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Application of hydrophobic solvents based on L-menthol, as greener alternatives to classical solvents for Pb(II) ions extraction

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Abstract: Deep eutectic solvents (DESs) as a new-generation of solvents are receiving increasing attention as environmentally friendly solvents in various analytical techniques. These solvents are new generation solvents, and based upon what they are derived from, they can be the safest, cheapest, and most effective extraction methods available. With DES, the extraction efficiency and metal ion recycling are significantly improved. In this work, the potential application of these solvents for the extraction of Pb(II) ions was investigated. For that purpose, hydrophobic DESs (HDESs), based on L-menthol as H-acceptor and decanoic acid as H-donor, were prepared at molar ratios of acceptor to donor of 1:1 and 1:2. In the optimized extraction procedure, the Pb(II) ions were extracted into the organic phase with the efficiency of 94.3% and 97.3% for 1:1Men:DecA and 1:2 Men: Dec A, respectively. The results also showed that unlike of classical liquid-liquid extraction methods, in the original solutions, counterions are not required to transfer the analyte to the hydrophobic phase. Furthermore, no ligands were required to transfer the analyte ions to the HDES phase: the results show that the extraction efficiency of 1:1 HDES decreased to 88.65% in the presence of 18C6, and to 96.5% for 1:2 HDES. Comparable results for HDES (1:1 Men: DecA) extraction efficiency in the proposed method with the efficiency of 1,2-dichloroethane and chloroform in classical methods (96.7% and 92%, respectively), without counterions and without the requirement for ligands as carriers, make this HDES-based extraction method simpler, less expensive, and most importantly, more environmentally friendly.

INTRODUCTION

Deep eutectic solvents (DESs) as a new generation of solvents are receiving increasing attention as environmentally friendly solvents in various analytical techniques. The concept of a "deep" eutectic solvent (DES) first appeared in the scientific world in 2003. when it was announced that a group of designed solvents could meet the principles of "green" chemistry, unlike the ionic liquids used at the time(Anastas and Eghbali, 2010).
Moreover, the possibility of synthesis of these solvents from non-toxic ingredients, as well as components of natural origin (NADES, Natural DES) allows overcoming the limitation of ionic liquids, such as toxicity and poor biodegradability (Tuzen et al., 2016). Hydrophobic deep eutectic solvents (HDES) prepared from terpenes (menthol, thymol) and fatty acids are considered relatively non-toxic, less volatile, more environmentally friendly, and renewable (Abbot et al., 2004), (Florindo et al., 2014). Their hydrophobicity makes them promising alternatives to traditional organic solvents used in sample preparation, as well as solvents used in the field of LLE of non-polar analytes and transition metals from aqueous environments.

In this paper, hydrophobic "deep" eutectic solvents based on natural neutral ingredients (L-menthol and natural organic acids) were prepared and their effect on the extraction of metal cations was studied. Only chemically stable DESs were selected to be used as solvents in the extraction. Practical applications of HDES in a sample preparation include conventional liquid-liquid extraction

(Zhao et al., 2015). The aim of this work is to examine all factors that affect the efficiency of Pb(II) ions removal, i.e. defining the conditions for the extraction of cations from the initial aqueous solution into a hydrophobic solution, all using a menthol-based solvent. Considering the low viscosity of the prepared menthol-based HDES, which makes them suitable for use in extraction techniques, L-menthol was also chosen in this work as an H-bond acceptor in the synthesis of HDES solvents (Ribeiro et al., 2015).

The final result is compared with the results of classical extraction of Pb(II) ions with hydrophobic organic solvents. Considering the relevance of such research and the still insufficiently researched area of application of hydrophobic eutectic solvents as alternative extracts for heavy metal ions as pollutants, the concept of this research was created. The obtained results will make a significant contribution to the expansion of knowledge in the field of application of hydrophobic eutectic solvents in liquid-liquid extraction.

