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Enhanced removal of lead from contaminated soil by polyol-based deep eutectic solvents and saponin

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Abstract

Deep eutectic solvents (DESs) are a class of green solvents analogous to ionic liquids, but much cheaper and easier to prepare. The objective of this study is to remove lead (Pb) from a contaminated soil by using polyol based DESs mixed with a natural surfactant saponin for the first time. The DESs used in this study were prepared by mixing a quaternary ammonium salt choline chloride with polyols e.g. glycerol and ethylene glycol. A natural surfactant saponin obtained from soapnut fruit pericarp, was mixed with DESs to boost their efficiency. The DESs on their own did not perform satisfactory due to higher pH; however, they improved the performance of soapnut by up to 100%. Pb removal from contaminated soil using mixture of 40% DES-Gly and 1% saponin and mixture of 10% DES-Gly and 2% saponin were above 72% XRD and SEM studies did not detect any major corrosion in the soil texture. The environmental friendliness of both DESs and saponin and their affordable costs merit thorough investigation of their potential as soil washing agents.

Keywords: soil washing; soapnut; deep eutectic solvents; Sapindus mukorossi; lead; DES; choline chloride.
1 Introduction

Recently, Deep Eutectic Solvents (DESs), a new class of ILs analogue, have been at the centre of scientific interest. DESs share many physical properties with ILs and can be synthesized by mixing a hydrogen bond donor with a salt and have melting points lower than either of its components. The charge delocalisation occurring through hydrogen bonding between the hydrogen bond donor moiety and the halide anion is responsible for the decrease in the freezing point of the mixture relative to the melting points of the individual components (Smith et al., 2014). DESs have attracted attention in the fields of chemical synthesis, metal-catalyzed organic reactions, biological catalysis (Durand et al., 2012), lubrication (Shi et al., 2013), electrochemical processes (Abbott et al., 2007), production and purification of biodiesel (Hayyan et al., 2013a; Hayyan et al., 2010), enhanced oil recovery (Hadj-Kali et al., 2015) and separation of aliphatic and aromatics (Hizaddin et al., 2015). Until now, DESs have not been used for soil washing except some preliminary work (Mukhopadhyay et al., 2016). In-vitro and in-vivo toxicity studies on ammonium based DESs with HBD e.g. ethylene glycol, triethylene glycol, glycerine and urea have been performed and these were found to be less toxic than ionic liquids (Hayyan et al., 2013b; Hayyan et al., 2015). Recently, lower concentrations of glycerol ethylene and glycol DESs with choline chloride were found to be biodegradable (Juneidi et al., 2015).

Pollution of soil and groundwater have far reaching impact on human civilizations around the world resulting in unproductive land, desertification, poisoning of food crops and contamination of surface and groundwater (Peters, 1999). Industrial, agricultural and mining activities release various contaminants such as organics, oils and heavy metals in soil matrix, threatening the soil ecosystem These harmful chemicals then permeate through unsaturated soil to enter the subsurface aquifer. The contaminant transport processes in soil which are strongly influenced by a range of site-specific variables, such as soil or sediment composition, contaminants of concern, and available human or ecological receptor(s) play a crucial role in determining extent of groundwater contamination (Ayvaz, 2010; Liang et al., 2016). A direct or indirect exposure pathway for contaminants in soil matrix is via pore-water solution though the structured and chemically reactive medium of soils. Soil matrix contains the plant root system and host a complete ecosystem. Therefore, the issues of preferential flow, spatially heterogeneous nature of point sources and active role of vegetation in influencing the hydraulic impetus for transport of contamination are important for understanding contamination of aquifers (Clothier et al., 2010). Some other factors influencing contamination of aquifer...
through soil pollution are change in soil redox conditions, a variety of biological and abiotic redox processes of dissolution/precipitation of minerals, complex formation, ion exchange and sorption (Vodyanitskii, 2016). Additionally, such hydrological transport processes are highly influenced by the soil clay content, prone to the presence of preferential flow paths due to alternating swelling/cracking in response to wetting/drying natural conditions (Veizaga et al., 2015). Therein lie both the importance and challenge in cleaning the soil matrix and thus preventing contamination of groundwater resources.

Lead (Pb) is one of the heavy metals which has been historically released in the soil environment in significant amount (Navarro et al., 2008). The USEPA standard for lead in bare soil in play areas is 400 mg Kg$^{-1}$ by weight and 1200 mg Kg$^{-1}$ for non-play areas (ATSDR, 2007). Toxicity of Pb has been well documented (Needleman and Bellinger, 1991). Therefore, excess Pb needs to be removed from affected soils and aquifer for reducing public health risk.

