

1 Application of colloidal gas aphron suspensions produced from 2 *Sapindus mukorossi* for arsenic removal from contaminated soil

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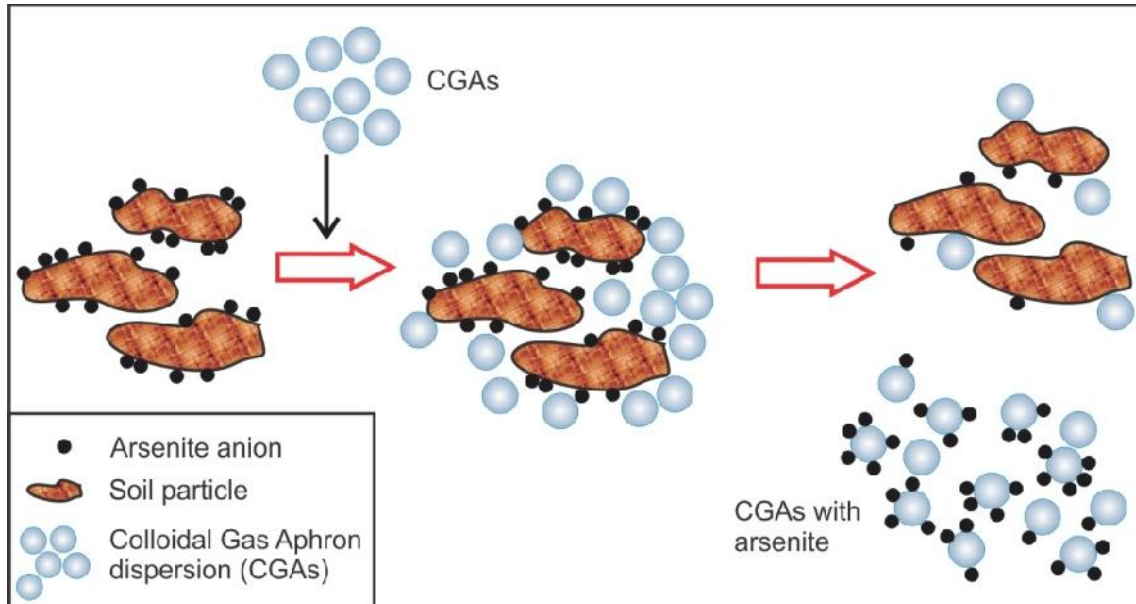
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18 Abstract

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

31 solution by precipitating the arsenic. Damage to soil was minimal arsenic confirmed by metal
32 dissolution from soil surface and SEM micrograph.



33

34 **Keywords:** soil washing; soapnut; *Sapindus mukorossi*; arsenic; CGAs, microbubbles

35

36 **1 Introduction**

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

44 Saponin, a natural surfactant was extracted from the pericarp of the soapnut fruit. It has been used as
45 medicine and detergent for many decades (Song et al., 2008; Suhagia et al., 2011). Earlier, Cd, Zn,
46 Ni and a number of organic pollutants were successfully removed by saponin (Kommalapati et al.,
47 1997; Roy et al., 1997; Chen et al., 2008; Song et al., 2008; Poletini et al., 2009). Soapnut is
48 biodegradable as well as non-toxic for soil environment (Kommalapati and Roy, 1997). However,
49 saponin extracted from soapnut has never been used for removal of soil arsenic, which has entirely
50 different chemical characteristics from heavy metals. Arsenic is a known human carcinogen
51 (USEPA, 2001). In soil, arsenic is accumulated through unsafe irrigation and industrial practices
52 such as mining, smelting and illegal waste dumping activities (Tokunaga and Hakuta, 2002). Soil
53 washing by acids, alkaline reagents, surfactants, phosphates and chelates for removing arsenic from
54 contaminated soil have been reported in literature (Jang et al., 2005; Alam and Tokunaga, 2006; Jang
55 et al., 2007; Brammer, 2009; Wang and Mulligan, 2009; Yamaguchi et al., 2011). Removal of toxic
56 metals from soil matrix using biosurfactants is also currently being assessed (Chen et al., 2008;
57 Poletini et al., 2009; Wang and Mulligan, 2009). Surfactants may be used for soil washing in a
58 number of physical forms viz. solution, foams and colloidal gas aphrons (CGAs) (Roy et al., 1995;
59 Wang and Mulligan, 2004).

60 In this work, low level of arsenic(V) removal has been attempted. It is established that pollutant
61 removal becomes difficult at lower concentrations (Sundstrom et al., 1989). Arsenic(V) from soil
62 containing Fe (III) bearing minerals is much more difficult to remove than As(III) (Yamaguchi et al.,
63 2011). The soil sample used in this work contains maghemite, which has a high affinity for arsenic
64 (V) (Chowdhury and Yanful, 2010). Different concentrations of soapnut solutions and CGAs were
65 compared with a widely used anionic synthetic surfactant Sodium Dodecyl Sulphate (SDS;
66 $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) at soil pH of 5 and 6 (Kommalapati et al., 1997). The objectives of this research were
67 to study arsenic removal performance of CGAs in comparison to solutions; effect of surfactant
68 concentration, flow mode and soil pH on the soil washing process; and environment friendliness of
69 the process by measuring the damage to the soil by soapnut solution and recovering soapnut solution
70 after removing arsenic from the effluent.

