Application of colloidal gas aphron suspensions produced from *Sapindus mukorossi* for arsenic removal from contaminated soil

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Abstract

Colloidal gas aphron dispersions (CGAs) can be described as a system of microbubbles suspended homogenously in a liquid matrix. This work examines the performance of CGAs in comparison to surfactant solutions for washing low levels of arsenic from an iron rich soil. Sodium dodecyl sulfate (SDS) and saponin, a biodegradable surfactant, obtained from *Sapindus mukorossi* or soapnut fruit were used for generating CGAs and solutions for soil washing. Column washing experiments were performed in down-flow and up flow modes at a soil pH of 5 and 6 using varying concentration of SDS and soapnut solutions as well as CGAs. Soapnut CGAs removed more than 70% arsenic while SDS CGAs removed up to 55% arsenic from the soil columns in the soil pH range of 5-6. CGAs and solutions showed comparable performances in all the cases. CGAs were more economical since it contains 35% of air by volume, thereby requiring less surfactant. Micellar solubilisation and low pH of soapnut facilitated arsenic desorption from soil column. FT-IR analysis of effluent suggested that soapnut solution did not interact chemically with arsenic thereby facilitating the recovery of soapnut.
solution by precipitating the arsenic. Damage to soil was minimal arsenic confirmed by metal
dissolution from soil surface and SEM micrograph.

Keywords: soil washing; soapnut; Sapindus mukorossi; arsenic; CGAs, microbubbles
1 Introduction

Colloidal gas aphron dispersions (CGAs) can be described as a system of microbubbles suspended homogeneously in a liquid matrix, first described by (Sebba, 1971). CGAs have shown good potential for contaminant separations (Hashim et al., 2012). In this work, solutions and CGAs prepared from a natural surfactant obtained from Sapindus mukorossi, or soapnut plant and sodium dodecyl sulphate (SDS), an inorganic anionic surfactant were used to remove low concentration of arsenic(V) from a soil matrix having high level of iron (Fe) rich mineral maghemite, which has a good affinity for As(V) (Yamaguchi et al., 2011).

Saponin, a natural surfactant was extracted from the pericarp of the soapnut fruit. It has been used as medicine and detergent for many decades (Song et al., 2008; Suhagia et al., 2011). Earlier, Cd, Zn, Ni and a number of organic pollutants were successfully removed by saponin (Kommalapati et al., 1997; Roy et al., 1997; Chen et al., 2008; Song et al., 2008; Polettini et al., 2009). Soapnut is biodegradable as well as non-toxic for soil environment (Kommalapati and Roy, 1997). However, saponin extracted from soapnut has never been used for removal of soil arsenic, which has entirely different chemical characteristics from heavy metals. Arsenic is a known human carcinogen (USEPA, 2001). In soil, arsenic is accumulated through unsafe irrigation and industrial practices such as mining, smelting and illegal waste dumping activities (Tokunaga and Hakuta, 2002). Soil washing by acids, alkaline reagents, surfactants, phosphates and chelates for removing arsenic from contaminated soil have been reported in literature (Jang et al., 2005; Alam and Tokunaga, 2006; Jang et al., 2007; Brammer, 2009; Wang and Mulligan, 2009; Yamaguchi et al., 2011). Removal of toxic metals from soil matrix using biosurfactants is also currently being assessed (Chen et al., 2008; Polettini et al., 2009; Wang and Mulligan, 2009). Surfactants may be used for soil washing in a number of physical forms viz. solution, foams and colloidal gas aphrons (CGAs) (Roy et al., 1995; Wang and Mulligan, 2004).
In this work, low level of arsenic(V) removal has been attempted. It is established that pollutant removal becomes difficult at lower concentrations (Sundstrom et al., 1989). Arsenic(V) from soil containing Fe (III) bearing minerals is much more difficult to remove than As(III) (Yamaguchi et al., 2011). The soil sample used in this work contains maghemite, which has a high affinity for arsenic (V) (Chowdhury and Yanful, 2010). Different concentrations of soapnut solutions and CGAs were compared with a widely used anionic synthetic surfactant Sodium Dodecyl Sulphate (SDS; NaCl$_2$H$_2$SO$_4$) at soil pH of 5 and 6 (Kommalapati et al., 1997). The objectives of this research were to study arsenic removal performance of CGAs in comparison to solutions; effect of surfactant concentration, flow mode and soil pH on the soil washing process; and environment friendliness of the process by measuring the damage to the soil by soapnut solution and recovering soapnut solution after removing arsenic from the effluent.