Washing of contaminated soil is a widely accepted practice (Dermont et al., 2008). Saponin, a plant based surfactant has been effectively used for contaminant removal from soil without corroding the soil (Mukhopadhyay et al., 2013a; Mukhopadhyay et al., 2015; Mulligan et al., 2001). Saponin (SN) is environment friendly and has been used as soft detergent and medicine for many decades. It can be extracted from the fruit pericarp of *Sapindus mukorossi* which contains natural surfactant triterpenoidal saponins viz oleanane, dammarane and tirucullane (Suhagia et al., 2011).

The objective of this study is to use polyol based DESs e.g. choline chloride: ethylene glycol (DES-EtGl) and choline chloride: glycerol (DES-Gly) for removing a heavy metal lead from a contaminated landfill soil. Among the DESs used in this study, DES-Glycerol is of plant origin and this has been compared with a synthetic DES i.e. DES-Ethylene Glycol. These DESs have been combined with a natural surfactant (saponin) for investigation of their synergistic effect on the process, thereby adding a new dimension to the study. The use of plant based DES and surfactant is the focus of this work due to their biodegradability and because they are environmentally benign.
2 Materials and methods

2.1 Soil sample

Jeram Sanitary Landfill (JSL) in Selangor, Malaysia receives waste from seven major municipalities including Kuala Lumpur and Selangor. A composite soil sample was collected from JSL for this study. The soil was dried in an oven overnight at 105ºC following the protocol of Roy et al. (1997). It was crushed and passed through a 2 mm sieve and classified according to USDA soil classification. The soil pH was measured by USEPA SW-846 Method 9045D and Eh was measured by an ORP electrode following ASTM Method D 1498-93 after preparing the sample by USEPA Method 9045 for soil samples as suggested in SW-846 series. The Loss by Ignition study was performed to determine the organic matter content following Storer (1984). Cation exchange capacity (CEC) in MeQ/100gm was measured using ammonium acetate method for acidic soil (Chapman, 1965). XRD analysis of the soil mineralogy was performed by a Panalytical Empyrean diffractometer using Highscore Plus software (Scan Axis: Gonio; Start Position 10.0118 °2Th; End Position 49.9868 °2Th; Step Size 0.013 °2Th; Scan Step Time of 13.77 sec at Continuous Scan Type).

2.2 Spiking of soil sample

The soil was spiked with 1000 mg L⁻¹ concentrations of Pb using Pb(NO₃)₂ solution at room temperature by mixing it for 7 days at weight: volume ratio of 3:2. The mixing protocol also involved washing of excess Pb with 2 pore volumes of artificial rainwater of pH 5.9 consisting of 5 × 10⁻⁴ M CaCl₂, 5 × 10⁻⁴ M Ca(NO₃)₂, 5 × 10⁻⁴ M MgCl₂, 10⁻⁴ M Na₂SO₄, and 10⁻⁴ M KCl following the method proposed by Oorts et al. (2007). This procedure was followed for increasing field relevance (Mukhopadhyay et al., 2013b; Mukhopadhyay et al., 2015). This contaminated soil was then air dried at 25ºC for 24 hours and sieved through 2 mm mesh screen. It was digested following USEPA method 3050B in order to measure metal contents by ICP-OES (Perkin-Elmer Optima 7000DV) using Perkin-Elmer multi-metal standard solutions. All the samples were analysed in triplicate and the results were reproducible within ± 3.5%.

2.3 Preparation of DESs and saponin solutions

The compositions of two DESs (DES:Gly and DES:EtGl) used in this study are given in Table 1. Glycerol and ethylene glycol were mixed with choline chloride to synthesize DES:Gly and DES:EtGl respectively. All chemicals used for DESs’ preparation were dried at 60ºC under vacuum. A glass jacketed vessel with a magnetic stirrer was used to prepare DES samples in a fume hood at 70ºC and stirrer speed of 350 rpm for 3 hour mixing time. The DESs were then
diluted in water with different volume ratios (i.e. 10, 20, 30, and 40% v/v) and used for further experiments. Soapnut solution of 1% concentration (w/v) was used in combination with the 2 DESs for Pb desorption from the soil and were compared against water blank. Saponin was extracted from the soapnut fruit pericarp by water following Roy et al. (1997). The pH of 1% soapnut solution was 4.44 and surface tension was 40 mN m$^{-1}$ measured by a ring type surface tensiometer (Fisher Scientific Manual Model 20).