71 **2 Materials and methods**

72 **2.1 Soil sample, surfactants and analytical methods**

73 A composite soil sample was collected from the first layer aquifer in Hulu Langat area, Selangor,
74 Malaysia. The soil was dried in an oven overnight at 105°C , crushed and passed through a 2 mm
75 sieve (Roy et al., 1997). The soil was then classified according to USDA soil classification. XRD
76 analysis was performed by a Panalytical Empyrean diffractometer using Highscore Plus software.
77 The soil pH was measured by USEPA SW-846 Method 9045D whilst Eh was measured by an ORP
78 electrode following ASTM Method D 1498-93 after preparing the sample by USEPA Method 9045
79 (SW-846 series) for soil samples. Arsenic(V) salt ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was used for spiking the soil
80 matrix depending on the Eh and pH of the unspiked soils (Tokunaga and Hakuta, 2002). Although
81 arsenic(V) salt is soluble in water, it binds strongly with Fe (III) minerals and cannot be removed by
82 water alone. The soil was spiked with 200 mgL^{-1} concentrations of sodium arsenate solution at room
83 temperature by mixing it for 7 days at a weight:volume ratio of 3:2. The arsenic spiked soil samples

84 were leached with 2 pore volumes of artificial rainwater of pH 5.9 to mimic field leaching conditions
 85 (Oorts et al., 2007). Pore volume was calculated to be approximately 80 mL for every 300 gm of
 86 soil. The spiked soils were air dried at 25°C for 24 h and sieved through a 2 mm mesh. They were
 87 digested following USEPA method 3050B to measure metal contents by ICP-OES (Perkin -Elmer
 88 Optima 7000DV). All the samples were analyzed in triplicate and the results were reproducible
 89 within ±3.5%. The soil was classified as sandy soil according to USDA soil classification

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

90 ((1)

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

94 Table 1a). XRD analysis of both spiked and unspiked soils revealed that the soil samples contained
 95 Silicon Dioxide as quartz (SiO₂, XRD displacement 0.158), Magnesium Aluminum Silicate
 96 Hydroxide as mica ((Mg, Al)₆ (Si, Al)₄O₁₀ (OH)₈, XRD displacement 0.119), Sylvine, sodium
 97 (Cl₁K_{0.9}Na_{0.1}, XRD displacement -0.171), Maghemite Q (Isometric Fe_{21.333} O₃₂, XRD displacement
 98 0.001), Feldspar Albite (Al Na O₈ Si₃, XRD displacement -0.053). Arsenic in the spiked soil was
 99 speciated by the solvent extraction process (Appendix A) and was found to be in +5 state as shown

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

100 in (1)

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

104 Table 1(b) (Chappell et al., 1995). Sequential extraction of arsenic from spiked as well as washed
105 soils were performed according to Hall et al. (1996).

106 Based on some preliminary experiments, 20 mM of SDS, 0.5 and 1% (w/v) of soapnut extractions
107 were selected for the study and were compared against a standard blank sample. All of the surfactant
108 concentrations used exceeded the critical micelle concentration (CMC) of the respective surfactants.
109 The natural saponin was extracted from the soapnut fruit pericarp by water and found to contain 65%
110 saponin using UV-vis spectrophotometer (Roy et al., 1997). The characteristics of the washing

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

111 agents are described in

112 (1)

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

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

123 $K = \left(\frac{R}{a}\right) / \left[\frac{P/(\rho X g)}{ht}\right]$ (1)

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

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

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)		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)		1.45					
Total porosity (%)		39	(Di Palma et al., 2003)				
Total arsenic (mg kg ⁻¹)		3					
Total iron (mg kg ⁻¹)		3719					
Total silicon (mg kg ⁻¹)		~390,000					
Aluminium (mg kg ⁻¹)		2400	USEPA 3050B				
Total manganese (mg kg ⁻¹)		185					
Magnesium (mg kg ⁻¹)		635					
Lead (mg kg ⁻¹)		11					
Zinc (mg kg ⁻¹)		18					
Soil particle size distribution							
Sand (< 50 μ m)		92.66 %					
Silt (50-2 μ m)		5.2 %	Sandy soil according to USDA Soil Classification				
Clay (> 2 μ m)		2 %					
b. arsenic speciation in spiked soil							
Total arsenic (mg kg ⁻¹)		85.63					
As (III) (mg kg ⁻¹)		2.65	Solvent extraction (Chappell et al., 1995)				
As (V) (mg kg ⁻¹)		82.98					
c. Characterization of wash agents							
washing agents	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	3	7.5	1.4 cP

129

130 2.2 Column washing experiments

131 The 10 cm long section of contaminated soil was packed in a 15 cm long plexiglass column having
 132 5.5 cm internal diameter (Roy et al., 1997). Approximately 300 gm of soil could be packed in each

133 column. Coarse sands were packed on top and bottom of the soil column for even distribution of the
134 flow. Circular plexiglass discs with perforations were inserted at 3 cm intervals to avoid preferential
135 flow pathways. The porosity of the packed column was calculated as 39% (Wasay et al., 2001). The
136 packed column was flooded with water from the bottom at the rate of 5 mL min⁻¹ to remove air
137 spaces. Arsenic desorption from column was then induced by pumping 6 pore volumes (PV ~ 80
138 mL) of surfactant solution or CGAs, at a constant flow rate of 10 mLmin⁻¹ by a peristaltic pump in
139 down-flow and up flow modes. The eluted samples were collected for each PV and arsenic
140 concentrations were measured by ICP-OES. The scheme of experiment has been shown in Figure
141 1(a).