MATERIALS AND METHODS

Chemicals:

- Standard Pb(II), solution (1000 mg/L), Merck
- Picric acid ($C_6H_3N_3O_7$), 99%, Kemika

Hydrophobic deep eutectic solvents prepared from:

- $C_{10}H_{20}O$, L(-)-mentol, 99,5%; Acros Organic
- $C_8H_{16}O_2$, octanoic acid; 99%, Acros Organics
- $C_{10}H_{20}O_2$, decanoic acid; 99%, Alfa Aesar
- $C_{12}H_{24}O_2$,dodecanoic acid ; 99%, Acros Organics

Macrocyclic ligands:

- $C_{12}H_{24}O_6$ (18-crown-6); 99%, ACROS OGANICS,

Stripping solution:
Triton X-100 surfactant; purrum.p.a. Sigma-Aldrich
Disodium-EDTA, > 99%; Sigma-Aldrich

Acetic acid buffer solution (pH=5), prepared from:
CH_3COOH (purris. p.a., Fluka) NaOH (g.r., Merck)

DES preparation

The preparation of hydrophobic DESs, as homogeneous liquids immiscible with water, was done by mixing two solid components (L-menthol as HBA and different HBDs) in different molar ratios, e.g. 2:1, 1:1 and 1:2. Different molar ratios were chosen to test whether DES solvents could be prepared in a wide or small range of compositions. The first component was weighed directly in the flask, and the second component was first weighed on a scale, after which the entire amount was transferred to the flask. (Rajabi et al., 2018).

The components in the flask were previously mixed with a glass rod and heated in a metal heating block. The formation of hydrophobic DESs was investigated using a standard procedure. After preparation and mixing, the flasks were heated and mixed at a temperature of approximately 40°C until the melting of the solid components was achieved and stability of the resulting solvent was determined (Cao et al., 2017). For mixtures that have not turned into a liquid state, the temperature is first increased to 60°C, and if (according to the previously explained procedure) this is not enough, the mixture is further heated up to 80°C (Phelps et al., 2018). During the experiments, in some cases after 24 h at room temperature, crystals were visible in the solvent, so these solvents were discarded from the study and not further analyzed (SalA:Men; tDecA:Men).

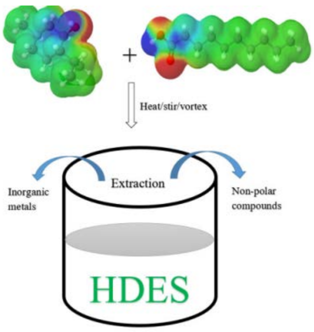

Figure 1. Synthesis of hydrophobic deep eutectic solvents (HDES) from DL-Menthol (HBA) and decanoic acid (HBD) at 1:1 molar ratio (Dwamen, 2019)

Extraction procedure

DES hydrophobicity was introduced in 2015 by van Osch and co-workers, although the authors acknowledged earlier work involving menthol-based hydrophobic eutectic mixtures. For the optimized liquid-liquid extraction procedure, 5 mL of standard feed solutions containing the analyte (standard metal solutions ($1\cdot10^{-4}$mol/L) and counterions (picrates, $1\cdot10^{-3}$mol/L) were mixed with a hydrophobic organic phase (volume of 3-5 mL) which represents the solvent used for the extraction. 5 mL of a buffered aqueous solution of "stripping agent" (thiosulfate, concentration 0.10 mol/L or EDTA concentration $1\cdot10^{-3}$ and $1\cdot10^{-2}$ mol/L) represents the final water phase - RP (eng. receiving phase). The aqueous phase and the organic hydrophobic phase (HDES solvent) were mixed for different periods of time (15 min to 2 h) on an automatic shaker (rotation: 300 rpm), after which the two phases of different polarity were physically separated. In the aqueous phase, the ion concentration of the analyte is then measured by AAS.