*Table 1: Composition of DESs and their pH in presence of saponin

2.4 Batch experiments

Batch tests were conducted in 50 mL conical flasks. For each experiment, 1 gm of soil was washed with 10, 20 or 30 mL of wash solution (DESs and DES-saponin mixtures) of different concentrations. The conical flasks were shaken in an orbital shaker in horizontal position for 4 hours. Wash solutions were then poured into test tubes, centrifuged, filtered and preserved with 1 drop of nitric acid for ICP analysis to measure Pb concentration.

2.5 Soil corrosion

XRD spectroscopy and SEM were used to inspect the damage to the mineral structure of soil. 10 gm of soil was washed with 100 mL of 10% DES-EtGl and mixture of 10% DES-EtGl and 1% saponin for 4 hours. Following this, they were filtered and the soil samples were dried at 45°C. Along with unwashed soil sample, they were subjected to XRD and SEM analysis to check for any mineralogical change of the soil. XRD analysis of original soil, Pb spiked soil and these washed soils were performed by a Panalytical Empyrean diffractometer using Highscore Plus software as described in sub-section 2.1. SEM was performed using a Zeiss Auriga 39-22 SEM under accelerating voltage of 1.00 kV, System Vacuum = 2.35 e-006 mbar - 1.86e-006 mbar. A size distribution analysis using sieve was performed on the 10 gm of weighed soil before and after the washing.
3 Results and discussion

3.1 Soil characterisation

The soil type has been classified as sandy according to USDA soil classification. Table 2 summarizes the characteristics of the soil. The soil experienced ignition loss of 1.21% signifying presence of some organic matters supported by the fact that it was blackish in colour. The organic matter acts as an electron donor and binds with the heavy metal cation (i.e. lead in this case). The soil redox potential value of 333 mV made it slightly oxidized, indicating minor electron deficiency. A moderately high electrical conductivity value of 8.25 mS/cm suggests presence of charged species in the soil matrix. A value of CEC (9 MeQ/100gm) indicated moderate cation retention capacity by the soil, lower than clay (>15 MeQ/100gm) but higher than sandy soils (>2 MeQ/100gm). This is due to presence of organic matter and presence of cations and lower pH value (Moore et al., 1998). The soil had high concentrations of Al, Mg and Fe in its mineralogical structure which was revealed by acid digestion and XRD analysis. This XRD analysis of unspiked and spiked soil revealed presence of Silicon Oxide (Si O2), Potassium Magnesium Iron Aluminum Silicate Hydrate (K - Mg - Fe - Al - Si - O - H2 O), Aluminum Silicate Hydroxide (Al2 Si2 O5 (O H )4), Zeolite NdY (H42 Al52.45 Nd18.258 O405 Se32 Si139.55), Sodium Aluminum Silicate Hydroxide Hydrate (Na0.3 Al6 ( Si , Al )8 O20 ( O H )10 14 H2 O) and Magnesium Silicate Hydroxide Hydrate (Mg4 Si6 O15 ( O H )2 16 H2 O). Absence of carbonates indicate that the ignition loss of 1.21% was principally due to organic matter. Presence of Fe and Mn minerals is significant due to their ability to retain Pb2+ cation (Cerqueira et al., 2011). After spiking, the Pb content of soil was found to be 1427 mg Kg\(^{-1}\) which is present as the soil contamination. The soil pH is 3.45 indicating acidic nature of the soil. Therefore, the overall soil was found to have electron deficiency despite of presence of organic carbonaceous compounds, which act as electron donor centres and bind readily with lead cations. It was revealed by researchers that good Pb2+ fixation capacity of soil depended on higher pH values, CEC values, and presence of iron and manganese oxides as soil mineral (Cerqueira et al., 2011). Since this specific soil from Jeram landfill has moderately high CEC value, organic content, and high Fe and Mn mineral content as seen from XRD spectra, therefore the Pb2+ fixation/retention is on the stronger side. The success of lead extraction would depend upon the ability of the washing agent to break the bond between organic carbon, Fe and Mn mineral phases and lead.
3.2 Pb removal by DESs and saponin

Lead removal by 10% solutions of DES-Gly and DES-EtGl in the absence or presence of 1% soapnut solution has been plotted in Figure 1. The soil: solution ratio used was 1:20. Performance of water and 1% soapnut solutions are shown for comparisons. The fact that water could remove only about 6% of the bound Pb from soil emphasizes the requirement of adding other agents e.g. saponin and DESs for Pb removal. A solution of 1% soapnut removed up to about 36% Pb. A 10% solution of DES-Gly removed only about 17.33% Pb and 10% DES-EtGl removed only 16.54% Pb. However, on addition of saponin solution, their performances improved by a large extent. For DES-Gly, lead removal ability enhanced by 40% on addition of 1% saponin. DES-EtGl, recorded an improvement of 41.51% on addition of 1% soapnut.