142 **2.3 Sustainability of the process**

143 Damage to soil caused by soapnut and SDS was investigated by washing 10 gm of arsenic
144 contaminated soil with 200 ml washing agents for 6 hours. The wash solutions were analyzed for Ca,
145 Mg, Si, Fe, Al to check for any structural damage of soil following (Zeng et al., 2008). Change in
146 soil surface morphology by 1.5% soapnut washing was analyzed by SEM. Coagulation-flocculation
147 process was used for separating arsenic from soapnut wash effluents (Jang et al., 2005). Jar tests
148 were performed with 200 mL of 0.5, 1 and 1.5% soapnut solutions containing 10 mg/L arsenic in
149 500 mL beakers by adding different doses of FeCl₃. The pH of soapnut solutions were adjusted by
150 HCl or NaOH. The mixing sequence was 1 min of rapid mixing at 120 rpm, 30 min of slow mixing
151 at 40 rpm, followed by 30 min of settling. At the end of the settling period, samples are taken from
152 supernatants using a 0.45 µm pore size membrane filter and analyzed for arsenic content in ICP-
153 OES.

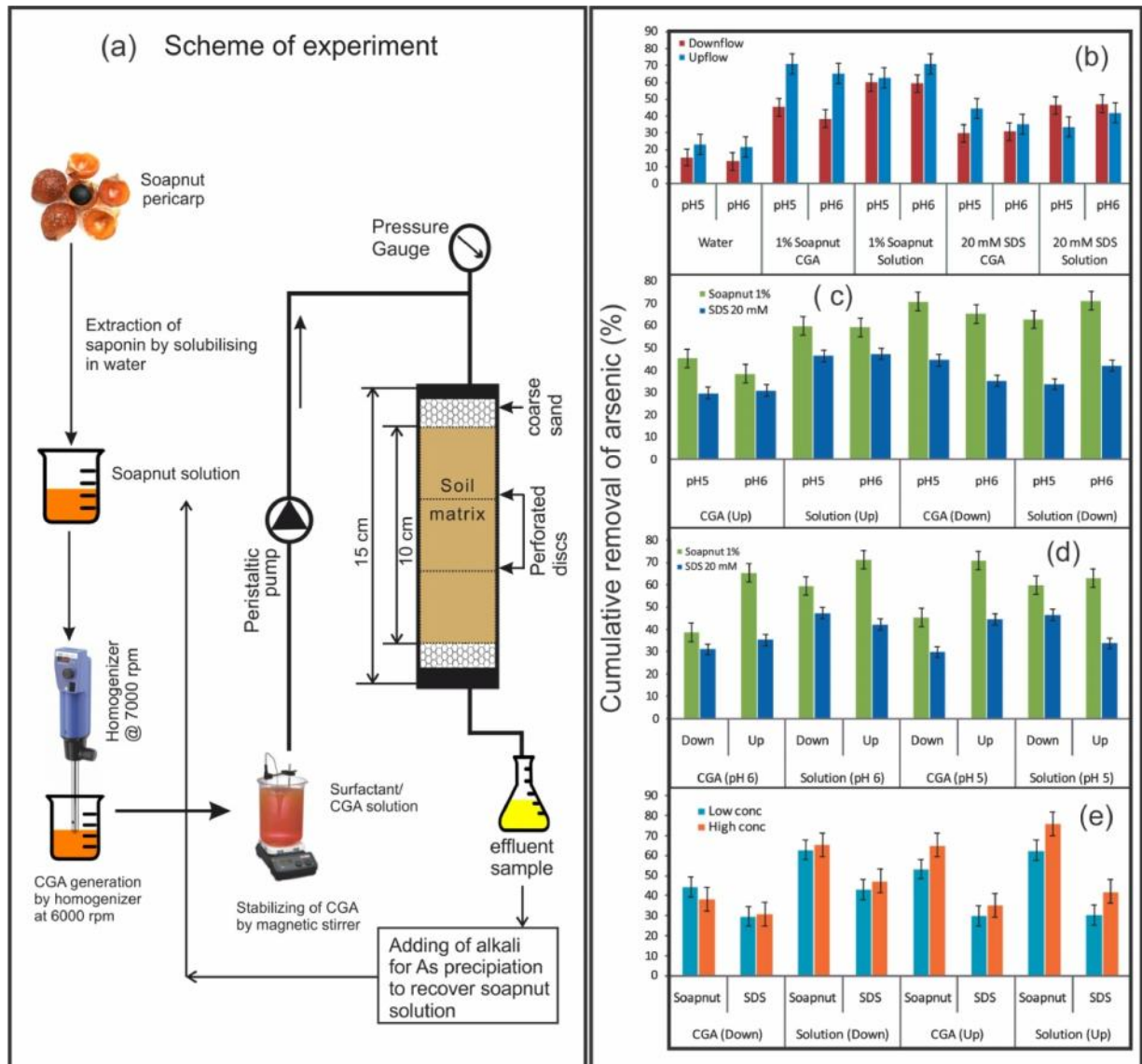
154 **3 Results and discussion**

155 **3.1 Propagation of CGA through soil column**

156 CGAs prepared from different concentrations of surfactants were injected into the soil column to
157 determine the pressure build-up and their hydraulic conductivities at various flow rates. Pressure
158 build-up in columns resulted from clogging of the soil pores due to dispersion of colloids and
159 trapping of air bubbles inside the soil pores. These obstructed the flow of flushing solution through
160 the contaminated area, reducing the efficiency of pollutant removal from the soil matrix (Roy et al.,
161 1995). Increasing the flow rates from 10 mLmin⁻¹ to 20 mLmin⁻¹ increased the pressure gradient in
162 an almost linear fashion for 0.5, 1 and 1.5% soapnut solutions (Figure A1). Other researchers
163 recommended that, flow rate should not exceed 10 to 15 mLmin⁻¹ for maintaining lower pressure
164 gradient in the column (Mulligan and Eftekhari, 2003). Accordingly, the flow rates were maintained
165 at 10 mLmin⁻¹ for the remaining experiments. Hydraulic conductivity followed exactly opposite
166 trend of pressure gradient and it increased with higher flow rate.

167 **3.2 Cumulative arsenic removal by soapnut solution and CGA**

168 There are a number of factors influencing the arsenic removal efficiency such as soil pH, flow modes
169 and concentration of surfactant and physical state of surfactants (CGAs and solution). The effect of
170 all these factors has been discussed separately. Six pore volumes of water were used as blank at soil
171 pH 5 and 6. It was observed that water could remove only up to 23% arsenic at pH5 in up flow mode
172 (Figure 1b). Other flow modes removed even less amount of arsenic indicating strong bonding in the
173 soil column. Therefore, additional reagents were necessary to remove rest of the arsenic. 1% soapnut
174 solution and CGAs removed 3 to 4 times more arsenic (up to 71%) than water flood. Solutions and
175 CGAs of 20 mM SDS solutions removed much less arsenic (up to only 46%) compared to soapnut,
176 possibly due to higher pH of 10 which did not favour arsenic solubilisation. No further comparisons
177 between SDS and soapnut are done since SDS does not match up against soapnut.



178

