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Ammonium-based deep eutectic solvents as novel soil washing agent for lead removal

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Abstract

Deep eutectic solvents (DESs) are a new class of biodegradable and low cost solvents analogous to ionic liquids. In this study, DESs have been used to remove lead from a landfill soil for the first time. The DESs used in this study were prepared by mixing choline chloride, a quaternary ammonium salt with different hydrogen bond donors such asfructose, sucrose, glycerol and ethylene glycol. A natural biodegradable surfactant saponin extracted from soapnut fruit pericarp, was mixed with DESs to enhance their efficiency. The 10% solution of fruit-based DESs containing fructose and sucrose demonstrated lead removal of about 31% and 25% respectively, which increased on additionof saponin. Up to 72% Pb could be removed with a combination of 40% fructose-based DES and 1% saponin or 10% fructose-based DES and 2% saponin. For synthetic DESs containing glycerol and ethylene glycol, saponin addition resulted in marked improvement of up to 54%. Mildly alkaline DESs supplied H^+ acting as Lewis acid which replaced the lead cations from the organic carbon electron donors. Slightly alkaline DESs performed better when mixed with acidic saponin solution which supplied H^+. This study will open up new possibilities into the application of natural compound basedDESs for soil remediation.

Keywords: soil washing; deep eutectic solvents; *Sapindus mukorossi*; lead; fructose-based DES; choline chloride.

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1 Introduction

Soil and groundwater pollution affects millions of lives around the world [1]. Modern industrial, agricultural and mining activities affect soil by releasing various contaminants such as organics, oils and heavy metals which eventually leach to the aquifer. Lead (Pb) is one of the heavy metals which has been released in the soil environment in large amount [2]. As a consequence, soil contains lead concentrations less than 50 mg Kg^{-1}, but in many urban areas lead levels exceed 200 mg Kg^{-1}. The USEPA's 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 [3]. Toxicity of Pb is well researched[4]. Therefore excess Pb needs to be removed from affected soils for reducing public health risk. Washing of soil contaminated with heavy metals and organics is a widely accepted practice[5-8] and saponin, a plant based surfactant has been effectively used for contaminant removal from soil [9-11]. Saponin (SN)is environment friendly and has been used as detergent and medicine for many decades[12]. It can be extracted from the fruit pericarp of *Sapindus mukorossi* which contains natural surfactant triterpenoidal saponins viz oleanane, dammarane and tirucullane[12].

Ionic liquids (ILs) have emerged as potentially versatile solvents for various applications including those for liquid extraction processes[13-17]. Properties of ILs include high thermal and electrochemical stabilities, wide liquid phase range and high ionic conductivity [17]. Recently, a new class of ILs analogue, namely Deep Eutectic Solvents (DESs) which consist of a mixture of two or more compounds that have melting points lower than that of either of its components [15]. DESs share many physical properties with ILs and can be synthesized by mixing a hydrogen bond donor with a salt [18]. The charge delocalisation occurring through hydrogen bonding between the halide anion and the hydrogen bond donor moiety is responsible for the decrease in the freezing point of the mixture relative to the melting points of the individual components [19]. This significant depression of the freezing point stems from an interaction between the halide anion of the salt and the hydrogen bond donor (HBD) component [15, 20]. Choline chloride has been used earlier as HBD [21] to synthesize DESs. Natural DESs or NADESs, a class of DESs obtained from mixing natural plant derivatives such as glucose, fructose and citric acid with choline chloride have been described earlier [22-24]. The NMR data showed that hydrogen bonding was the key to the formation of NADES, allowing the creation of supramolecular structures between the components.

Toxicity aspects of ammonium based DESs with HBD e.g. glycerine, ethylene glycol, triethylene glycol and urea have been studied through in-vitro and in-vivo studies and they were found to be less toxic than ionic liquids[25, 26]. Choline chloride: glucose and choline chloride: glycerol displayed low cytotoxic effects[27]. Recently, ethylene glycol and glycerol DESs with choline chloride were found to be biodegradable under lower concentrations [28].

DESs have attracted attention in the fields of chemical synthesis, metal-catalyzed organic reactions, biological catalysis [29], lubrication [30], electrochemical processes [31], production and purification of biodiesel [15, 18], separation of aliphatic and aromatics [32]. However, DESs have never been used as washing agent for contaminant removal from soil matrices. Therefore, this study used a group of ammonium-based DES for soil washing. Different HBDs were used to prepare NADES such as fructose, sucrose and glycerol. NADES and ethylene glycol-based DES (DES-EtGl) have been combined with natural surfactant (saponin) for investigation of their synergistic effect on the process, adding a new dimension to the study.

2 Materials and methods

A composite soil sample was collected from Jeram Sanitary Landfill (JSL) in Selangor, Malaysia. JSL receives waste from seven major municipalities, mostly from Kuala Lumpur and Selangor Municipality. The soil was dried in an oven overnight at 105^{O}C following the protocol presented by Roy et al. [33]and was crushed and passed through a 2 mm sieve. It was classified according to USDA soil classification. The soil pH was measured by USEPA SW-846 Method 9045D while 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 soil was spiked with1000 mg L^{-1} concentrations of Pb in $Pb(NO_3)_2$ solution at room temperature by mixing it for 7 days at weight: volume ratio of 3:2, 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%. A set of 4 DESs were used for the preliminary study.The compositions of these DESs are given in Table 1 and their structures are shown in Figure 1. 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 at 70ºC and stirrer speed of 350 rpm for 3 hour mixing time. The DES preparation was carried out in a fume hood. Soapnut solution of 1% concentration (w/w) was used in combination with the 4 DESs for Pb desorption from the soil and were compared against water blank. Saponin was extracted from the soapnut fruit pericarp by water and the saponin concentration was measured by UV-Visible spectra to be 65% following Roy et al [33]. 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).