2 Materials and methods

2.1 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, crushed and passed through a 2 mm sieve (Roy et al., 1997). The soil was then classified according to USDA soil classification. XRD analysis was performed by a Panalytical Empyrean diffractometer using Highscore Plus software. The soil pH was measured by USEPA SW-846 Method 9045D whilst Eh was measured by an ORP electrode following ASTM Method D 1498-93 after preparing the sample by USEPA Method 9045 (SW-846 series) for soil samples. Arsenic(V) salt (Na$_2$HAsO$_4$·7H$_2$O) was used for spiking the soil matrix depending on the Eh and pH of the unspiked soils (Tokunaga and Hakuta, 2002). Although arsenic(V) salt is soluble in water, it binds strongly with Fe (III) minerals and cannot be removed by water alone. The soil was spiked with 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. The arsenic spiked soil samples
were leached with 2 pore volumes of artificial rainwater of pH 5.9 to mimic field leaching conditions (Oorts et al., 2007). Pore volume was calculated to be approximately 80 mL for every 300 gm of soil. The spiked soils were 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 ±3.5%. The soil was classified as sandy soil according to USDA soil classification

\[ K = \frac{R}{a} \left[ \frac{P}{(\rho \times g \times h_t)} \right] \]

where "K" is hydraulic conductivity in cm/sec, "R" is the foam flow rate, "P" is pressure inside column, "\( \rho \)" is density of fluid, "g" is gravitational acceleration, "a" is cross sectional area of column, "ht" is column height.

Table 1a). 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 Aluminum Silicate Hydroxide as mica ((Mg, Al)\(_6\) (Si, Al)\(_4\)O\(_{10}\) (OH)\(_8\), XRD displacement 0.119), Sylvine, sodium (Cl\(_1\)K\(_{0.9}\)Na\(_{0.1}\), XRD displacement -0.171), Maghemite Q (Isometric Fe\(_{21.333}\)O\(_{32}\), XRD displacement 0.001), Feldspar Albite (Al Na O\(_8\) Si\(_3\), XRD displacement -0.053). Arsenic in the spiked soil was speciated by the solvent extraction process (Appendix A) and was found to be in +5 state as shown

\[ K = \frac{R}{a} \left[ \frac{P}{(\rho \times g \times h_t)} \right] \]

where "K" is hydraulic conductivity in cm/sec, "R" is the foam flow rate, "P" is pressure inside column, "\( \rho \)" is density of fluid, "g" is gravitational acceleration, "a" is cross sectional area of column, "ht" is column height.
Table 1(b) (Chappell et al., 1995). Sequential extraction of arsenic from spiked as well as washed soils were performed according to Hall et al. (1996).

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 used exceeded the critical micelle concentration (CMC) of the respective surfactants.

The natural saponin was extracted from the soapnut fruit pericarp by water and found to contain 65% saponin using UV-vis spectrophotometer (Roy et al., 1997). The characteristics of the washing agents are described in

\[ K = \left( \frac{R}{a} \right) \left[ \frac{P}{(\rho X g / h_t)} \right] \]  

where "K" is hydraulic conductivity in cm/sec, "R" is the foam flow rate, "P" is pressure inside column, "\( \rho \)" is density of fluid, "\( g \)" is gravitational acceleration, "\( a \)" is cross sectional area of column, "\( h_t \)" is column height.

Table 1. CGAs were generated from surfactant solutions by stirring them at 7000 rpm by an IKA T50 homogenizer for 5 minutes. The functional groups present in the soapnut extract and the effluent solution were characterized by FT-IR spectroscopy (PerkinElmer Spectrum 100 Series). Zetasizer Nano ZS (Malvern) was used to measure zeta potential of the soil particles in the presence of different surfactant solutions (Mulligan et al., 2001). The average hydraulic conductivity of the CGAs was calculated for all surfactant concentrations based on Darcy's equation for the various pressure readings and flow rates as shown in Equation 1 (Mulligan and Wang, 2006)

\[ K = \left( \frac{R}{a} \right) \left[ \frac{P}{(\rho X g / h_t)} \right] \]  

(1)
where "K" is hydraulic conductivity in cm/sec, "R" is the foam flow rate, "P" is pressure inside column, "ρ" is density of fluid, "g" is gravitational acceleration, "a" is cross sectional area of column, "ht" is column height.

