed to any free phase pollutant in the column. Any loosely bound As(V) may get easily detached from the soil particles by the initial spurge of the surfactant having enhanced wettability than water and high micelle forming ability. The later PVs experience extraction of strongly bound As. However, opposite observations were made by other researchers who experienced less removal in initial PVs (Kommalapati et al., 1997; Roy et al., 1997; Wang and Mulligan, 2009b). This might be due to presence of strongly attached pollutants which required higher desorption time to leach out from the soil particles.

The soapnut concentration in the effluent increased after the third or fourth PV, signifying that during the initial stages the extractant solutions underwent adsorption on the soil particles thereby extracting the pollutant by micellar solubilisation. As the washing process progressed, the surfactant absorbance in the soil reached saturation. At the 5th and 6th PV, the concentration of effluent soapnut solution resembled that of influent solution. Roy et al. (1997) also observed that the soapnut concentration was less than the influent in the initial effluents and increased gradually with each pore volume.

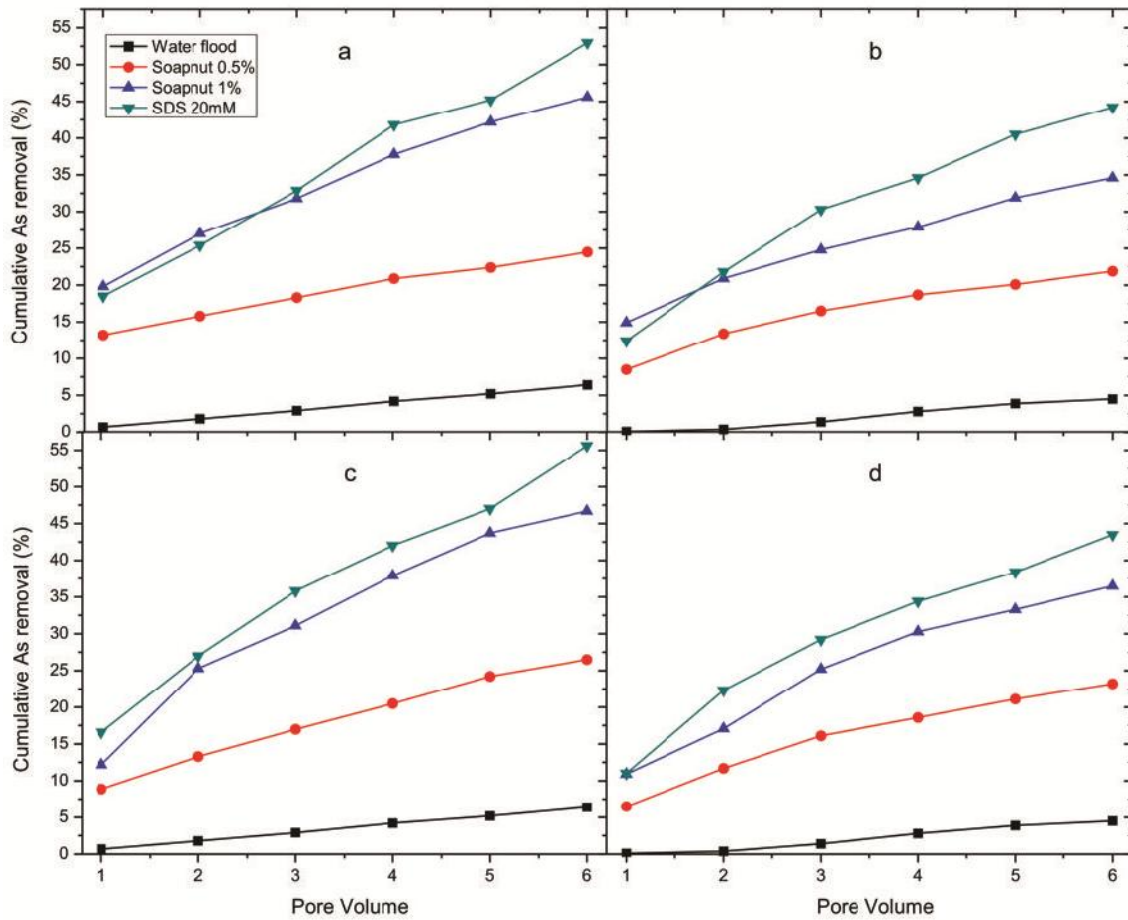


Fig. 4. Cumulative As removal from (a) D, L (b) D, H (c) S, L (d) S, H

Fig. 5 compares the overall performance of all the surfactants. The anionic surfactant SDS was the better extractant. However, soapnut at 1% concentration achieved 78-86% of the performance of SDS under all conditions. Considering that soapnut is an environment friendly biodegradable non-ionic surfactant, this performance is encouraging and it merits further investigation. Washing 1 ton of low level arsenic contaminated soil in the ratio of 300:480 (corresponding to washing of 300 gm soil with 6 PV liquid of 80 mL each) by 1% SN and 20 mM SDS solutions under similar conditions will require 22.86 Kg of soapnut and 9.23 Kg of SDS, both of which will cost roughly 30 USD at the current market price. Preliminary experiments and previously published work indicate that soapnut concentration higher than 1% developed excess pressure inside the column and the process slowed down (Roy et al., 1997).