Batch tests were conducted in 15 mL test tubes. For each experiment, 1 gof soil was washed with 5 mL of wash solution (DESs and DES-saponin mixtures) of different concentrations as shown inFigure 2. The test tubes were shaken in an orbital shaker in horizontal position for 4 hours. Wash solutions were then centrifuged, filtered and preserved with 1 drop of nitric acid for ICP analysis for Pb concentration.

XRD spectroscopy and SEM were used to inspect the damage to the mineral structure of soil. 10 g 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 was performed by a Panalytical Empyrean diffractometer using Highscore Plus software and 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.

Table 1: List of different DESs and their pH

Figure 1: Structure of different DESs used in the study

3 Results and discussion

3.1 Soil characterisation

Table 2 summarizes the characteristics of the soil, which was classified as sandy soil following USDA soil classification. The soil redox potential value of 333 mV made it slightly oxidized, indicating minor electron deficiency. The soil was blackish in colour signifying presence of some organic matter which was supported by a small ignition loss of 1.21%. The organic matter tends to act as an electron donor and binds with the heavy metal cations i.e. lead in this case. A moderately high electrical conductivity value of 8.25 mS/cm suggests presence of charged species in the soil matrix.

On acid digestion, the mineralogical metals were extracted and Al, Mg and Fe were detected in high concentration. A background concentration of 218 mg Kg^{-1}Pb was measured in unspiked soil, probably in mineralogical state. After spiking, the Pb content of soil was found to be 1500 mg Kg^{-1} which is present as the soil contamination. The soil pH is 3.45 indicating acidic nature of the soil. Low pH value of soil can be the result of rainwater leaching away basic ions (calcium, magnesium, potassium and sodium) and formation of carbon dioxide from decomposing organic matter and from root respiration; dissolving in soil water to form a weak organic acid. Therefore, the overall soil was found to have electron deficiency in spite of presence of organic carbonaceous compounds, which act as electron donor centres and bind readily with lead cations. The success of lead extraction would depend upon the ability of the washing agent to break the bond between organic carbon and lead.

Table 2: Characterisation of the contaminated soil

3.2 Pb removal by DESs and saponin

The Pb removal by a 10% solution of individual DESs in the absence or presence of saponin has been shown in Figure 2. Water and 0.5% saponin solutions were used as blanks. The Pb was strongly bound with soil organic carbon and water could remove only up to 5% of Pb signifying the necessity of adding other extractants. A 1% soapnut removed up to about 31% Pb. A 10% solution of DES-Fr showed the best performance in terms of Pb removal on its own, removing up to 31% of Pb followed by 10% DES-Su (Sucrose), which removed 25.21% Pb from soil. DES-EtGl and DES-Gly, both at 10 % concentration, did not show promising performance on their own, removing only 6.55 and 3.44% Pb respectively. However, on addition of saponin solution, their performances improved by a large extent. For DES-Gly, lead removal ability enhanced up to 54% compared with 4% observed earlieron addition of 0.5% saponin. DES-EtGl is another notable case, which recorded an improvement of 34% more than its previous result.

The Pb removal has a strong correlation with the pH of the solution, signifying a Lewis acid-base reaction. The slightly acidic DESs i.e. DES-Fr and DES-Su could remove more Pb by attacking electron rich organic carbon sites thereby releasing Pb^{2+}cations, than the slightly alkaline DESs e.g. DES-Gly and DES-EtGl. In presence of saponin solution which is also 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 $Pb^{2+}$from soil particles (c) dilution of DESs and introduction of more H_2O molecules, which can act as a media to leach out the already loosened Pb from soil surface.

Figure 2: Lead removal by DESs, DES+saponin mixtures, water and saponin

Fruit sugar based DESs such asDES-Fr and DES-Su were further investigated with different concentrations in presence and absence of saponin. Figure 3(a) depicts the increase in Pb^{2+}removal when DES-Fr and DES-Su concentrations are increased from 5 to 40% both in absence of saponin and in presence of 1% saponin. Figure 3(b) clearly shows the increase in lead removal when saponin concentration was increased from 0.5 up to 2% in presence of 10% solutions of DES-Fr and DES-Su without any exception. Therefore, the general trend is that the performance of DESs as well as DES-saponin mixtures improves with increasing the concentration of any of them, thereby proving a direct relationship between the activities of these two agents behind removal of Pb^{2+}.