Table 1: (a) Characterization of unspiked soil (b) arsenic speciation in spiked soil and (c) characterization of washing agents

<table>
<thead>
<tr>
<th>a. Characterization of natural soil sample</th>
<th>Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.5</td>
<td>USEPA SW-846 Method 9045D</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.64</td>
<td>ASTM D 854 - Water Pycnometer method</td>
</tr>
<tr>
<td>CEC (Meq)</td>
<td>5</td>
<td>Ammonium acetate method for acidic soil (Chapman, 1965)</td>
</tr>
<tr>
<td>Organic matter content</td>
<td>0.14 %</td>
<td>Loss of weight on ignition (Storer, 1984)</td>
</tr>
<tr>
<td>Bulk Density (gm cc⁻¹)</td>
<td>1.45</td>
<td>(Di Palma et al., 2003)</td>
</tr>
<tr>
<td>Total porosity (%)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Total arsenic (mg kg⁻¹)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Total iron (mg kg⁻¹)</td>
<td>3719</td>
<td></td>
</tr>
<tr>
<td>Total silicon (mg kg⁻¹)</td>
<td>~390,000</td>
<td></td>
</tr>
<tr>
<td>Aluminium (mg kg⁻¹)</td>
<td>2400</td>
<td></td>
</tr>
<tr>
<td>Total manganese (mg kg⁻¹)</td>
<td>185</td>
<td>USEPA 3050B</td>
</tr>
<tr>
<td>Magnesium (mg kg⁻¹)</td>
<td>635</td>
<td></td>
</tr>
<tr>
<td>Lead (mg kg⁻¹)</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Zinc (mg kg⁻¹)</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Soil particle size distribution</td>
<td></td>
<td></td>
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<tr>
<td>Sand (&lt; 50 μm)</td>
<td>92.66 %</td>
<td>Sandy soil according to USDA Soil Classification</td>
</tr>
<tr>
<td>Silt (50-2 μm)</td>
<td>5.2 %</td>
<td></td>
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<tr>
<td>Clay (&gt; 2 μm)</td>
<td>2 %</td>
<td></td>
</tr>
</tbody>
</table>

| b. arsenic speciation in spiked soil     |       | |
| Total arsenic (mg kg⁻¹)                  | 85.63 | Solvent extraction (Chappell et al., 1995) |
| As (III) (mg kg⁻¹)                       | 2.65  | |
| As (V) (mg kg⁻¹)                         | 82.98 | |

c. Characterization of wash agents        |       | |

<table>
<thead>
<tr>
<th>washing agents</th>
<th>Empirical Formula</th>
<th>Molecular Wt</th>
<th>CMC at 25°C</th>
<th>Concentration</th>
<th>Surface Tension (mN m⁻¹)</th>
<th>pH</th>
<th>Viscosity (at 25°C) cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>71.2</td>
<td>7</td>
<td>0.89 cP</td>
</tr>
<tr>
<td>Soapnut</td>
<td>C₅₂H₆₄O₂₁₂H₂O</td>
<td>1081.24</td>
<td>0.1%</td>
<td>0.5%</td>
<td>41</td>
<td>4.33</td>
<td>1.1 cP</td>
</tr>
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<td></td>
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<td></td>
</tr>
<tr>
<td>SDS</td>
<td>NaC₃₂H₃₅SO₄</td>
<td>288.38</td>
<td>8.2 mM</td>
<td>20 mM</td>
<td>3</td>
<td>7.5</td>
<td>1.4 cP</td>
</tr>
</tbody>
</table>

2.2 Column washing experiments

The 10 cm long section of contaminated soil was packed in a 15 cm long plexiglass column having 5.5 cm internal diameter (Roy et al., 1997). Approximately 300 gm of soil could be packed in each
column. Coarse sands were packed on top and bottom of the soil column for even distribution of the flow. Circular plexiglass discs with perforations were inserted at 3 cm intervals to avoid preferential flow pathways. The porosity of the packed column was calculated as 39% (Wasay et al., 2001). The packed column was flooded with water from the bottom at the rate of 5 mL min\(^{-1}\) to remove air spaces. Arsenic desorption from column was then induced by pumping 6 pore volumes (PV \(\sim\) 80 mL) of surfactant solution or CGAs, at a constant flow rate of 10 mL min\(^{-1}\) by a peristaltic pump in down-flow and up flow modes. The eluted samples were collected for each PV and arsenic concentrations were measured by ICP-OES. The scheme of experiment has been shown in Figure 1(a).