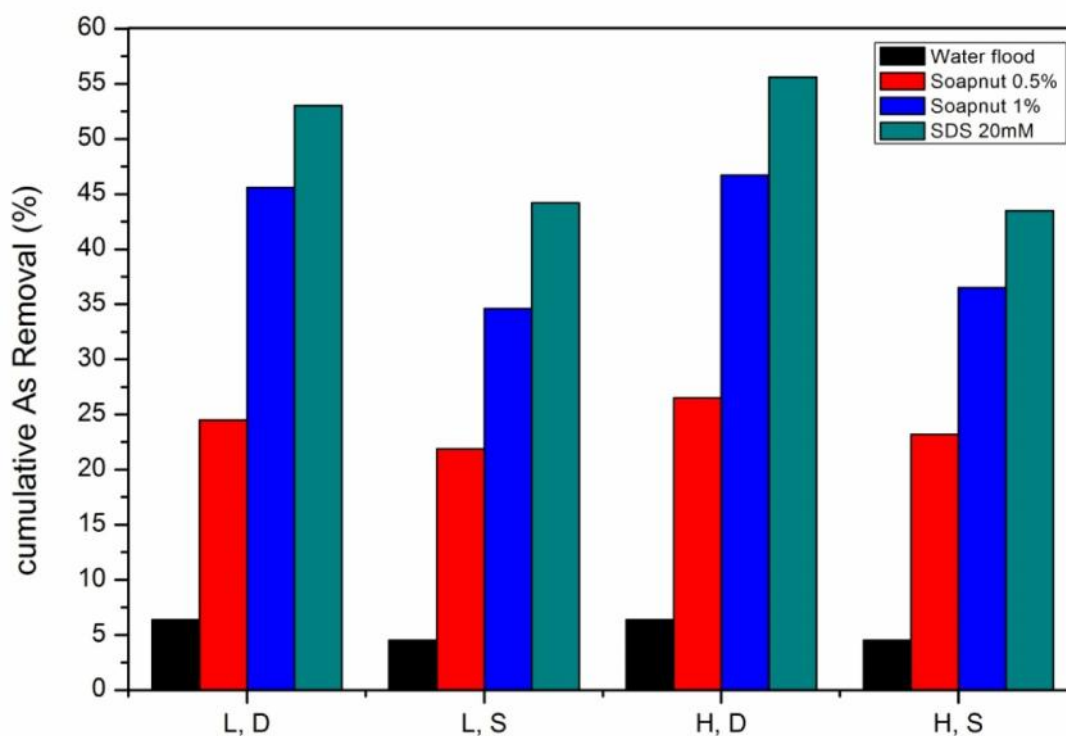


Fig. 5. Comparison of As removal performance by surfactants under different flow modes (L: Low contaminated soil; H: High contaminated soil; S: Suction mode; D: Down-flow mode)

Statistical Analysis: ANOVA for As removal in each PV

Analysis of variance (ANOVA) is shown in Table 4. The F Value for a term is the test for comparing the variance associated with that term with the residual variance. It is the mean square for the term divided by the mean square for the residual. The Model F-value of 38.484 implies the proposed model is significant. There is a 0.01% chance that a "Model F-Value" this large could occur due to noise. Model terms were evaluated by the *P*-value (probability) with 95% confidence level. This is the probability value that is associated with the F Value for this term. It is the probability of getting an F Value of this size if the term did not have an effect on the response. In general, a term that has a probability value less than 0.05 would be considered a significant effect. A probability value greater than 0.10 is generally regarded as not significant. A, C, D, AD, BD, CD are significant model terms. However, the factor B was also included to maintain the hierarchy of the design. The "Pred R-Squared" of 0.891 is in reasonable agreement with the "Adj R-Squared" of 0.933. The AP value of

28.537 indicates an adequate signal fit to be used for navigating the design space. The interaction graphs for sqrt of As removal at different PVs are given in Fig A1. From the normal probability plot of the residuals (Fig. A2) it can be seen that the data points are fairly close to the straight line indicating that the experimental results conform to a normally distributed population (Antony, 2003). Diagnostic plots of predicted versus actual values aids in judging the quality of the model. Table A1 enlists the actual and predicted values of the experimental data points. Figure A3 indicates a good agreement between actual data and data predicted by the model which is not shown here. The overall statistical analysis indicates the robustness of the experimental data.