The Pb removal has a strong correlation with the pH of the solution, signifying a Lewis acid-base reaction. More acidic an agent is (e.g. DES+SN mixture), more Pb removal has been achieved by attacking electron rich organic carbon sites thereby releasing Pb²⁺ cations, than the alkaline agents e.g. DES-Gly and DES-EtGl. In presence of saponin solution which is acidic, a number of factors come into play that increased the Pb removal such as (a) lowering in pH thereby supplying more H⁺, (b) introduction of saponin resulting in micellar solubilisation of Pb²⁺ from soil particles (c) dilution of DESs and presence of more H₂O molecules, which can act as a media for leaching out the already loosened Pb from soil surface.

Figure 1: Lead removal by 10% DESs, 10% DES+ 1% soapnut mixtures, water and 1% soapnut solution at 1:20 soil: solution ratio.

DES-Gly and DES-EtGl were further investigated for various concentrations in the presence of soapnut solution. Three different soil:solution ratios were used for washing the soil, namely 1:10, 1:20 and 1:30. Soapnut concentrations tested were 0.5, 1, 1.25, 1.5 and 2% while DES concentrations were 5, 10, 12.5, 15 and 20%. Factorial experiments were conducted for both DES-EtGl and DES-Gly using all these combinations and the obtained data have been represented as Box-Whisker plot in Figure 2 and Figure 3, respectively.

The Box-Whisker plot shown in Figure 2 describes the range of variation in lead removal performance by DES-EtGl and saponin, and it investigates the relative importance of different factors on lead removal process. Figure 2a-b, 2c-d and 2e-f represent the experiments under
soil: solution ratios of 1:10, 1:20 and 1:30 respectively. The improvement in the lead removal with increase in soil: solution ratio can be comprehended from the range of the X-axis of the figures. Lead removal reached up to 70.45% under 1:30 ratio, 20% DES-EtGl and 2% soapnut concentrations. Figure 2a, 2c, and 2e clearly show the increase in lead removal when saponin concentration was increased from 0.5 up to 2% under different concentrations of DES-EtGl. However, at soil:solution ratio of 1:10, the performance improvement with increase in soapnut concentration is not very obvious. Again, Figure 2b, 2d and 2f depicts the increase in lead removal when DES-EtGl concentration was increased from 5 to 20% under various concentrations of saponin. Although the general trend is that Pb removal increases with both soapnut and DES concentrations, increase in DES-EtGl concentrations has a more prominent effect on the process. The Box-Whisker plot shown in Figure 3 describes the variation in lead removal by DES-Gly. The improvement in the lead removal with increase in soil: solution ratio can be comprehended from the range of the X-axis of the Figure 3a-b, 3c-d and 3e-f. Lead removal reached up to 76.50% under 1:30 ratio, 20% DES-Gly and 2% soapnut concentrations. Figure 3a, 3c, and 3e clearly demonstrate the increase in lead removal when saponin concentration is increased from 0.5 up to 2% under different concentrations of DES-Gly. Figure 3b, 3d and 3f depicts the increase in lead removal when DES-Gly concentration was increased from 5 to 20% under various concentrations of saponin. The general trend is that Pb removal increases with both soapnut and DES concentrations.

These findings indicate that the soil washing by DESs and saponin solutions represent a Lewis acid-base interaction. While the soil has a deficiency of electrons, the organic carbons produce electron donating points, thereby acting as an electron pair donating Lewis base, attracting and bounding Pb$^{2+}$ cations which act as Lewis acid. Electron transfer reactions tend to occur through an adsorbed layer (Cruz and Mishra, 2011). The DESs used in this study are slightly alkaline in the pH range of 8-8.20. Therefore, when the alkaline DES-Gly and DES-EtGl were introduced into the system, they could not supply any H$^+$ or H$_3$O$^+$ ions since they are alkaline in nature. Therefore, the Pb$^{2+}$ removals were negligible for these two DESs. However, on mixing acidic soapnut with DESs, more H$^+$ or H$_3$O$^+$ ions were introduced in the system and then DES-Gly and DES-EtGl. Once the H$^+$ or H$_3$O$^+$ ions sourced from the saponin solution compete with the Pb$^{2+}$, loosening their bond, DES anions remove them from the soil surface. Saponins also attack the Pb$^{2+}$ forming micelle which capture the loose Pb$^{2+}$ increasing the functionality of the mixture. The synergistic effect of saponin and DES therefore improves the performance of the DES-saponin mixtures. Higher the saponin concentration, higher is the rate of micelle formation leading to dissociation of Pb$^{2+}$ from soil. Higher the DES concentration, higher is the
rate of formation of DES-Pb complex. Thus the trends demonstrated in Figure 2 and Figure 3 are justified.