Figure 3: (a) Variation of DES concentration at 1% saponin concentration (b) Variation of saponin concentration at 10% DES concentration

Figure 4: FTIR spectra of DES glucose before and after soil washing

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 carbon produces 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 [34]. The DESs used in this study had either acidic pH (e.g. DES-Fr and DES-Su), or slightly alkaline pH (e.g. DES-Gly and DES-EtGl). Therefore, when the acidic DESs i.e. DES-Fr and DES-Su were added with the Pb^{2+} contaminated soil, H^+ or H_3O^+ ions were introduced, a powerful Lewis acid. The H^+ ions attacked the electron rich sites of the soil, mostly the organic carbon and competed with the Pb^{2+} for electrons, thereby pulling them out of the soil surface and attaching them with DES anions already present in the solution. However, when the alkaline DES-Gly and DES-EtGl were introduced into the system, H^+ or H_3O^+ ions were not supplied since they are alkaline in nature. Therefore, the Pb^{2+}removals were negligible for these two DESs. Following that, when DESs were mixed with saponin, which is naturally acidic in nature, more H^+ or H_3O^+ ions were introduced in the system and all the DESs demonstrated better performance. Saponin also contributed by trapping the Pb^{2+} inside micelle. In earlier works, Song et al [35] suggested complexation of saponin molecule with heavy metals. However, the FTIR spectra in Figure 4 do not detect any complexation between DES-glucose, soapnut and Pb^{2+} . The FTIR spectra of all the solutions give similar peaks and no shift of peaks could be detected after introduction of Pb in the DES and DES-SN solutions. Once the H^+ or H_3O^+ ions sourced from the saponin solution compete with the Pb^{2+}, loosening their bond, DES anions remove them from the soil surface. The synergistic effect of saponin and DES therefore improves the performance of the DES-saponin mixtures.

3.3 Damage of soil mineralogical structure

XRD spectra of Pb contaminated soil and the soils washed with DES-EtGl as well as a mixture of DES-EtGl and saponin did not detect any change in the location of the peaks (Figure5a). This indicates that the soil minerals did not undergo corrosion or mineralogical changes when they were subjected to soilwashing. Figure5b, c and d show the SEM micrographs of Pb contaminated soil,washed with a mixture of DES-EtGl + saponin and a 10% DES-EtGl respectively. Minor roughness of underlying soil surface can be noticed for both DES+saponin and DES. However, no major corrotion could be observed. Therefore, DESs can be safely used for soil washing without destroying the soil texture.

Figure5: (a) XRD Spectra and (b,c,d) SEM imagery of soil before and after washing with DES-EtGl and DES EtGl-soapnut mixture

4 Conclusion

This study demonstrates the suitability of using 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^{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. Micellar solubilisation by saponin adds an edge to the process. Also, the process improves when the concentrations of both DESs and saponin were increased.Pb^{2+}removal of above 72.65% was obtained while using 40% DES-Fr and 1% saponin mixture and 72.54% $Pb^{2+}$was removed by 10% DES-Fr and 2% saponin mixture. These results are promising and demand further investigation into the application of DESs for soil washing. The biological origin of natural deep eutectic solvents and natural saponin make the process of soil washing promising and sustainable.