Table 4: ANOVA for selected factorial model for cumulative As removal

Analysis of variance table [Partial sum of squares]

(Run no 62 was ignored during the analysis due to bad data points)

Source	Sum of Squares	DF	Mean Square	F Value	p-value	
Model	75.57	35	2.159	38.484	< 0.0001	significant
A-wash solution	47.89	3	15.962	284.492	< 0.0001	
B-Washing Mode	0.068	1	0.068	1.216	0.2745	
C-Contamination	1.07	1	1.068	19.033	< 0.0001	
D-Pore Volume	14.17	5	2.835	50.525	< 0.0001	
AD	10.37	15	0.691	12.322	< 0.0001	
BD	0.92	5	0.183	3.265	0.0114	
CD	1.13	5	0.226	4.031	0.0033	
Residual	3.31	59	0.056			
Lack of Fit	3.082	58	0.053	0.232	0.9575	not significant
Pure Error	0.229	1	0.229			
Cor Total	78.88	94				
Std. Dev.	0.237		R-Squared			0.958
Mean	2.015		Adj R-Squared			0.933
C.V. %	11.757		Pred R-Squared			0.891
PRESS	8.575		Adeq Precision			28.537

Pressure build-up in soil column

Table 5 illustrates the variation in pressure development for the surfactant runs for low contaminated soils in both down-flow and suction modes. The pressure build-up was highest for 1% soapnut

solution, followed by 20 mM SDS solution, 0.5% soapnut solution and water. Previous studies also experienced the development of pressure in down-flow mode in the soil column (Kommalapati et al., 1998; Roy et al., 1995). However, for the suction mode, the pressure build-up was much lower than down-flow mode. The maximum pressure build-up recorded by 1% soapnut at the sixth PV was only 83 kPa compared to 214 kPa at down-flow mode, resulting in a much faster operation in down-flow mode. Therefore, a fast process with low pressure development makes the suction mode more advantageous than down-flow mode. The development of higher pressure in down-flow mode resulted from clogging of the soil pores due to a dispersion of colloids and trapping of air bubbles inside the soil pores, which obstructed the flow of flushing solution through the contaminated area, reducing the efficiency of As removal from the soil matrix (Nash, 1987; Roy et al., 1995). Suction mode also produced channelized flow and pore clogging, however the entrapment of air bubbles was negligible due to the suction pressure provided at the outlet. The surfactant solutions easily flowed through the channels to the outlet point without building up undesirable pressure, making the operation easier. The cumulative As removal was similar in both suction and down-flow modes.

Table 5: Pressure build-up in low contaminated soil column

	PV	Pressure build-up (kpa)			
		Water flood	SN 0.5%	SN 1%	SDS 20 mM
Down-flow Mode	1	0	7	21	14
	2	7	21	55	28
	3	10	48	103	55
	4	14	69	131	117
	5	21	90	159	145
	6	34	110	214	193
Suction mode	1	0	7	14	7
	2	7	14	17	14
	3	8	28	28	21
	4	10	31	48	34
	5	12	38	69	62
	6	14	48	83	76

SN: soapnut; PV: pore volume; SDS: sodium dodecyl sulphate

Kinetics of As extraction from soil column

Whilst performing the column washing procedure, the time taken for each PV to pass through the column was recorded. The time increased with each subsequent PV. As_t was calculated from the samples collected at the end of each PV. As_t values are provided in the appendix in Table A2. $\ln(As_t/As_0)$ was plotted against time and the graph showed linearity. This confirmed that the kinetics of desorption phenomenon to be of first order for the entire period of column washing. Table 6 summarizes the k_d' values which ranged from 0.001 to 0.010 min^{-1} . Satisfactory fits were obtained and, with a few exceptions, R^2 values were above 0.9. The k_d' values for suction modes were much higher than down-flow mode due to a faster rate of washing. Whilst down-flow mode took up to 170 mins for passing 6 PV, suction mode took only up to 75 mins of time at the maximum. In general, SDS demonstrated highest k_d' , followed by 1% and 0.5% soapnut solutions.

Table 6: Apparent desorption rate coefficients (k_d') and R^2 for As desorption from the soil columns

		Low contamination		High Contamination	
		k_d'	R^2	k_d'	R^2
Down-flow mode	SN 0.5%	0.001	0.997	0.001	0.964
	SN 1%	0.002	0.978	0.001	0.979
	SDS 20 mM	0.004	0.970	0.003	0.926
Suction mode	SN 0.5%	0.006	0.967	0.005	0.990
	SN 1%	0.008	0.903	0.006	0.900
	SDS 20 mM	0.010	0.948	0.007	0.916