Figure 2: Variation in Pb removal at different saponin and DES-Ethylene Glycol concentrations at soil: solution ratios of 1:10, 1:20 and 1:30. The Box-whisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score

Figure 3: Variation in Pb removal at different saponin and DES-Glycerol concentrations at soil: solution ratios of 1:10, 1:20 and 1:30. The Box-whisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score

3.3 Damage of soil mineralogical structure

XRD spectra of Pb contaminated soil as well as the soils washed with DES-EtGl, DES-Gly and their mixture with saponin did not detect any change in the location of the peaks. Figure 4 shows the XRD spectra of spiked soil and the soil washed with DES-Gly and DES-Gly+saponin. This phenomenon indicates that the soil minerals did not undergo corrosion or mineralogical changes when they were subjected to soil washing. Figure 5a-c show the SEM micrographs of Pb contaminated soil, washed with a mixture of DES-Gly+saponin and a 10% DES-Gly respectively. Minor roughness of underlying soil surface can be noticed for both DES-Gly+saponin and DES-Gly. However, no major corrosion could be observed. On measuring the size distribution of particle size before and after washing the soil using DES-Gly and DES-Gly+saponin solutions, it was found that there was an overall loss of soil sample in course of experiment and sample handling (Table 3). There was an overall loss of ~6% soil samples after the experiment. Among the soil components, the loss of silt was highest, in the range of 10% justifiable due to loss of fine particles during filtration and transfer of solutions. Loss of coarse, medium and fine sands were in the range of 4-7%. These values indicate that not much difference was noticed among size distribution and the coarser sand did not undergo noticeable disintegration into finer particles on washing. If such were the case, a large variation of size distribution would have been noticed. Therefore, DESs can be safely used for soil washing without destroying the soil texture.
Figure 4: XRD Spectra before and after washing with DES-Gly, DES-Et Gl and their combination with saponin

Figure 5: SEM image before and after washing with DES-Gly and DES-Gly+soapnut mixture

Table 3: Comparison of the particle size distribution before and after the soil corrosion batch experiments

4 Conclusion

This study demonstrates the suitability of using polyol-based DESs for soil washing purpose alongside saponin. The DESs and saponin performed well when used as a mixture rather than on their own, indicating a synergistic behaviour where they both contribute towards Pb\textsuperscript{2+} removal from soil. The soil washing process represents a Lewis acid-base reaction and therefore pH of the wash solution plays an important role. While saponin lowers the pH of the mixture and causes micellar solubilisation of Pb\textsuperscript{2+} from the soil, DESs influence the Pb removal by capturing the loosened Pb\textsuperscript{2+}. The process improves when the concentrations of both DESs and saponin were increased. More than 72% of Pb\textsuperscript{2+} removal from contaminated soil were obtained while using mixture of 40% DES-Gly and 1% saponin and mixture of 10% DES-Gly and 2% saponin. These results are promising and demand further investigation into the application of DESs for soil washing.

Acknowledgements

The authors would like to express their thanks to the University of Malaya, Centre for Ionic Liquids (UMCiL) and University of Malaya Grant no: UM-QUB6A-2011 for their support to this research.