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LIST OF FIGURES

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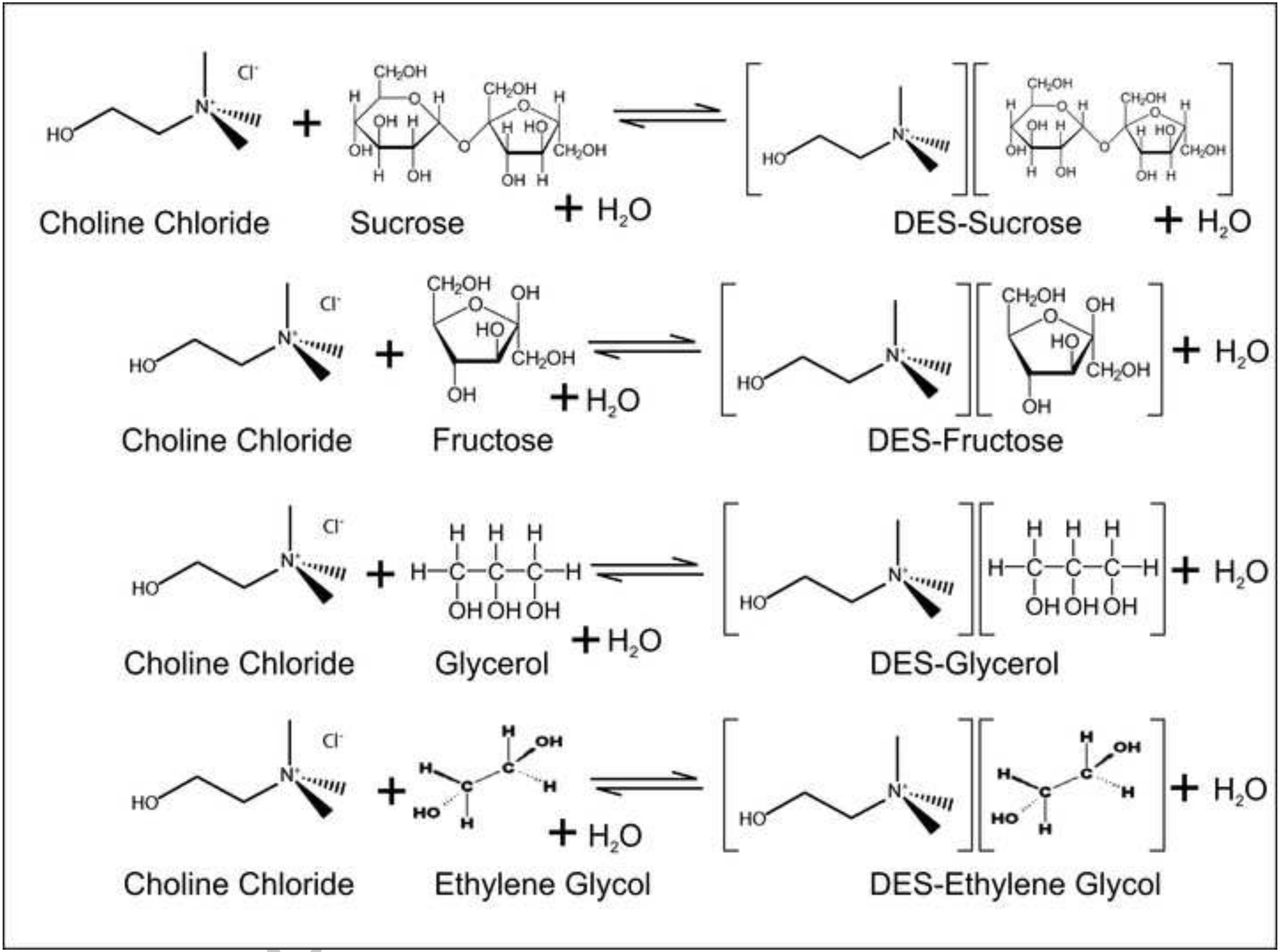
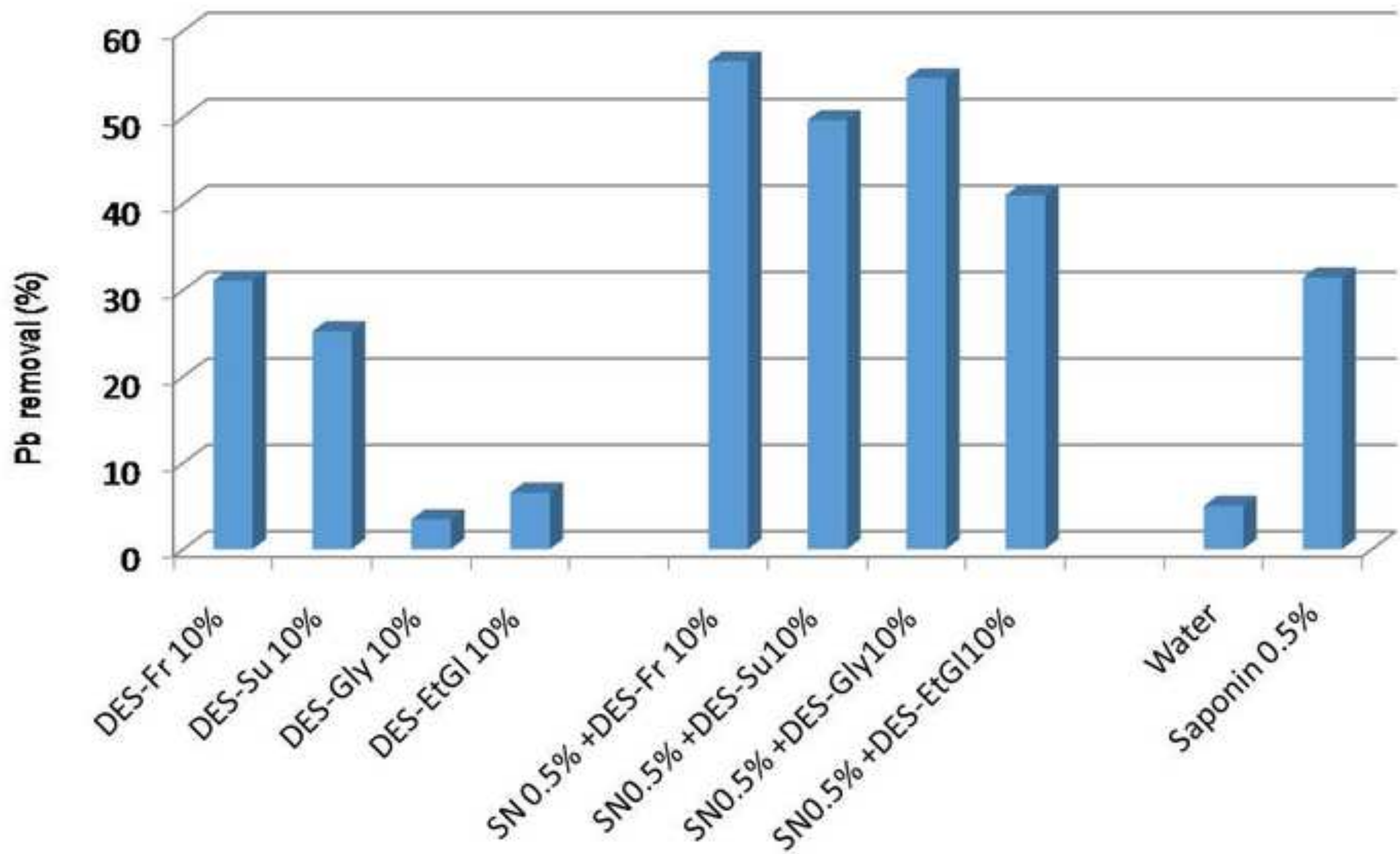
Table 3: List of different DESs and their pH

	1st Component (quaternary ammonium salt)	2nd Component (HBD)	3rd Component	Ratio of Components (1: 2: 3)	pH of DES	pH (10 mL DES+ 1 g soil)	pH (5 mL DES-5 mL 1% SN + 1 g soil)
DES-Fr	Choline chloride	Fructose	Water	5:2:5	6.26	7.28	4.45
DES-Su	Choline chloride	Sucrose	Water	4:1:4	6.76	6.86	4.41
DES-Gly	Choline chloride	Glycerol	Water	1:2:1	8.10	6.99	4.49
DES-EtGl	Choline chloride	Ethylene glycol	Water	1:3:1	8.12	7.52	4.58