Zeta potential, FT-IR spectral data and mechanism of As removal by soapnut

The zeta potential values of the soil particles were measured in de-ionized water, 20 mM SDS, 0.5% and 1% soapnut solutions and were found to have values of -34.3, -61.8, -17.1 and -11.8 mV respectively. Therefore, in the case of both SDS and soapnut, zeta potential values underwent significant change. Compared to water, the zeta potential decreased significantly for 20 mM SDS, which indicates adsorption of the anionic surfactant SDS on the surface of soil particles. A similar decrease in zeta potential of kaolinite was observed when it sorbed SDS on its already negative basal plane, because of the original negative kaolinite charge plus the negative charge due to sorbed SDS

head groups (Ko et al., 1998). However, the zeta potential value was much higher for soapnut due to the non-ionic tails of saponin molecules, which were adsorbed on the soil particles, thereby reflecting higher zeta potential values. It was postulated that surfactant adsorption is essential for the removal of soil contaminants, and surfactants that adsorb at the soil–water inter-phases are better detergents (Raatz and Härtel, 1996). Therefore, soapnut and SDS, both were adsorbed on soil particle and were effective detergents.

FT-IR spectral data as exhibited in Fig. 6, displayed the differences in average absorbance spectra for the influent and the effluent soapnut solutions, together with the absorption range of different molecular vibrations present in phenolic-OH at 3436 cm^{-1} , carbonyl groups of carboxylic acid at 2092 cm^{-1} and alkene groups at 1642 cm^{-1} , similar to earlier observations (Pradhan and Bhargava, 2008). No shifting of peaks in FT-IR spectra was observed in the soapnut solution in presence of As in the soil column. Similar analysis in UV-Visible frequency range also did not show any shift in the peaks. The UV-Vis spectra are not shown here due to absence of significant observations. Thus in this study, no suggestion of chemical interaction of As with soapnut was obtained. However, earlier works suggested complexation of saponin molecule with heavy metals (Hong et al., 2002; Song et al., 2008). A mechanism for arsenic removal by nonionic soapnut can be proposed as in Fig 7. The nonionic surfactant gets adsorbed onto the soil surface and gets attached to the arsenic by physical force. Arsenic which is in turn adsorbed on soil particle gets detached and goes into the solution and subsequently gets associated with surfactant micelles.