179 Figure 1: (a) Scheme of experiment, (b) Comparison of Arsenic removal performance by CGAs and
 180 solutions under different flow modes at pH5 and 6 at 1% soapnut concentration; (c) Arsenic removal
 181 in up flow and down flow modes by solution and CGAs prepared from 1% soapnut at pH5 and pH 6;
 182 (d) Arsenic removal in different flow modes by Down flow and Up flow modes by CGAs and
 183 solutions with 1% soapnut and 20mM SDS at pH5 and 6; (e) Arsenic removal in different surfactant
 184 concentrations at pH 5 (Soapnut: L= 0.5%, H=1%; SDS: L=10mM, H=20mM) (with standard errors)
 185

186 3.2.1 CGAs vs solution

187 The cumulative arsenic removal efficiency by CGA and solution of soapnut and SDS are shown in
 188 Figure 1(c). There was no clear winner among solution and CGAs. The performance of solution was
 189 much better than CGAs in up flow mode at pH5 where soapnut CGAs removed 45.42% arsenic
 190 while soapnut solution removed 60%. The scenario was different at pH5 soil in down flow mode

191 where soapnut CGAs removed 71% arsenic compared to 63% by soapnut solution. In the case of
192 SDS at soil pH of 5 at up flow mode, CGAs removed 30% arsenic and solution removed 46%. But
193 for down flow mode at pH5, SDS CGAs and solutions removed 44.68 and 33.87% arsenic
194 respectively. So, it can be concluded that both CGAs and solution had comparable performances. In
195 the experiments involving CGAs, it was seen to perform better in up flow modes rather than down
196 flow mode. It is understandable due to the higher buoyancy of the microbubbles of CGAs when they
197 are introduced from the bottom of the column. However, it should be noted that 1 PV of CGAs
198 actually contained only 65% of surfactant solution and 35% air, while surfactant solutions had no air
199 content. So, CGAs are more economical compared to solutions.

200 **3.2.2 Dependency on Flow modes**

201 The arsenic removal also depends heavily upon the mode of flow of wash solutions. In these
202 experiments, two different wash modes were used, viz down flow and up flow modes in soil pH of 6.
203 In down flow mode, CGAs are pumped from the top of the column and forced to come out from the
204 bottom of the column. CGAs resist the process due to high buoyancy of the constituent
205 microbubbles, thus resulting in some pressure gradient. In this mode, only 38% arsenic removal
206 could be obtained using soapnut and 31% by SDS CGAs. This is shown in Figure 1(d). However,
207 solutions of the same agents enjoyed a clear advantage due to the assistance of gravity that drags the
208 liquid down the column. The arsenic removal by soapnut and SDS solutions are 60 and 47.5%
209 respectively, which are much better than that with CGAs in down flow mode. In down flow mode,
210 minute channels are formed inside the column through which the solution and CGAs flow
211 conveniently, missing out a large part of the contaminated soil matrix. In the up flow mode, both
212 solutions and CGAs are introduced from the bottom of the column and the effluent are collected
213 from the top after they rise through the column. In this mode, the CGAs and solutions performed
214 equally well. The CGAs, due to higher air content and higher buoyancy, have a tendency to rise up in
215 a flooded column when introduced from the bottom. Air pockets are less likely to form. Although