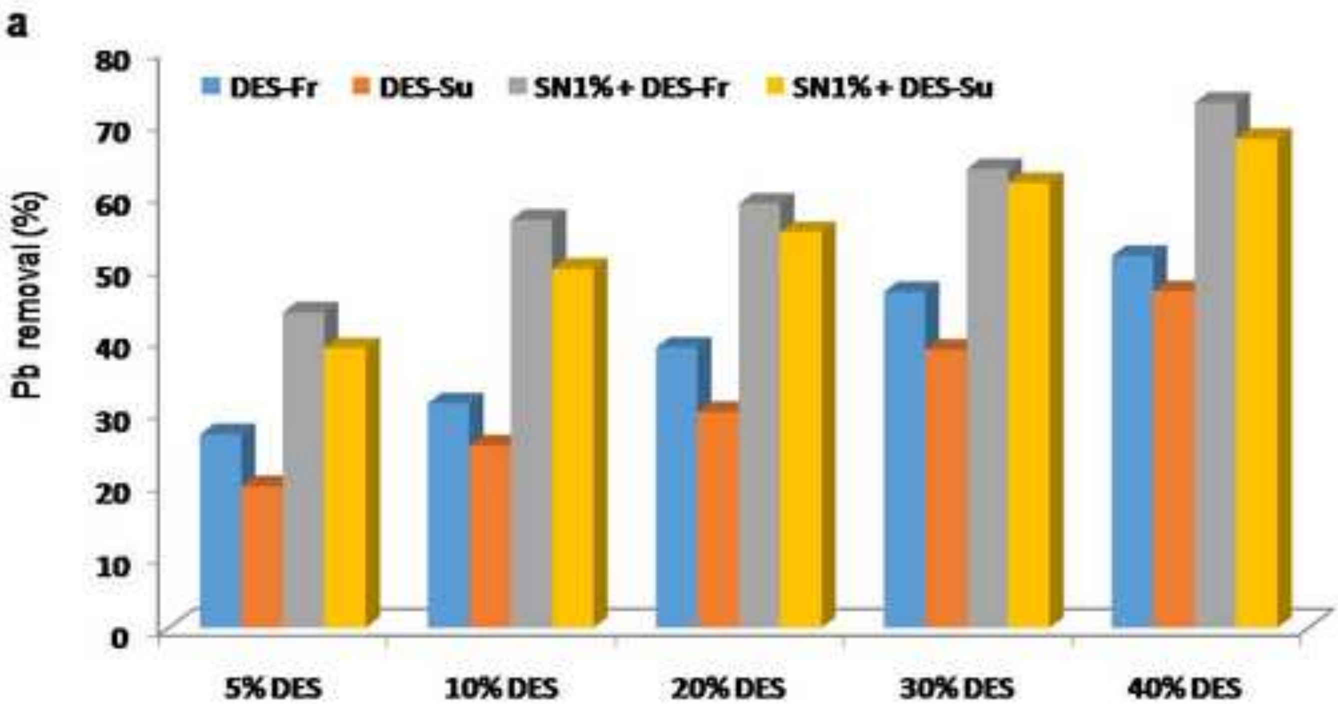
Table 4: Characterisation of the contaminated soil

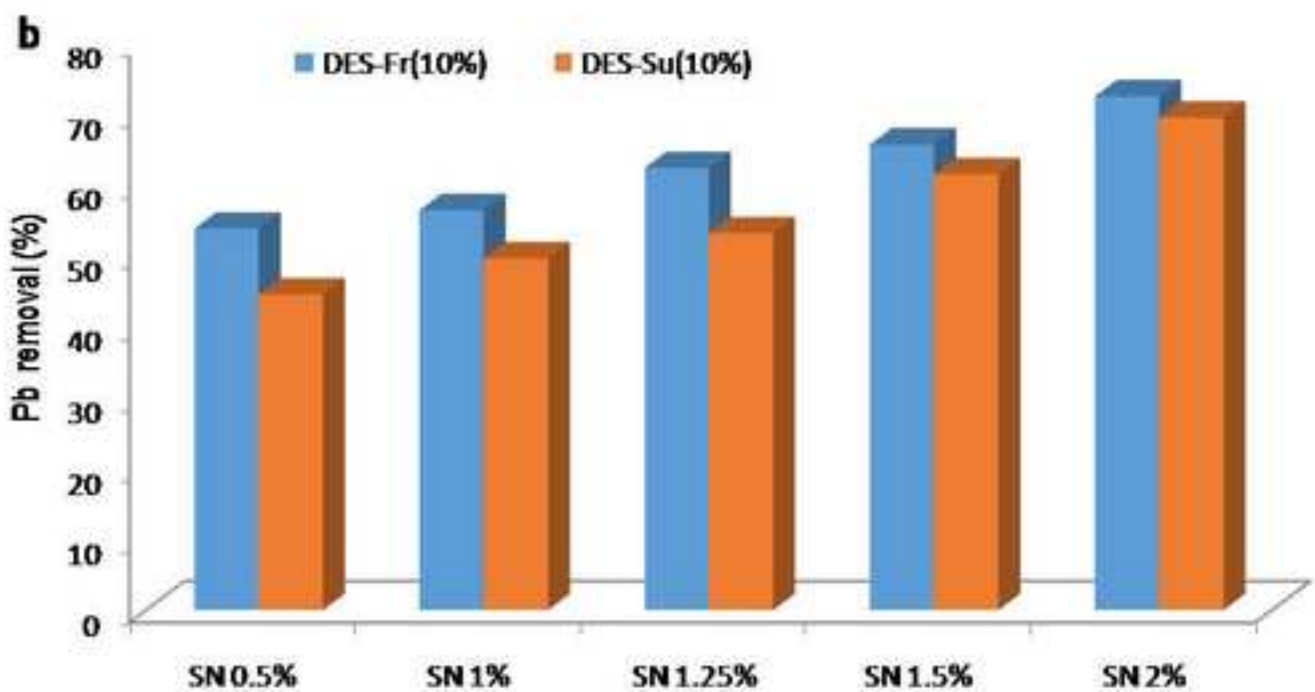
a. Size distribution of soil particles		
	mm	%
Gravel/Rock	>2	5.750
Very Coarse sand	0.85 < x < 2	17.180
Coarse sand	0.71 < x < 0.85	3.582
Medium sand	0.25 < x > 0.71	36.951
Fine sand	0.045 < x < 0.25	34.140
Silt	<0.045	2.397
b. Physical characteristics		
Moisture content (% wt)		3.60
Loss by ignition (% wt)		1.21
Density (Kg L^{-1})		2.52
pH		**3.45**
ORP (mV)		333
EC (mS cm^{-1})		8.25
c. Metal content (mg Kg^{-1})		
Pb		**1500**
Al		11893.94
Fe		1000
Mg		464.393
Ca		220.758
Na		71.960
Mn		42.121
Zn		10.303
As		6.771