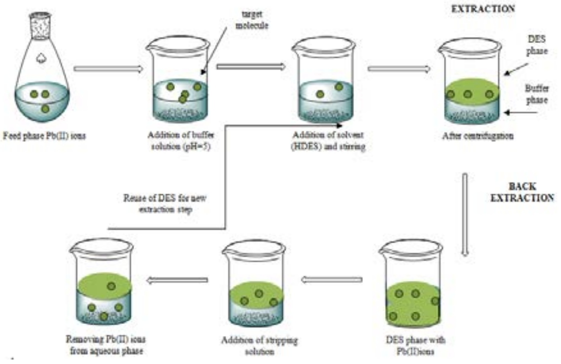

Figure 2. Extraction procedure

The efficiency of extraction was calculated:

$$\%\,of E = \frac{(analyte\ conc.\ before\ extraction) - (analyte\ conc.\ after\ extraction)}{analyte\ conc.\ before\ extraction} . 100$$

Instruments

The pH of the aqueous solutions was measured using a pH meter (GLP31 Crison Instruments).

Quantification of metal ions removed during the transport experiments was obtained by the Flame Atomic Absorption Spectrometry technique, using a Perkin Elmer AAnalyst 200 instrument.

RESULTS AND DISCUSSION

Various parameters were studied in order to optimize the conditions for selective extraction and the most efficient removal of Pb(II) ions. Factors affecting the selective extraction of Pb(II) ions were analyzed: the type of solvent used and its volume, the counterion concentration in the feed solution, the pH value of the feed and stripping solutions, and the extraction equilibrium time,.

The influence of analyte concentration on extraction efficiency was investigated.

Given that the increase in lead concentration has no significant effect on the extraction efficiency, the analyte concentration of 20 mg/L ($1\cdot10^{-4}$mol/L) was taken as optimal for further research. A study by Zolgharnein, Hosseini, Sangi et al. (2002) also confirmed the significant effect of different concentrations of counterions in the original solution on the efficiency of ion removal during transport. In this paper, the results showed that there is no significant effect of counter-ions on the extraction of Pb(II) ions. Namely, even in the absence of counter-ions, a satisfactory extraction efficiency is achieved (96.7%). It can be concluded that it is possible to achieve a high extraction efficiency even without the use of picric acid.

Since the amount of solvent used directly affects the cost of the extraction process, the effect of HDES volume on the removal of ions from the source phase was also investigated. Initially a volume of 5 mL was used, but smaller volumes (1 to 4 mL) were also tested. Treatment of samples with HDES volumes of 1 and 2 mL resulted in significantly reduced extraction efficiency compared to treatment of samples with DES volumes of 5 mL, performed under the same conditions. These results are consistent with the principles of mass transfer, since the driving force is the concentration gradient between the aqueous and organic phases.

However, using a volume of 3 mL, as well as 4 mL of solvent, achieves extraction efficiency comparable to the results of using 5 mL of solvent. Considering that reducing the amount of solvent did not significantly change the amount of ions removed, 3 mL was chosen as the optimal parameter for further experiments.

The effect of pH was tested by extraction experiments with Men/OctA (1:1) solvent, in the pH range between 3 and 6. At pH=3, there is no significant removal of Pb(II) ions in the HDES phase, which is probably due to the greater stability of menthol-based solvents in the pH 4-6 range.

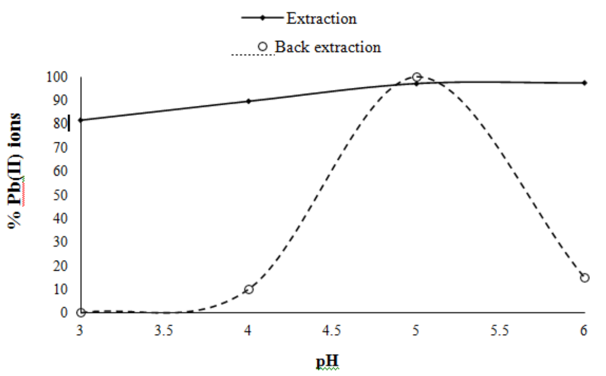

Figure 3. Dependence of extraction/back extraction efficiency on the pH value of aqueous solutions
SP contains: $[Pb^{2+}] = 1\cdot10^{-4}$ mol/L and $[Pic^{-}] = 4\cdot10^{-3}$ mol/L; RP contains: $[EDTA] = 1\cdot10^{-3}$ mol/L; time of mixing : 2h; HDES : Men:OctA; V(HDES) = 3 mL; V(SP)= 5 mL