2.3 Sustainability of the process

Damage to soil caused by soapnut and SDS was investigated by washing 10 gm of arsenic contaminated soil with 200 ml washing agents for 6 hours. The wash solutions were analyzed for Ca, Mg, Si, Fe, Al to check for any structural damage of soil following (Zeng et al., 2008). Change in soil surface morphology by 1.5% soapnut washing was analyzed by SEM. Coagulation-flocculation process was used for separating arsenic from soapnut wash effluents (Jang et al., 2005). Jar tests were performed with 200 mL of 0.5, 1 and 1.5% soapnut solutions containing 10 mg/L arsenic in 500 mL beakers by adding different doses of FeCl\(_3\). The pH of soapnut solutions were adjusted by HCl or NaOH. The mixing sequence was 1 min of rapid mixing at 120 rpm, 30 min of slow mixing at 40 rpm, followed by 30 min of settling. At the end of the settling period, samples are taken from supernatants using a 0.45 \(\mu\)m pore size membrane filter and analyzed for arsenic content in ICP-OES.

3 Results and discussion
3.1 Propagation of CGA through soil column

CGAs prepared from different concentrations of surfactants were injected into the soil column to determine the pressure build-up and their hydraulic conductivities at various flow rates. Pressure build-up in columns resulted from clogging of the soil pores due to dispersion of colloids and trapping of air bubbles inside the soil pores. These obstructed the flow of flushing solution through the contaminated area, reducing the efficiency of pollutant removal from the soil matrix (Roy et al., 1995). Increasing the flow rates from 10 mLmin\(^{-1}\) to 20 mLmin\(^{-1}\) increased the pressure gradient in an almost linear fashion for 0.5, 1 and 1.5% soapnut solutions (Figure A1). Other researchers recommended that, flow rate should not exceed 10 to 15 mLmin\(^{-1}\) for maintaining lower pressure gradient in the column (Mulligan and Eftekhari, 2003). Accordingly, the flow rates were maintained at 10 mLmin\(^{-1}\) for the remaining experiments. Hydraulic conductivity followed exactly opposite trend of pressure gradient and it increased with higher flow rate.

3.2 Cumulative arsenic removal by soapnut solution and CGA

There are a number of factors influencing the arsenic removal efficiency such as soil pH, flow modes and concentration of surfactant and physical state of surfactants (CGAs and solution). The effect of all these factors has been discussed separately. Six pore volumes of water were used as blank at soil pH 5 and 6. It was observed that water could remove only up to 23% arsenic at pH5 in up flow mode (Figure 1b). Other flow modes removed even less amount of arsenic indicating strong bonding in the soil column. Therefore, additional reagents were necessary to remove rest of the arsenic. 1% soapnut solution and CGAs removed 3 to 4 times more arsenic (up to 71%) than water flood. Solutions and CGAs of 20 mM SDS solutions removed much less arsenic (up to only 46%) compared to soapnut, possibly due to higher pH of 10 which did not favour arsenic solubilisation. No further comparisons between SDS and soapnut are done since SDS does not match up against soapnut.
Figure 1: (a) Scheme of experiment, (b) Comparison of Arsenic removal performance by CGAs and solutions under different flow modes at pH 5 and 6 at 1% soapnut concentration; (c) Arsenic removal in up flow and down flow modes by solution and CGAs prepared from 1% soapnut at pH 5 and pH 6; (d) Arsenic removal in different flow modes by Down flow and Up flow modes by CGAs and solutions with 1% soapnut and 20mM SDS at pH 5 and 6; (e) Arsenic removal in different surfactant concentrations at pH 5 (Soapnut: L=0.5%, H=1%; SDS: L=10mM, H=20mM) (with standard errors)