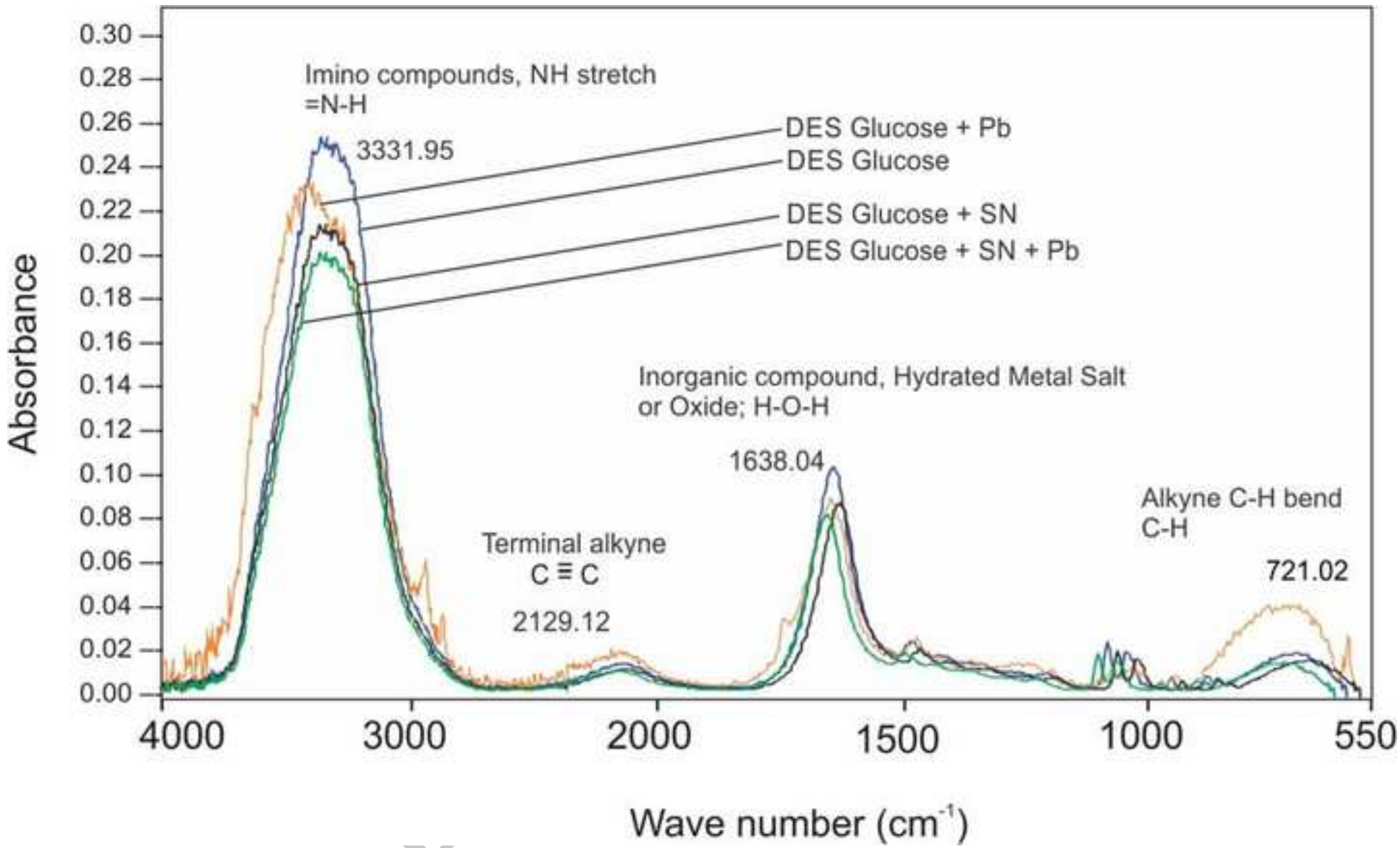

Choline Chloride
Sucrose
+ H2O
DES-Sucrose
+ H2O
Choline Chloride
Fructose
+ H2O
DES-Fructose
+ H2O
Choline Chloride
Glycerol
+ H2O
DES-Glycerol
+ H2O
Choline Chloride
Ethylene Glycol
+ H2O
DES-Ethylene Glycol
+ H2O