216 higher pressure was developed in this mode of washing, the arsenic removal was better for up flow
217 by both CGAs and solutions compared to down flow mode. CGAs of soapnut and SDS removed 65.5
218 and 35.4% arsenic respectively and the corresponding values for the solutions are 71 and 42%
219 respectively. Thus, up flow mode is found to be the better performer than down flow mode and both
220 CGAs and solutions had comparable performance in up flow mode. Similar trends are observed in
221 soil of pH 5.

222 3.2.3 Dependency on surfactant concentrations

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

229 3.2.4 Cumulative arsenic removal in subsequent pore volumes

230 Cumulative arsenic removal by the low concentration surfactant solutions and CGAs from soil of pH
231 6 in subsequent pore volumes in down flow mode was calculated (data not shown). In most cases,
232 more arsenic was removed during the initial pore volumes than the final pore volumes. Roy et al.
233 (1995) attributed the initial higher pollutant removal to any free phase pollutant in the column. Any
234 loosely bound arsenic(V) will easily detach from the soil particles by the initial spurge of the
235 surfactant. In the later pore volumes, new channels opened up while old channels close down to
236 remove arsenic from a virgin area. Thus sometimes more arsenic was removed during the
237 intermediate pore volumes. However, it was observed that cumulative arsenic removal increased
238 linearly in subsequent pore volumes. The R^2 values of the linear trend lines are above 0.9 in all the
239 cases. The soapnut concentration in the effluent increased after the third or fourth PV, signifying that

240 during the initial stages, the washing agent underwent adsorption on the soil particles thereby
241 extracting the pollutant by micellar solubilisation. Earlier, it was postulated that adsorption of
242 surfactant on soil particle is essential for the removal of soil contaminants, and surfactants that
243 adsorb at the soil–water inter-phases are better detergents (Raatz and Härtel, 1996).

244 3.3 Sequential extraction of arsenic

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

245 In arsenic contaminated soil having chemical composition as described in

246 (1)

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

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

259 3.4 Zeta potential and FT-IR spectral data

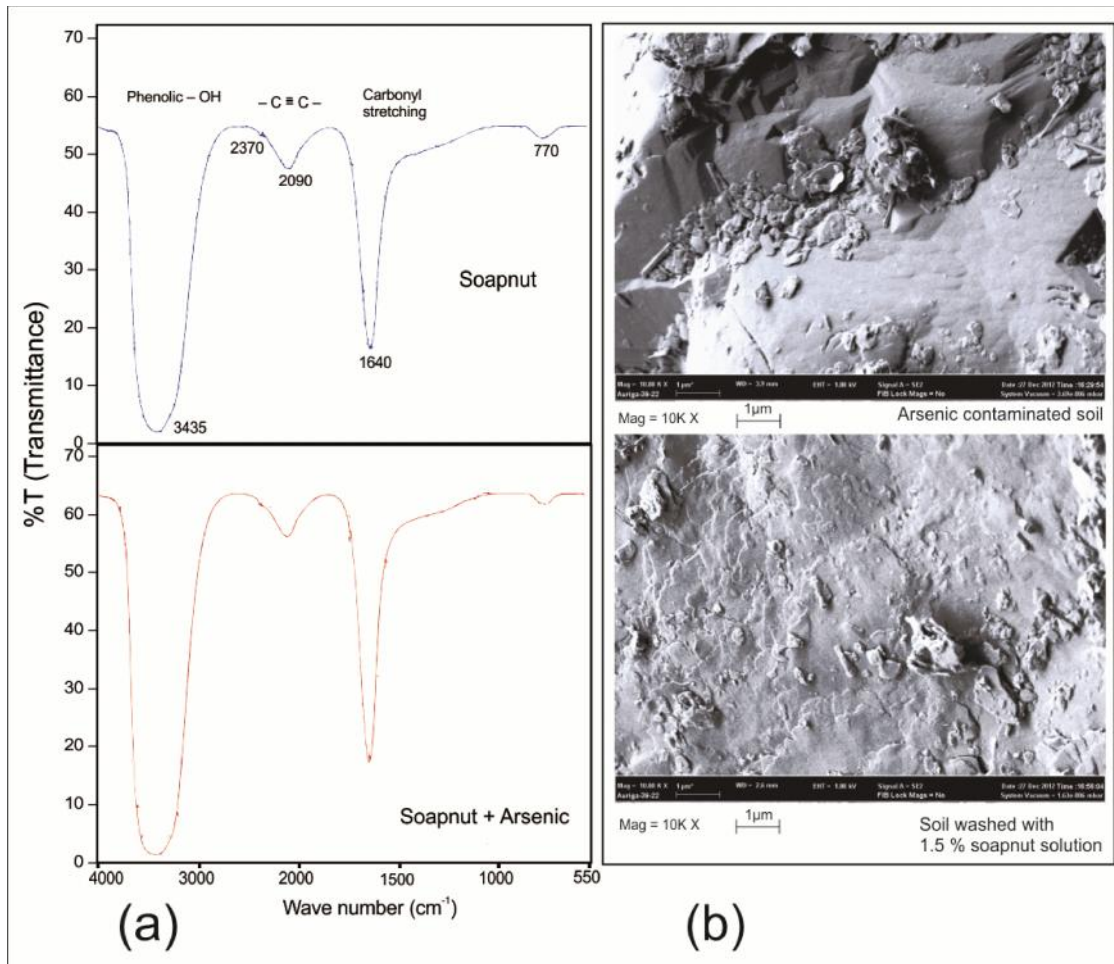
260 The zeta potential values of the soil particles in de-ionized water, 20 mM SDS, 0.5% and 1% soapnut
261 solutions are -34.3, -61.8, -17.1 and -11.8 mV respectively. In comparison to water, the zeta potential