3.2.1 CGAs vs solution

The cumulative arsenic removal efficiency by CGA and solution of soapnut and SDS are shown in Figure 1(c). There was no clear winner among solution and CGAs. The performance of solution was much better than CGAs in up flow mode at pH 5 where soapnut CGAs removed 45.42% arsenic while soapnut solution removed 60%. The scenario was different at pH 5 soil in down flow mode...
where soapnut CGAs removed 71% arsenic compared to 63% by soapnut solution. In the case of SDS at soil pH of 5 at up flow mode, CGAs removed 30% arsenic and solution removed 46%. But for down flow mode at pH5, SDS CGAs and solutions removed 44.68 and 33.87% arsenic respectively. So, it can be concluded that both CGAs and solution had comparable performances. In the experiments involving CGAs, it was seen to perform better in up flow modes rather than down flow mode. It is understandable due to the higher buoyancy of the microbubbles of CGAs when they are introduced from the bottom of the column. However, it should be noted that 1 PV of CGAs actually contained only 65% of surfactant solution and 35% air, while surfactant solutions had no air content. So, CGAs are more economical compared to solutions.

3.2.2 Dependency on Flow modes

The arsenic removal also depends heavily upon the mode of flow of wash solutions. In these experiments, two different wash modes were used, viz down flow and up flow modes in soil pH of 6. In down flow mode, CGAs are pumped from the top of the column and forced to come out from the bottom of the column. CGAs resist the process due to high buoyancy of the constituent microbubbles, thus resulting in some pressure gradient. In this mode, only 38% arsenic removal could be obtained using soapnut and 31% by SDS CGAs. This is shown in Figure 1(d). However, solutions of the same agents enjoyed a clear advantage due to the assistance of gravity that drags the liquid down the column. The arsenic removal by soapnut and SDS solutions are 60 and 47.5% respectively, which are much better than that with CGAs in down flow mode. In down flow mode, minute channels are formed inside the column through which the solution and CGAs flow conveniently, missing out a large part of the contaminated soil matrix. In the up flow mode, both solutions and CGAs are introduced from the bottom of the column and the effluent are collected from the top after they rise through the column. In this mode, the CGAs and solutions performed equally well. The CGAs, due to higher air content and higher buoyancy, have a tendency to rise up in a flooded column when introduced from the bottom. Air pockets are less likely to form. Although
higher pressure was developed in this mode of washing, the arsenic removal was better for up flow
by both CGAs and solutions compared to down flow mode. CGAs of soapnut and SDS removed 65.5
and 35.4% arsenic respectively and the corresponding values for the solutions are 71 and 42%
respectively. Thus, up flow mode is found to be the better performer than down flow mode and both
CGAs and solutions had comparable performance in up flow mode. Similar trends are observed in
soil of pH 5.

3.2.3 Dependency on surfactant concentrations

The arsenic removal also increased with the concentration of surfactant in wash solution and CGAs.
Figure 1(e) shows arsenic removal by CGAs and solutions of high and low concentration surfactant
solutions in down flow mode at pH 6. Except for soapnut CGAs in down flow mode, all the other
CGAs and solutions experienced better removal at higher concentration of surfactant. Similar to the
down flow mode, all the surfactant CGAs and solutions showed better result at higher concentration
due to increase in the number of micelles (Mulligan, 2005).

3.2.4 Cumulative arsenic removal in subsequent pore volumes

Cumulative arsenic removal by the low concentration surfactant solutions and CGAs from soil of pH
6 in subsequent pore volumes in down flow mode was calculated (data not shown). In most cases,
more arsenic was removed during the initial pore volumes than the final pore volumes. Roy et al.
(1995) attributed the initial higher pollutant removal to any free phase pollutant in the column. Any
loosely bound arsenic(V) will easily detach from the soil particles by the initial spurge of the
surfactant. In the later pore volumes, new channels opened up while old channels close down to
remove arsenic from a virgin area. Thus sometimes more arsenic was removed during the
intermediate pore volumes. However, it was observed that cumulative arsenic removal increased
linearly in subsequent pore volumes. The $R^2$ values of the linear trend lines are above 0.9 in all the
cases. The soapnut concentration in the effluent increased after the third or fourth PV, signifying that
during the initial stages, the washing agent underwent adsorption on the soil particles thereby extracting the pollutant by micellar solubilisation. Earlier, it was postulated that adsorption of surfactant on soil particle 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).