Although experiments at pH 6 resulted in the highest extraction of analyte ions, the efficiency of the back extraction procedure (15%) does not justify working at this pH value. Therefore, pH=5 was chosen as the optimal pH value, for the proposed extraction procedure. In this work, it was also examined whether the use of macrocyclic ligands has an effect on the extraction of Pb(II) ions (Figure 4).

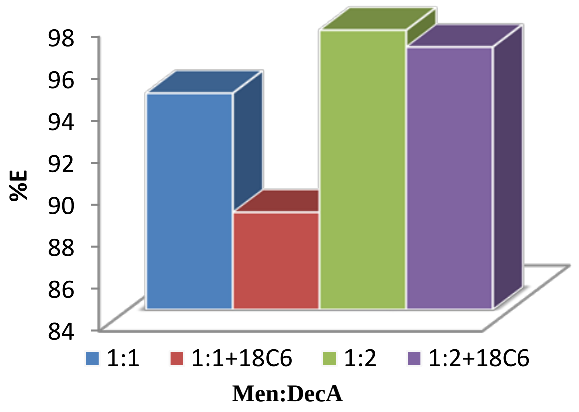

Figure 4. Comparison of Pb(II) ion extraction efficiency using Men:DecA solvent, with and without macrocyclic ligand 18C6 (SP contains: $[Pb^{2+}] = 1\cdot10^{-4}$ mol/L and [Pic-] $= 4\cdot10^{-3}$ mol/L; pH=5; mixing time: 2h; used V(HDES)=5 mL, V (SP)=5 mL)

In the classic LLE process, ligands are necessary as "carriers" of metal ions. In this work, the use of macrocyclic ligands is not necessary, it even has a negative effect on the removal of analyte ions, based on which we can assume that analyte ions enter into direct interactions with the hydrophobic solvent, without ligands as mediators. The results showed, that Pb(II) ions were extracted into the organic phase with the efficiency of 94.3% and 97.3% for 1:1 Men:DecA and 1:2 Men:DecA, respectively. For the HDES solvent Men:DecA (1:1) the extraction efficiency of 94.3% was reduced in the presence of 18C6 (88.65%), while in the case of the HDES solvent Men:DecA (1:2) the extraction efficiency of 97.3% decreased to 96.5% in the presence of 18C6. Therefore, it did not make sense to the macrocyclic ligand 18C6 for further research. It is also evident that the greater hydrophobicity of the solvent Men:DecA (1:2) enables a higher extraction efficiency (97.3% > 94.3%) compared to Men:DecA (1:1).

In order to emphasize the advantage of the proposed method for the extraction of Pb(II) ions, we make a comparison with the results of classical liquid-liquid extraction with chloroform and 1,2-dichloroethane as solvents. The results obtained from this research are shown in Figure 5. A comparison was made between the results obtained using the HDES solvent Men-OctA (1:1), without the use of ligands, at pH=5 (for both aqueous phases SP and RP), and with equimolar concentrations of analyte ions and counterions within the SP, as well as the stripping agent in the RP. The mixing time was the same for the compared techniques (120 min), as was the mixing speed (300 rpm). It should be noted that for classical extraction in chloroform and 1,2-DCE, 18-crown-6 was used as a macrocyclic ligand for complexation of analyte ions (extraction is not possible without a ligand).

The results show a higher extraction efficiency (97%) for the procedure with HDES solvent (Men:OctA) even without ligand, and compared to chloroform (92%) and dichloroethane (96.7%) as classical solvents, under the same experimental conditions (120 min stirring at 300 rpm). In particular, a higher back-extraction efficiency (98%) from HDES compared to chloroform (55%) and dichloroethane (16.7%) is evident.