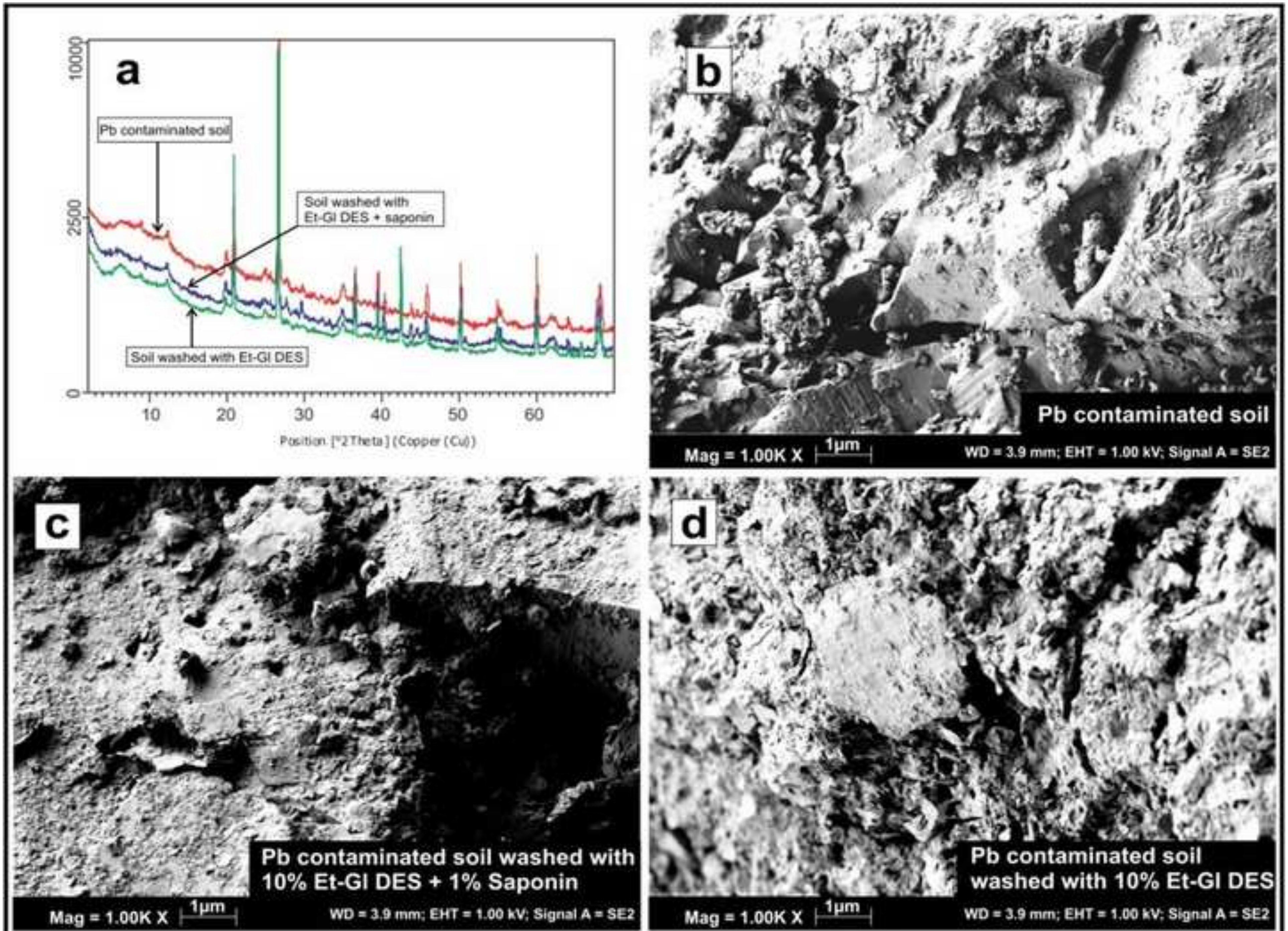


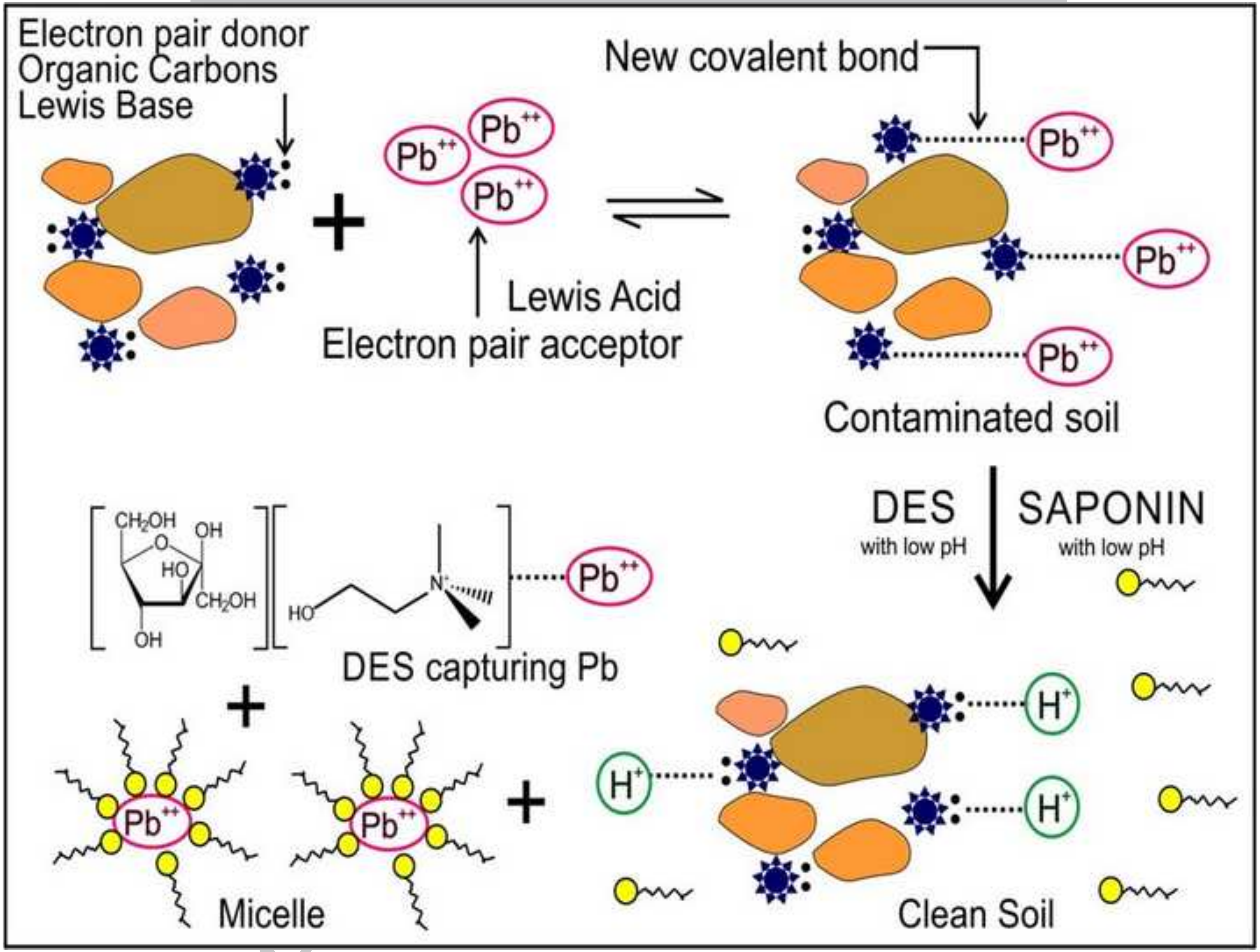
Pb removal (%)
0
10
20
30
40
50
60
DES-Fr 10%
DES-Su 10%
DES-Gly 10%
DES-EtGl 10%
SN 0.5% +DES-Fr 10%
SN0.5% +DES-Su10%
SN0.5% +DES-Gly10%
SN0.5% +DES-EtGl10%
Water
Saponin 0.5%


a
80
70
60
50
40
30
20
10
0
Pb removal (%)
DES-Fr
DES-Su
SN1% + DES-Fr
SN1% + DES-Su
5% DES
10% DES
20% DES
30% DES
40% DES


b
80
70
60
50
40
30
20
10
0
Pb removal (%)
DES-Fr(10%)
DES-Su(10%)
SN 0.5%
SN 1%
SN 1.25%
SN 1.5%
SN 2%


0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absorbance
Imino compounds, NH stretch
=N-H
3331.95
DES Glucose + Pb
DES Glucose
DES Glucose + SN
DES Glucose + SN + Pb
Inorganic compound, Hydrated Metal Salt
or Oxide; H-O-H
1638.04
Alkyne C-H bend
C-H
721.02
Terminal alkyne
C ≡ C
2129.12
4000
3000
2000
1500
1000
550
Wave number (cm-1)


a
Pb contaminated soil
Soil washed with
Et-Gl DES + saponin
Soil washed with Et-Gl DES
Position [°2Theta] (Copper (Cu))
b
Pb contaminated soil
Mag = 1.00K X
1μm
WD = 3.9 mm; EHT = 1.00 kV; Signal A = SE2
c
Pb contaminated soil washed with
10% Et-Gl DES + 1% Saponin
Mag = 1.00K X
1μm
WD = 3.9 mm; EHT = 1.00 kV; Signal A = SE2
d
Pb contaminated soil
washed with 10% Et-Gl DES
Mag = 1.00K X
1μm
WD = 3.9 mm; EHT = 1.00 kV; Signal A = SE2


Electron pair donor
Organic Carbons
Lewis Base
Pb++
Pb++
Pb++
Lewis Acid
Electron pair acceptor
New covalent bond
Pb++
Pb++
Pb++
Contaminated soil
DES
with low pH
SAPONIN
with low pH
CH2OH
OH
O
HO
CH2OH
OH
HO
N+
Pb++
DES capturing Pb
Pb++
Pb++
Micelle
H+
H+
H+
Clean Soil

Ammonium-based deep eutectic solvents as novel soil washing agent for lead removal

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.
- Natural DESs formed with choline chloride & fructose/sucrose examined in details.
- Up to 72% Pb was removed with a combination of 40% DES-fructose & 1% saponin
- Soil corrosion by DES washing is negligible.