3.3 Sequential extraction of arsenic

\[ K = \frac{R}{a}/\left[\frac{P \times g}{ht}\right] \]

In arsenic contaminated soil having chemical composition as described in

\begin{equation}
K = \frac{R}{a}/\left[\frac{P \times g}{ht}\right]
\end{equation}

where "K" is hydraulic conductivity in cm/sec, "R" is the foam flow rate, "P" is pressure inside column, "p" is density of fluid, "g" is gravitational acceleration, "a" is cross sectional area of column, "ht" is column height.

Table 1, arsenic(V) is retained mainly in amphoteric ferric oxy-hydroxide (Am-Fe-ox), adsorbed-exchangeable-carbonate(AEC) fraction and crystalline Fe oxide (Cry-Fe-ox) fractions (Figure A2). Other fractions such as sulphide and organics fraction and residual fraction had very little amount of arsenic(V). The AEC fraction is the easiest to remove and both SDS and soapnut removed almost all of it. By 20mM SDS treatment, 47.43% of As(V) was extracted and the remaining arsenic in the soil was fractionated into 43.87% Am-Fe-ox form, 6.47% in Cry-Fe-ox form. After 1% soapnut treatment, 31.36% arsenic remained in Am-Fe-ox form and 4.36% in Cry-Fe-ox form. So soapnut was able to extract highest amount of arsenic(V) from the Am-Fe-oxide hydroxides and was the better washing agent.

3.4 Zeta potential and FT-IR spectral data

The zeta potential values of the soil particles in de-ionized water, 20 mM SDS, 0.5% and 1% soapnut solutions are -34.3, -61.8, -17.1 and -11.8 mV respectively. In comparison to water, the zeta potential
decreased significantly for 20 mM SDS. This signifies that the anionic molecules of SDS adsorbed on the surface of soil particles, imparting them a much lower charge of -61.8 mV. Both soapnut and SDS are prospective detergents for soil washing, while arsenic cations are more likely to get attached to the anionic heads of SDS. Soapnut solution performs better due to lower operating pH of 4.5 that helps to desorb arsenic from soil.

FT-IR spectral data shown in Figure 2(a) displays the absorbance spectra for the influent and the effluent soapnut solutions. 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\(^{-1}\) are observed and are similar to earlier findings (Pradhan and Bhargava, 2008). No shifting of peaks in FT-IR spectra was observed in the effluent soapnut solution in presence of arsenic compared to influent soapnut solution. Although earlier works suggested complexation of saponin molecule with heavy metals (Hong et al., 2002; Song et al., 2008), no chemical interaction of saponin and arsenic is observed in this work.

3.5 Damage to soil

SEM image in Figure 2(b) shows the surface morphology of the arsenic contaminated soil before and after treating with 1% soapnut solution for 6 hours in a shake flask, at a 10000 X magnification. It can be observed that the soil before washing contained finer particles on a smooth underlying surface, which are absent after washing while the smooth surface is exposed. Slight roughness of the underlying smooth surface is also observed after soapnut washing. However, the corrosion is not very high as indicated by the Table A1 which indicates that the amount of structural elements such as Ca, Mg, Fe, Al and Si leached in the wash solution after 6 hours of vigorous shaking. In this case, no considerable metal leaching was detected. With 1.5% soapnut solution, 1.95% Ca, 2.02% Mg and 0.44% Fe leached out. This indicates negligible chemical withering.
Figure 2: (a) FT-IR spectra of influent & effluent soapnut solutions, (b) SEM micrographs of soil matrix before and after washing with 1% soapnut solution

3.6 Recovery of wash solution

In earlier research, ferric chloride was found to be the best precipitating agent for arsenic (Bilici Baskan and Pala, 2010; Donmez and Akbal, 2011). Coagulation process has been used for removing soluble arsenic from soapnut solution at different pH under different ferric chloride dose. The probable mechanism of co-precipitation of arsenic with Fe(III) is shown in Equations 2 and 3.

\[
\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe(OH)}_3\text{Cl}_2^+ + 3\text{H}^+ + 3\text{Cl}^- \tag{2}
\]

\[
\text{H}_2\text{AsO}_4 + \text{Fe(OH)}_3 \rightarrow \text{Fe-As complex} \tag{3}
\]
The amorphous Fe-As complex is most stable in the pH range of 6-8 (Donmez and Akbal, 2011). Accordingly, arsenic removal efficiency with FeCl$_3$ is maximum in the pH range of 7-8. At pH of 8 with 15 mgL$^{-1}$ of ferric chloride, up to 87% of the arsenic is removed from the soapnut. However, after 8-10 mgL$^{-1}$ dose of ferric chloride, the improvement in arsenic removal does not increase too much, in agreement with earlier publications (Jang et al., 2005; Donmez and Akbal, 2011). Moreover, arsenic removal below pH of 7 and above pH of 8 are comparatively low, in the range of 60-70%.