262 decreased significantly for 20 mM SDS. This signifies that the anionic molecules of SDS adsorbed
263 on the surface of soil particles, imparting them a much lower charge of -61.8 mV. Both soapnut and
264 SDS are prospective detergents for soil washing, while arsenic cations are more likely to get attached
265 to the anionic heads of SDS. Soapnut solution performs better due to lower operating pH of 4.5 that
266 helps to desorb arsenic from soil.

267 FT-IR spectral data shown in Figure 2(a) displays the absorbance spectra for the influent and the
268 effluent soapnut solutions. The absorption range of different molecular vibrations present in
269 phenolic-OH at 3436 cm^{-1} , carbonyl groups of carboxylic acid at 2092 cm^{-1} and alkene groups at
270 1642 cm^{-1} are observed and are similar to earlier findings (Pradhan and Bhargava, 2008). No shifting
271 of peaks in FT-IR spectra was observed in the effluent soapnut solution in presence of arsenic
272 compared to influent soapnut solution. Although earlier works suggested complexation of saponin
273 molecule with heavy metals (Hong et al., 2002; Song et al., 2008), no chemical interaction of
274 saponin and arsenic is observed in this work.

275 **3.5 Damage to soil**

276 SEM image in Figure 2(b) shows the surface morphology of the arsenic contaminated soil before and
277 after treating with 1% soapnut solution for 6 hours in a shake flask, at a 10000 X magnification. It
278 can be observed that the soil before washing contained finer particles on a smooth underlying
279 surface, which are absent after washing while the smooth surface is exposed. Slight roughness of the
280 underlying smooth surface is also observed after soapnut washing. However, the corrosion is not
281 very high as indicated by the Table A1 which indicates that the amount of structural elements such as
282 Ca, Mg, Fe, Al and Si leached in the wash solution after 6 hours of vigorous shaking. In this case, no
283 considerable metal leaching was detected. With 1.5% soapnut solution, 1.95% Ca, 2.02% Mg and
284 0.44% Fe leached out. This indicates negligible chemical withering.

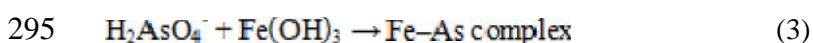
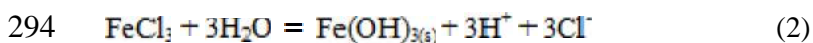


285
286
287
288

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

289 3.6 Recovery of wash solution

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



296 The amorphous Fe-As complex is most stable in the pH range of 6-8 (Donmez and Akbal, 2011).
297 Accordingly, arsenic removal efficiency with FeCl₃ is maximum in the pH range of 7-8. At pH of 8
298 with 15 mgL⁻¹ of ferric chloride, up to 87% of the arsenic is removed from the soapnut. However,
299 after 8-10 mgL⁻¹ dose of ferric chloride, the improvement in arsenic removal does not increase too
300 much, in agreement with earlier publications (Jang et al., 2005; Donmez and Akbal, 2011).
301 Moreover, arsenic removal below pH of 7 and above pH of 8 are comparatively low, in the range of
302 60-70%.

303 **4 Conclusions**

304 Soapnut solutions and CGAs are able to remove low level arsenic residues from soil. Inorganic
305 surfactant SDS showed poor performance in comparison to soapnut due to higher pH of 10 which
306 did not favour arsenic solubilisation. Soapnut CGAs and solutions showed comparable
307 performances. However CGAs comprises up to 35% of its volume of air indicating their economic
308 advantage over solutions. Flow mode and soapnut concentration were main influential parameters.
309 Soil pH had little influence on the process. Arsenic removal is highest in up flow mode for both
310 CGAs and solutions and the CGAs of 1% soapnut removed 71% arsenic from soil of pH 5. CGAs
311 prepared from high concentration soapnut solution showed better arsenic removal due to higher air
312 hold-up which exposes more interfacial area, facilitating mass transfer. Solution of lower
313 concentration performed better due to higher penetration for lower viscosity. Zeta potential values
314 showed that soapnut is adsorbed on soil particles and possess the quality of being an effective
315 detergent. From FT-IR spectra, no evidence of chemical complexation of saponin molecules and
316 arsenic can be found. The SEM image of the soapnut washed soil reveals no major corrosion of the
317 soil particles and negligible amount of Ca, Mg, Fe, Al and Si leached out in soapnut wash solution,
318 indicating minimal soil damage. Soapnut solution could be recovered from the wash effluent with 8-
319 10 mgL⁻¹ of ferric chloride at the pH of 8 by coagulation-flocculation-precipitation process. Soapnut