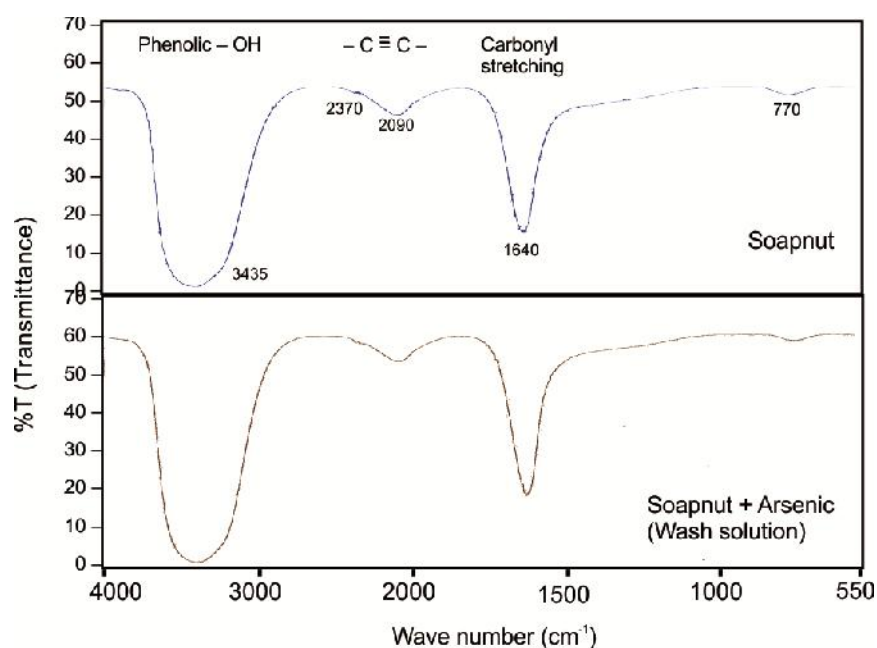


Fig. 6. FT-IR spectra of soapnut solutions before and after washing

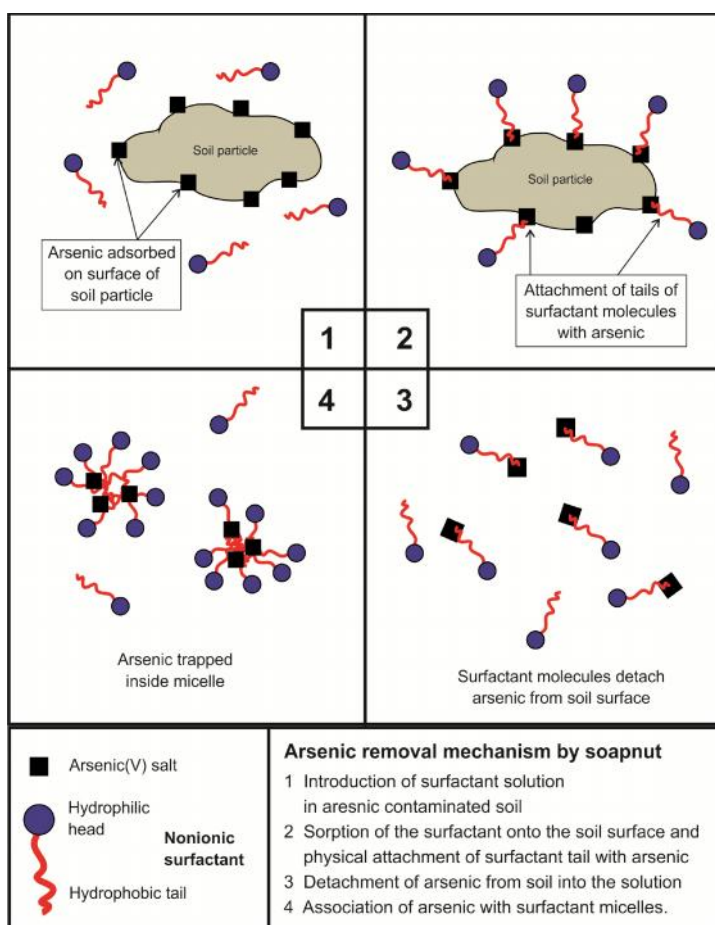


Fig. 7. Mechanism of arsenic removal from soil by soapnut solution

Conclusions

The performance of 1% soapnut solution reached an efficiency of 86% of the performance of 20 mM solution of anionic SDS both in low and high-contaminated soil in down-flow and suction modes. Considering the fact that soapnut is non-ionic, this performance is satisfactory. Arsenic desorption was found to occur mostly by micellar solubilisation following first order kinetics. The low contaminated soil column in suction mode had higher rate constants. A model was proposed for As desorption from each PV by Design expert software and the data fits were satisfactory indicating robustness of the experimental observations. The As removal during initial PVs were high, whilst it decreased during the later PVs in agreement with published literature (Roy et al., 1995). The performance of extractant solutions was similar in both down-flow and suction modes. Suction mode generated up to 50% less pressure inside the column and was more advantageous than the traditional down-flow mode, which experienced significant pore clogging, and air bubble entrapment (Roy et al., 1995). Zeta potential measurements confirmed very weak ionic charge in the hydrophobic tails of soapnut molecules, thus eliminating the ionic interaction mechanism behind As removal by soapnut. Absence of any chemical structure change in the soapnut solution, as evident from the FT-IR and UV-Vis spectra, opens up the possibility of reusing the same soapnut solution after separation of As from the wash liquid. A mechanism for As desorption has also been proposed. From economic perspective, it is estimated that soapnut will cost exactly like SDS under similar conditions of washing.

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Appendix

Table A1. Factorial design matrix of four variables along with experimental and predicted responses for As removal