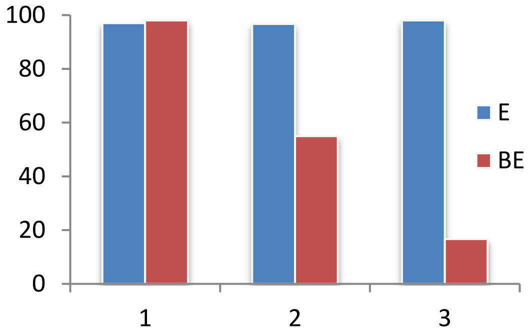

Figure 5. Comparison of extraction/back-extraction efficiency in procedures with HDES solvents and classic chlorinated organic solvents (1-HDES, 2-$CHCl_3$, 3-1,2-DCE)

CONCLUSIONS

The water-immiscible nature of HDES solvents makes them promising in the liquid-liquid extraction of non-polar analytes and transition metals from the aqueous phase.

Since the most HDES solvents are synthesized from natural raw materials, the solvent is considered relatively non-toxic, environmentally friendly and sustainable.

The use of menthol-based HDES solvent in the technique of liquid-liquid extraction of Pb(II) ions has a number of advantages: simplicity and shorter duration of the procedure, non-toxicity of the solvent and high efficiency of analyte ion removal.

In the series of H-donors used for the preparation of HDES with L-menthol, octanoic acid showed the best results, both for the extraction efficiency (97%) and for the back-extraction procedure (98%).

The most efficient extraction of Pb(II) ions is achieved using 3 mL of HDES solvent Men:OctA (1:1), without the use of ligands, without counterions in the original solution, at pH 5.

The higher efficiency of HDES solvent extraction, even without ligand, gives this procedure an advantage over the classical one.

Considering that the presence of other ions does not affect the Pb(II) removal efficiency , the proposed procedure can be used in Pb(II) removal procedures from real samples.

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Summary/Sažetak

U posljednjoj deceniji „duboki“ eutektički rastvarači (DES) naširoko su proučavani i primijenjivani u tehnikama pripreme uzoraka. Donedavno je većina sintetiziranih DES rastvarača bila hidrofilna, što je sprječavalo njihovu upotrebu u ekstrakciji vodenih uzoraka. HDES (hidrofobni DES) su obećavajuće alternative tradicionalnim organskim rastvaračima koji se koriste u pripremi uzoraka. Mogućnost HDES sinteze od netoksičnih sastojaka čini HDES da zadovolji sve standarde zelene analitičke hemije. U ovom radu pripremljeni su hidrofobni „duboki eutektički rastvarači“ na bazi prirodnih neutralnih sastojaka (L-mentol i prirodne organske kiseline), te je ispitan njihov uticaj na ekstrakciju metalnih kationa. Samo su hemijski stabilni DES-ovi odabrani da se koriste kao rastvarači u ekstrakciji. Praktične primjene HDES-ova u pripremi uzoraka uključuju konvencionalnu tečno-tečnu ekstrakciju. Cilj ovog rada je ispitati sve faktore koji utiču na efikasnost uklanjanja Pb(II) iona, tj. definisanje uslova za ekstrakciju kationa iz polaznog vodenog rastvora u hidrofobni rastvor, a sve to pomoću rastvarača na bazi mentola. Kvantitativno određivanje kationa u ovim slučajevima se uglavnom vrši nekom od spektrometrijskih metoda, a najčešće je to atomska apsorpciona spektroskopija (AAS). Konačni rezultat je kompariran sa rezultatima klasične ekstrakcije Pb(II) iona hidrofobnim organskim rastvaračima. S obzirom na aktuelnost ovakvih istraživanja i još uvijek nedovoljno istraženo područje primjene hidrofobnih eutektičkih rastvarača kao alternativnih ekstraktanata za ione teških metala kao polutante, napravljen je koncept ovog istraživanja. Dobijeni rezultati će dati značajan doprinos proširivanju znanja iz područja primjene hidrofobnih eutektičkih rastvarača u tečno-tečnoj ekstrakciji.