320 CGAs can be a safe, efficient and economical means to remediate sub-surface arsenic-contaminated
321 soil.

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

410 **Extraction of total arsenic from soil**

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

418 **Speciation of trivalent arsenic**

419 A 10 mL aliquot of the arsenic extract was transferred to a 100 mL separating funnel and 80 mL of
420 10M hydrochloric acid was added, adjusting the acid concentration to greater than 9M. This was
421 followed by extraction of arsenic(III) into chloroform with 4 x 10 mL washings. At this stage the
422 strongly acidic aqueous phase was discarded. The arsenic was then back-extracted from the organic
423 phase into 2 x 20 mL aliquots of water and diluted to 100 mL.

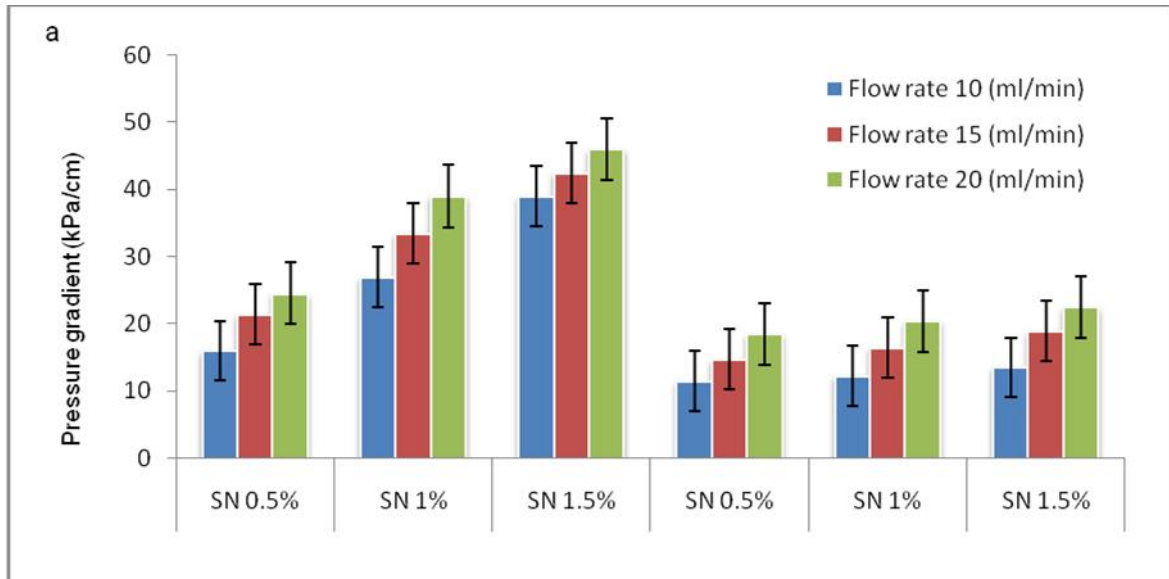
424 **Amount of pentavalent arsenic = Total arsenic - Trivalent arsenic**

425

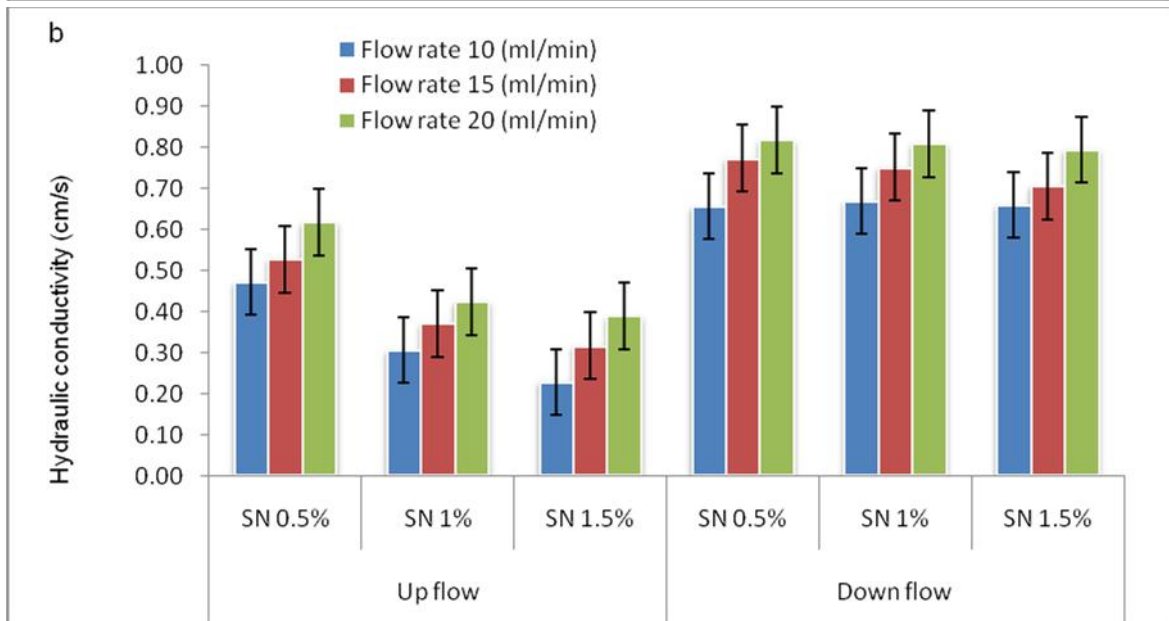
426 Table A1: Metal dissolution from washed soil