Diagnostics Case Statistics for As removal (Transform: Square root, Constant: 0.000)							
Run No	A: Wash Solution	B: Washing Mode	C: Soil contamination	D: Pore Volume	Square root of values		
					Observed	Predicted	Residual
1	Water	D	High	PV1	0.32	0.48	-0.16
2	SN 0.5%	D	High	PV1	2.92	2.92	-0.01
3	SN 1%	D	High	PV1	3.86	3.68	0.18
4	SDS 20 mM	D	High	PV1	3.52	3.71	-0.19
5	Water	S	High	PV1	0.32	0.11	0.21
6	SN 0.5%	S	High	PV1	2.55	2.55	0.00
7	SN 1%	S	High	PV1	3.30	3.31	-0.01
8	SDS 20 mM	S	High	PV1	3.32	3.34	-0.02
9	Water	D	Low	PV1	0.84	1.04	-0.21
10	SN 0.5%	D	Low	PV1	3.63	3.49	0.15
11	SN 1%	D	Low	PV1	4.45	4.24	0.21
12	SDS 20 mM	D	Low	PV1	4.30	4.27	0.03
13	Water	S	Low	PV1	0.84	0.67	0.16
14	SN 0.5%	S	Low	PV1	2.98	3.12	-0.13
15	SN 1%	S	Low	PV1	3.49	3.87	-0.38
16	SDS 20 mM	S	Low	PV1	4.07	3.90	0.17
17	Water	D	High	PV2	0.55	0.70	-0.16
18	SN 0.5%	D	High	PV2	2.21	1.96	0.26
19	SN 1%	D	High	PV2	2.45	2.48	-0.03
20	SDS 20 mM	D	High	PV2	3.07	2.97	0.09
21	Water	S	High	PV2	0.55	0.89	-0.34
22	SN 0.5%	S	High	PV2	2.28	2.14	0.14
23	SN 1%	S	High	PV2	2.49	2.66	-0.17
24	SDS 20 mM	S	High	PV2	3.36	3.16	0.20
25	Water	D	Low	PV2	1.05	0.71	0.34
26	SN 0.5%	D	Low	PV2	1.61	1.96	-0.35
27	SN 1%	D	Low	PV2	2.68	2.48	0.20
28	SDS 20 mM	D	Low	PV2	2.63	2.98	-0.35
29	Water	S	Low	PV2	1.05	0.89	0.16
30	SN 0.5%	S	Low	PV2	2.10	2.15	-0.05
31	SN 1%	S	Low	PV2	-	-	-
32	SDS 20 mM	S	Low	PV2	3.22	3.17	0.06
33	Water	D	High	PV3	1.00	0.94	0.06
34	SN 0.5%	D	High	PV3	1.76	1.75	0.01
35	SN 1%	D	High	PV3	1.97	2.27	-0.29
36	SDS 20 mM	D	High	PV3	2.92	2.72	0.19
37	Water	S	High	PV3	1.00	1.15	-0.15
38	SN 0.5%	S	High	PV3	2.10	1.97	0.13
39	SN 1%	S	High	PV3	2.85	2.48	0.36
40	SDS 20 mM	S	High	PV3	2.63	2.94	-0.31
41	Water	D	Low	PV3	1.05	0.90	0.15
42	SN 0.5%	D	Low	PV3	1.58	1.71	-0.13
43	SN 1%	D	Low	PV3	2.19	2.23	-0.04
44	SDS 20 mM	D	Low	PV3	2.74	2.69	0.05
45	Water	S	Low	PV3	1.05	1.11	-0.06
46	SN 0.5%	S	Low	PV3	1.92	1.93	0.00

**Diagnostics Case Statistics for As removal
(Transform: Square root, Constant: 0.000)**

Run No	A: Wash Solution	B: Washing Mode	C: Soil contamination	D: Pore Volume	Square root of values		
					Observed	Predicted	Residual
47	SN 1%	S	Low	PV3	2.41	2.44	-0.03
48	SDS 20 mM	S	Low	PV3	2.97	2.90	0.07
49	Water	D	High	PV4	1.18	0.96	0.22
50	SN 0.5%	D	High	PV4	1.48	1.44	0.05
51	SN 1%	D	High	PV4	1.76	2.07	-0.31
52	SDS 20 mM	D	High	PV4	2.07	2.26	-0.18
53	Water	S	High	PV4	1.18	1.05	0.13
54	SN 0.5%	S	High	PV4	1.58	1.53	0.05
55	SN 1%	S	High	PV4	2.26	2.16	0.10
56	SDS 20 mM	S	High	PV4	2.28	2.35	-0.07
57	Water	D	Low	PV4	1.14	1.27	-0.13
58	SN 0.5%	D	Low	PV4	1.61	1.75	-0.13
59	SN 1%	D	Low	PV4	2.45	2.38	0.07
60	SDS 20 mM	D	Low	PV4	2.98	2.57	0.42
61	Water	S	Low	PV4	1.14	1.36	-0.22
62	SN 0.5%	S	Low	PV4	1.87	1.84	0.03
63	SN 1%	S	Low	PV4	2.61	2.47	0.14
64	SDS 20 mM	S	Low	PV4	2.49	2.66	-0.17
65	Water	D	High	PV5	1.05	0.96	0.09
66	SN 0.5%	D	High	PV5	1.18	1.41	-0.23
67	SN 1%	D	High	PV5	2.00	1.90	0.10
68	SDS 20 mM	D	High	PV5	2.43	2.06	0.37
69	Water	S	High	PV5	1.05	1.05	0.00
70	SN 0.5%	S	High	PV5	1.58	1.50	0.08
71	SN 1%	S	High	PV5	1.73	1.99	-0.26
72	SDS 20 mM	S	High	PV5	2.00	2.15	-0.15
73	Water	D	Low	PV5	1.00	1.00	0.00
74	SN 0.5%	D	Low	PV5	1.22	1.45	-0.23
75	SN 1%	D	Low	PV5	2.10	1.94	0.16
76	SDS 20 mM	D	Low	PV5	1.84	2.10	-0.26
77	Water	S	Low	PV5	1.00	1.09	-0.09
78	SN 0.5%	S	Low	PV5	1.92	1.54	0.38
79	SN 1%	S	Low	PV6	2.41	2.08	0.33
80	SDS 20 mM	S	Low	PV5	2.24	2.19	0.04
81	Water	D	High	PV6	0.77	0.69	0.08
82	SN 0.5%	D	High	PV6	1.34	1.20	0.14
83	SN 1%	D	High	PV6	1.64	1.59	0.05
84	SDS 20 mM	D	High	PV6	1.92	2.24	-0.31
85	Water	S	High	PV6	0.77	0.82	-0.05
86	SN 0.5%	S	High	PV6	1.45	1.33	0.12
87	SN 1%	S	High	PV6	1.79	1.72	0.07
88	SDS 20 mM	S	High	PV6	2.26	2.36	-0.10
89	Water	D	Low	PV6	1.10	1.05	0.05
90	SN 0.5%	D	Low	PV6	1.45	1.55	-0.10
91	SN 1%	D	Low	PV6	1.84	1.95	-0.11
92	SDS 20 mM	D	Low	PV6	2.79	2.59	0.20
93	Water	S	Low	PV6	1.10	1.18	-0.08
94	SN 0.5%	S	Low	PV6	1.52	1.68	-0.16
95	SN 1%	S	Low	PV6	1.73	2.08	-0.34
96	SDS 20 mM	S	Low	PV6	2.93	2.72	0.21

