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

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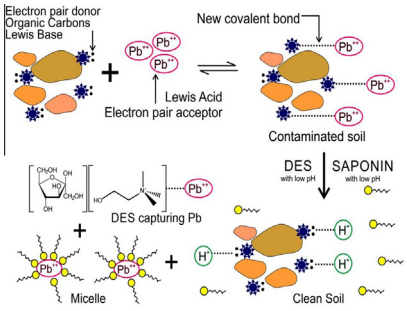
HIGHLIGHTS

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

GRAPHICAL ABSTRACT



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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 as fructose, 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 addition of 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 based DESs for soil remediation.

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

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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

Table 1
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

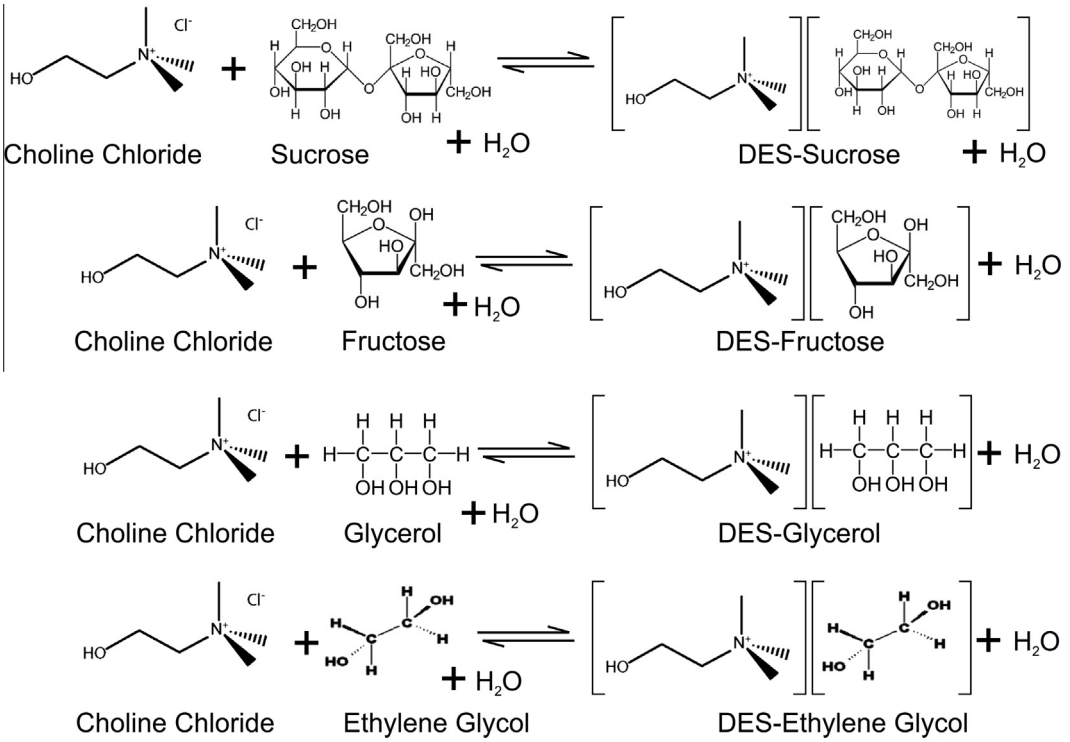

Fig. 1. Structure of different DESs used in the study.