Washing agent	Conc	Dissolution of metal from soil (% of total content)				
		Ca	Mg	Fe	Al	Si
Soapnut	1%	1.82	1.96	0.43	0.44	0.05
Soapnut	1.5%	1.95	2.02	0.44	0.48	0.05
SDS	30 mM	0.35	1.02	0.17	0.21	0.03

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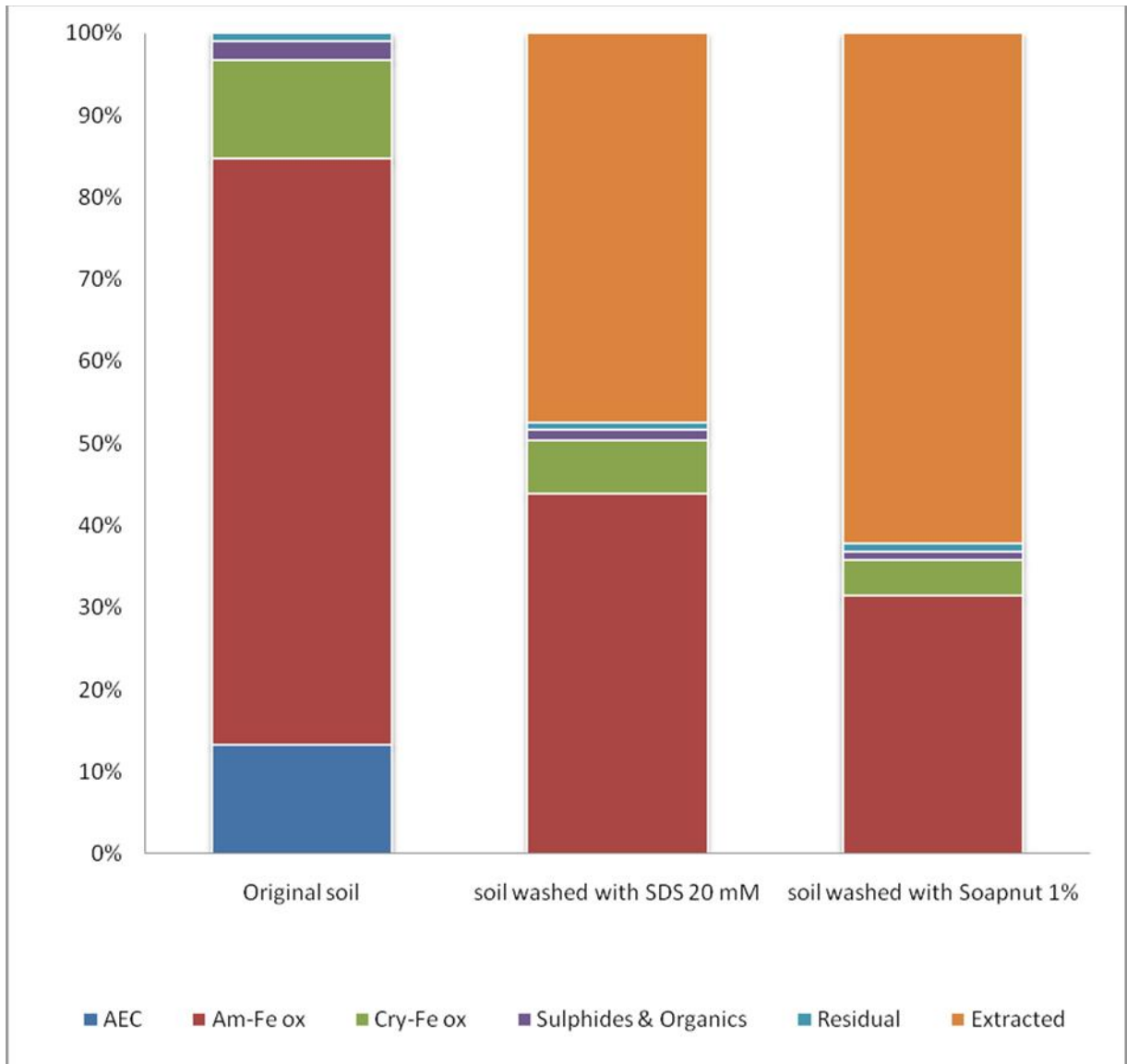


429

430 Figure A1: (a) Pressure build-up in the soil column as a function of flow mode and CGAs flow rate
 431 (b) Hydraulic conductivity through the soil column as a function of flow mode and CGAs flow rate,
 432 SN: soapnut (with standard error)

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435

436 Figure A2: Sequential extraction of As(V) following Hall et al. (1996) The following are represented
437 – AEC: adsorbed-exchangeable-carbonate fraction; Cry-Fe ox: Crystalline Fe oxide, Am-Fe ox:
438 Amphoteric Fe oxide.