S: Suction; D: Downflow

Table A2: Time and corresponding percentage of As remaining in soil column (As_i)

D, L					D, H			
time	H ₂ O	SN 0.5%	SN 1%	SDS	H ₂ O	SN 0.5%	SN 1%	SDS
10	99.3				99.9			
15	98.2	86.8			99.6	91.5		
20	97.1				98.6			
25	95.8			81.5	97.2			87.6
30	94.8	84.2	80.2		96.1	86.6	85.1	
35				74.6				78.2
40	93.6				95.5			
50		81.7				83.5		
55			73	67.1			79.1	69.7
65		79.1				81.3		
80		77.6				79.9		
90			68.2				75.2	
95		75.5				78.1		
100				58.2				65.4
110			62.2				72.1	
120				54.8				59.5
130			57.8				68.1	
155				47				55.8
170			54.4				65.4	

S, L					S, H			
time	H ₂ O	SN 0.5%	SN 1%	SDS	H ₂ O	SN 0.5%	SN 1%	SDS
10	99.3				99.9			
15	98.2	91.1		83.4	99.6	93.5		89
16	97.1				98.6			
20	95.8				97.2			
21	94.8				96.1			
25	93.6	86.7	87.8	73	95.5	88.3	89.1	77.7
27.5			74.7				82.9	
30				64.2				70.8
35		83	68.9			83.9	74.8	
37.5		79.5				81.4		
40				58				65.6
42.5		75.8				78.9		
50		73.5	62.1			76.8	69.7	
60				53				61.6
65			56.3				66.7	
70				44.4				56.5
75			53.3				63.5	