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Figure 3: Variation in Pb removal at different saponin and DES-Glycerol concentrations at soil: solution ratios of 1:10, 1:20 and 1:30. The Box-whisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score
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Figure 3
Figure 4
Figure 5
Table 1: Composition of DESs and their pH in presence of saponin

<table>
<thead>
<tr>
<th>Component</th>
<th>1st Component (quaternary ammonium salt)</th>
<th>2nd Component (HBD)</th>
<th>Ratio of Components (1:2)</th>
<th>pH of pure DES</th>
<th>pH of 10% DES + 1 gm soil</th>
<th>pH (5 mL 10% DES + 5 mL 1% SN + 1 gm soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DES-Gly</td>
<td>Choline chloride</td>
<td>Glycerol</td>
<td>1:2</td>
<td>8.10</td>
<td>6.99</td>
<td>4.49</td>
</tr>
<tr>
<td>DES-EtGl</td>
<td>Choline chloride</td>
<td>Ethylene glycol</td>
<td>1:3</td>
<td>8.12</td>
<td>7.52</td>
<td>4.58</td>
</tr>
</tbody>
</table>

Table 2: Characterisation of the contaminated soil

a. Size distribution of soil particles

<table>
<thead>
<tr>
<th>mm</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel/Rock</td>
<td>&gt;2</td>
</tr>
<tr>
<td>Very Coarse sand</td>
<td>0.85 &lt; x &lt; 2</td>
</tr>
<tr>
<td>Coarse sand</td>
<td>0.71 &lt; x &lt; 0.85</td>
</tr>
<tr>
<td>Medium sand</td>
<td>0.25 &lt; x &gt; 0.71</td>
</tr>
<tr>
<td>Fine sand</td>
<td>0.045 &lt; x &lt; 0.25</td>
</tr>
<tr>
<td>Silt</td>
<td>&lt;0.045</td>
</tr>
</tbody>
</table>

b. Physical characteristics

- Moisture content (% wt) 3.60
- Loss by ignition (% wt) 1.21
- Density (Kg L⁻¹) 2.52
- pH 3.45
- ORP (mV) 333
- EC (mS cm⁻¹) 8.25
- CEC (Meq/100gm) 9

c. Metal content (mg Kg⁻¹)

<table>
<thead>
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<th>Value</th>
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</tr>
<tr>
<td>Pb</td>
<td>1,472.00</td>
</tr>
<tr>
<td>Fe</td>
<td>982.00</td>
</tr>
<tr>
<td>Mg</td>
<td>457.11</td>
</tr>
<tr>
<td>Ca</td>
<td>218.34</td>
</tr>
<tr>
<td>Na</td>
<td>72.52</td>
</tr>
<tr>
<td>Mn</td>
<td>43.28</td>
</tr>
<tr>
<td>Zn</td>
<td>12.10</td>
</tr>
<tr>
<td>As</td>
<td>8.64</td>
</tr>
</tbody>
</table>
Table 3: Comparison of the particle size distribution before and after the soil corrosion batch experiments

<table>
<thead>
<tr>
<th>Size (mm)</th>
<th>Mass before washing (gm)</th>
<th>Mass after washing (gm)</th>
<th>Loss after washing (%)</th>
<th>Mass before washing (gm)</th>
<th>Mass after washing (gm)</th>
<th>Loss after washing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.71 &lt; x &lt; 0.85</td>
<td>Washed with DES-Gly</td>
<td>Washed with DES-Gly+saponin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>1.72</td>
<td>1.63</td>
<td>-5.23</td>
<td>1.68</td>
<td>1.57</td>
<td>-6.55</td>
</tr>
<tr>
<td>Medium sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 &lt; x &gt; 0.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.71</td>
<td>2.76</td>
<td>2.56</td>
<td>-7.25</td>
<td>2.89</td>
<td>2.75</td>
<td>-4.84</td>
</tr>
<tr>
<td>0.045 &lt; x &lt; 0.25</td>
<td></td>
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<tr>
<td>Fine sand</td>
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<tr>
<td>&lt; 0.25</td>
<td>3.86</td>
<td>3.65</td>
<td>-5.44</td>
<td>3.72</td>
<td>3.51</td>
<td>-5.65</td>
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<td>Silt</td>
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<td></td>
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<tr>
<td>&lt;0.045</td>
<td>1.66</td>
<td>1.49</td>
<td>-10.24</td>
<td>1.71</td>
<td>1.54</td>
<td>-9.94</td>
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<tr>
<td>Total mass</td>
<td>10.00</td>
<td>9.33</td>
<td>-6.70</td>
<td>10.00</td>
<td>9.37</td>
<td>-6.30</td>
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Graphical Abstract
Enhanced removal of lead from contaminated soil by polyol-based deep eutectic solvents and saponin

Highlights

- Deep eutectic solvents (DESs) are used for the first time for soil remediation.
- Saponins are used to enhance DESs performances for lead (Pb) removal.
- Polyol based DESs formed with choline chloride examined in details.
- Up to 76% Pb was removed with a combination of DES-glycerol and saponin.
- Soil corrosion by DES washing is negligible.