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Short communication

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

Soumyadeep Mukhopadhyay [a,*], Sumona Mukherjee [a], Adeeb Hayyan [b,c], Maan Hayyan [b], Mohd Ali Hashim [a,b], Bhaskar Sen Gupta [d]

[a] Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] University of Malaya Centre for Ionic Liquids, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] Institute of Halal Research University of Malaya (IHRUM), Academy of Islamic Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia
[d] Water Academy, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University, Edinburgh Campus, Scotland EH14 4AS, UK

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ABSTRACT

Deep eutectic solvents (DESs) are a class of green solvents analogous to ionic liquids, but less costly 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.

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, 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, 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,

* Corresponding author.
E-mail address: soumya_m@ymail.com (S. Mukhopadhyay).

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Table 1
Composition of DESs and their pH in presence of saponin.

	1st Component (quaternary ammonium salt)	2nd Component (HBD)	Ratio of components (1:2)	pH of pure DES	pH of 10% DES + 1 g soil	pH (5 mL 10% DES + 5 mL 1% SN + 1 g soil)
DES-Gly	Choline chloride	Glycerol	1:2	8.10	6.99	4.49
DES-EtGl	Choline chloride	Ethylene glycol	1:3	8.12	7.52	4.58

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, 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 105 °C 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/100 g 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 s at continuous scan type).

2.2. Spiking of soil sample

The soil was spiked with 1000 mg L^{-1} concentrations of Pb using $Pb(NO_3)_2$ 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 $CaCl_2$, 5×10^{-4} M $Ca(NO_3)_2$, 5×10^{-4} M $MgCl_2$, 10^{-4} M Na_2SO_4, 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, 2015). This contaminated soil was then air dried at 25 °C for 24 h 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 60 °C under vacuum. A glass jacketed vessel with a magnetic stirrer was used to prepare DES samples in a fume hood at 70 °C and stirrer speed of 350 rpm for 3 h 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 2
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
CEC (Meq/100 g)		9
c. Metal content (mg kg^{-1})		
Al		11,658.06
Pb		1472.00
Fe		982.00
Mg		457.11
Ca		218.34
Na		72.52
Mn		43.28
Zn		12.10
As		8.64