Interaction Graphs

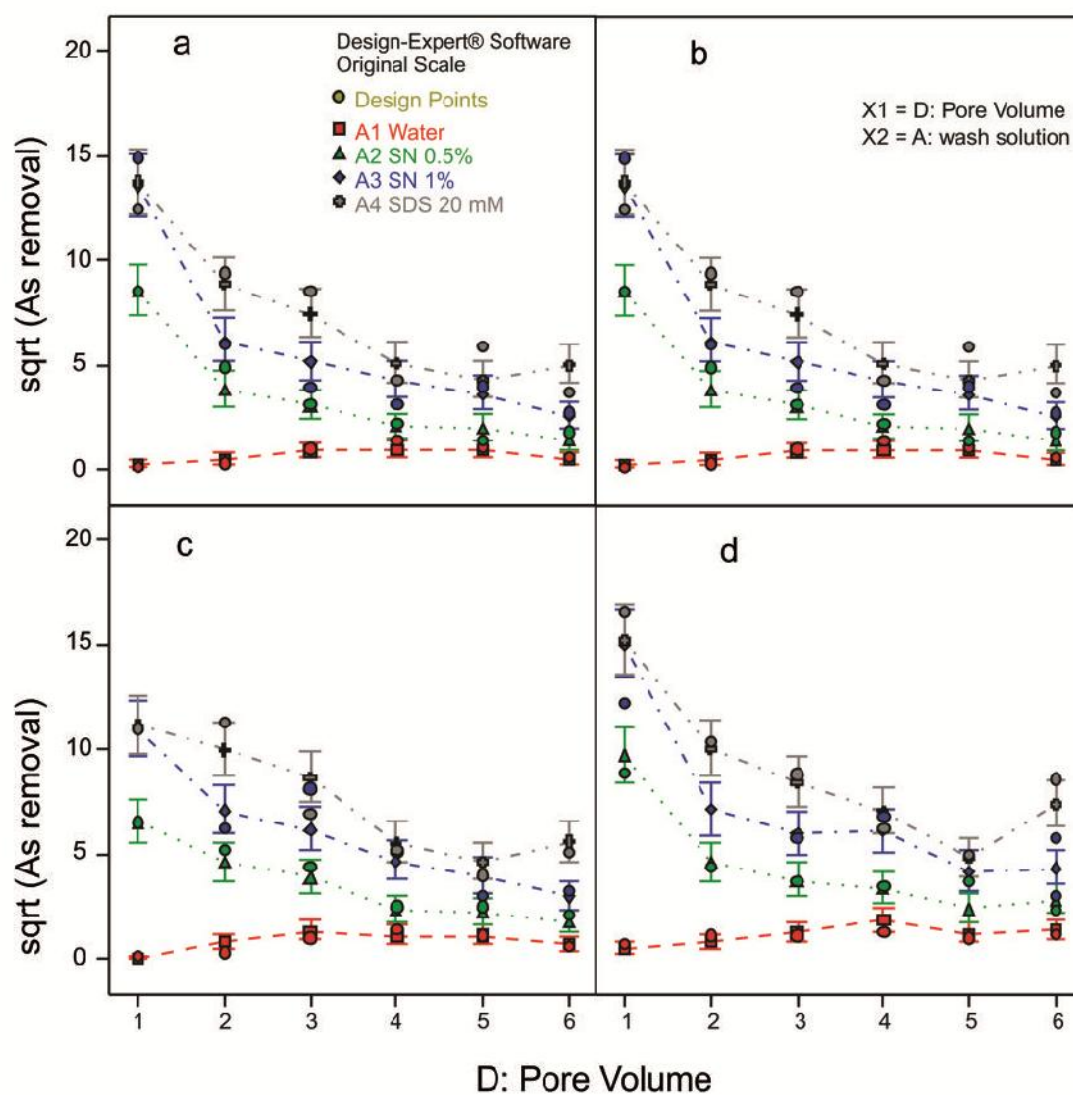


Fig A1: Interaction graph for sqrt(As removal) vs PV for all the extractants (a) D,H (b) D,L (c) S,H (d) S,L

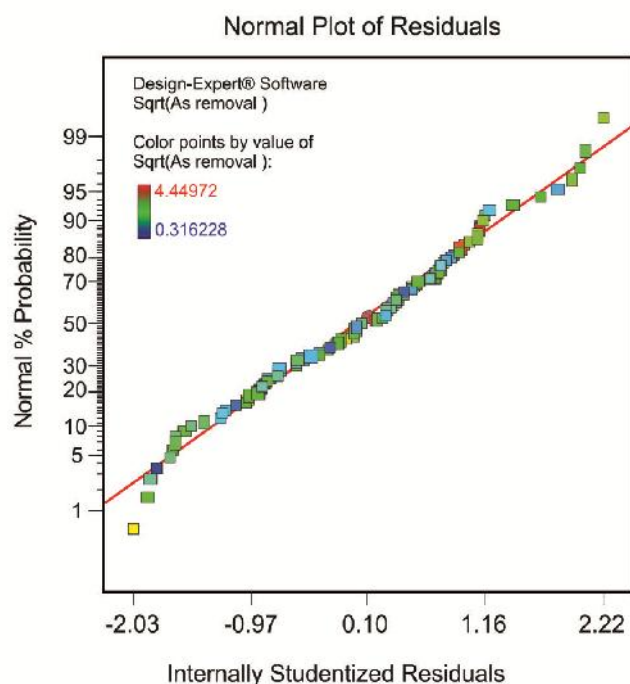


Fig A2: Normal probability plots of residuals for As removal in each PV

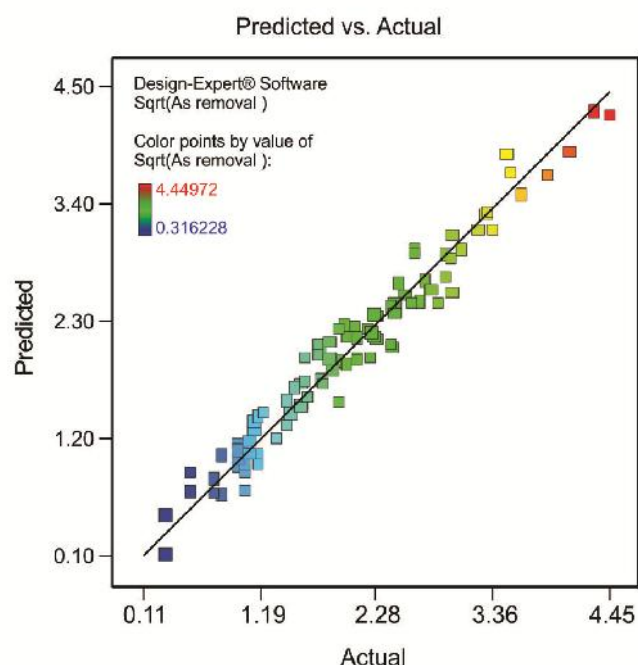


Fig. A3. Design-expert plot: predicted vs. actual values plot for As removal in each PV