### 4 Conclusions

Soapnut solutions and CGAs are able to remove low level arsenic residues from soil. Inorganic surfactant SDS showed poor performance in comparison to soapnut due to higher pH of 10 which did not favour arsenic solubilisation. Soapnut CGAs and solutions showed comparable performances. However CGAs comprises up to 35% of its volume of air indicating their economic advantage over solutions. Flow mode and soapnut concentration were main influential parameters. Soil pH had little influence on the process. Arsenic removal is highest in up flow mode for both CGAs and solutions and the CGAs of 1% soapnut removed 71% arsenic from soil of pH 5. CGAs prepared from high concentration soapnut solution showed better arsenic removal due to higher air hold-up which exposes more interfacial area, facilitating mass transfer. Solution of lower concentration performed better due to higher penetration for lower viscosity. Zeta potential values showed that soapnut is adsorbed on soil particles and possess the quality of being an effective detergent. From FT-IR spectra, no evidence of chemical complexation of saponin molecules and arsenic can be found. The SEM image of the soapnut washed soil reveals no major corrosion of the soil particles and negligible amount of Ca, Mg, Fe, Al and Si leached out in soapnut wash solution, indicating minimal soil damage. Soapnut solution could be recovered from the wash effluent with 8-10 mgL$^{-1}$ of ferric chloride at the pH of 8 by coagulation-flocculation-precipitation process. Soapnut
CGAs can be a safe, efficient and economical means to remediate sub-surface arsenic-contaminated soil.

Acknowledgements

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References


Appendix A: Chappell’s Speciation of Arsenic in soil (Chappell, et al., 1995)

Extraction of total arsenic from soil

Arsenic was removed from the soil by treating with concentrated hydrochloric acid. A 5 g sample of soil was accurately weighed into a centrifuge tube and 20 mL of 10M hydrochloric acid was added. The extraction was assisted by shaking vigorously for about 30 min. The resulting slurry was centrifuged at 3000 r.p.m. for approximately 5 min and the supernatant was gravity filtered (Whatman 44) into a 100 mL volumetric flask. This procedure was repeated a further two times on the same 5 g sample of soil. When the extraction was complete, the soil was washed into the filter paper with water and the solution diluted.

Speciation of trivalent arsenic

A 10 mL aliquot of the arsenic extract was transferred to a 100 mL separating funnel and 80 mL of 10M hydrochloric acid was added, adjusting the acid concentration to greater than 9M. This was followed by extraction of arsenic(III) into chloroform with 4 x 10 mL washings. At this stage the strongly acidic aqueous phase was discarded. The arsenic was then back-extracted from the organic phase into2 x 20 mL aliquots of water and diluted to 100 ml.

Amount of pentavalent arsenic = Total arsenic - Trivalent arsenic
Table A1: Metal dissolution from washed soil

<table>
<thead>
<tr>
<th>Washing agent</th>
<th>Conc</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soapnut 1%</td>
<td>1.82</td>
<td>1.96</td>
<td>0.43</td>
<td>0.44</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Soapnut 1.5%</td>
<td>1.95</td>
<td>2.02</td>
<td>0.44</td>
<td>0.48</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>SDS 30 mM</td>
<td>0.35</td>
<td>1.02</td>
<td>0.17</td>
<td>0.21</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

Figure A1: (a) Pressure build-up in the soil column as a function of flow mode and CGAs flow rate (b) Hydraulic conductivity through the soil column as a function of flow mode and CGAs flow rate, SN: soapnut (with standard error)
Figure A2: Sequential extraction of As(V) following Hall et al. (1996) The following are represented
- AEC: adsorbed-exchangeable-carbonate fraction; Cry-Fe ox: Crystalline Fe oxide, Am-Fe ox: Amphoteric Fe oxide.