

Deep Eutectic Solvents

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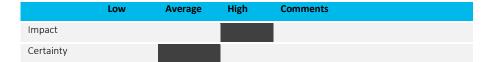
Summary

Deep Eutectic Solvents (DES) were initially treated as the second generation of Ionic Liquids (IL), however DES have lower production costs and environmental impacts. Hydrophobic natural DES are particularly useful for water treatment applications. Hydrophobic DES consist of a hydrophobic hydrogen bond acceptor, combined with a hydrogen bond donor, such as alcohol or carboxylic acid, with long alkyl chains. Since 2015, hydrophobic DES were manufactured and successfully applied in water for the extraction of micropollutants, membrane processes and as surface modifiers; all reporting improved performance. Most reported work refers to the microextraction of contaminants, therefore performed at analytical level. Applications to water treatment processes, as membrane processes, adsorption or advanced oxidation processes (AOP) are currently performed at lab-scale. Depending on the DES applied, discharges of halide ions (chloride and bromide ions) may occur.

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Consequences

Deep Eutectic Solvents



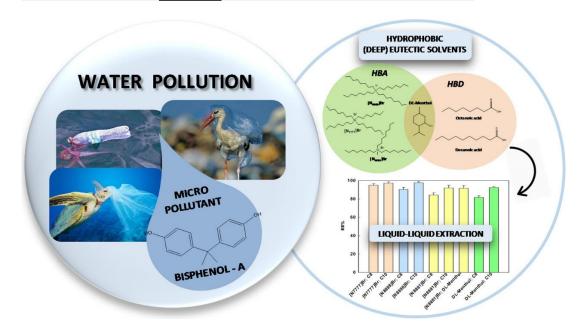


Figure 1- Deep Eutectic Solvents for extraction of Bisphenol-A in water (Source: graphical abstract in Florindo et al, 2020)

Background

Deep Eutectic Solvents (DES) were first reported in 2001. A DES is a mixture of two or more compounds, acting as hydrogen bond donors and hydrogen acceptors, which are able to self-associate and form a new eutectic phase, characterized by a melting point (below 100°C) lower than that of each individual compound (Tomé et al, 2018). In short, DES have a temperature depression that keeps the mixture in its liquid form (Chabib et al, 2022). DES were initially treated as the new generation of Ionic Liquids (ILs), and share several physiochemical properties, such as low volatility, high tunability, and ability to dissolve both organic and inorganic compounds due to high polarity. However, there are three main differences (Tomé et al, 2018):

- DES have lower production costs and much lower environmental impact; ILs are expensive, some of them present high toxicity, poor biodegradability, biocompatibility and sustainability.
- 2 The preparation process of DES and IL are different; DES are synthesized by mixing the components and do not generate waste or require purification steps; ILs preparation is more complex.
- 3 DES are the result of complexation between hydrogen bond acceptors and hydrogen bond donors, whose interactions involve mostly

hydrogen bonds; IL are composed entirely of ions, that interact through ionic bonds.

DES can be classified into natural DES and therapeutic DES, depending on its application or nature; both natural DES and therapeutic DES can be hydrophobic and hydrophilic. Therapeutic DES were introduced in the context of pharmaceutical sciences and were defined as bioactive eutectic systems composed of an active pharmaceutical ingredient, as one of the DES compounds. Therapeutic DES are applied in improved pharmaceutical drugs, to overcome issues of drug solubility and permeability. Natural DES, and in particular hydrophobic DES, have a greater number of applications in water treatment.

Natural DES were identified in 2011, while attempting to explain the solubility of intracellular compounds, that are insoluble in water and solid phases (Tomé et al, 2018). Natural DES are mixtures of compounds containing metabolites that occur in large amounts in cells, with crucial roles in biological processes, such as drought resistance, germination and dehydration. Since 2011, more than 100 natural DES have been identified, such as ChCl/organic acids, alcohols, sugars and amino acids/organic acids, therefore naturally occurring hydrogen bond donors. Natural DES show high solvation to non-water-soluble molecules (gluten, DNA, starch),

therefore they act as extraction media for bioactive molecules and as stabilizing agents (Chabib et al, 2022). The reporting of hydrophobic DES synthesis, associated to water purification processes and technologies, started in 2015. Most of the reported hydrophobic DES consist of a hydrophobic hydrogen bond acceptor, combined with a hydrogen bond donor, such as alcohol or carboxylic acid, with long alkyl chains. The hydrophobic DES can be classified as ionic or non-ionic, depending on the ionic nature of the hydrogen bond acceptor. So far, a limited number of hydrophobic DES have been reported, due to the low number of hydrogen bond donors that can form hydrophobic eutectic solvents with melting points close to room temperature (Chabib et al, 2022).

The mechanisms taking place in water treatment vary according to the DES applied, and pollutant to be extracted. Complex formation, ion exchanges, hydrogen bonding, hydrophobic interactions, aggregation of the DES, are reported as possible mechanisms (Chabib et al, 2022). Depending on the DES applied, discharges of halide ions (chloride and bromide ions) may occur.



Relevance

Extraction of micropollutants

DES are widely applied for micropollutants extraction (Chabib et al, 2022). At lab-scale level, extraction from water/wastewater of metal ions, pesticides, phenolic compounds and organic micropollutants, such as ciprofloxacin or bisphenol-A (Florindo et al 2020), has been achieved. However, the largest amount of references refers to microextraction, where a few microliters of DES solvent are applied, at some stage of an analytical or experimental procedure. Examples of improved microextraction in water, due to the use of a DES, are reported for extraction of compounds such as: aluminum ions, cadmium, lead, arsenic, antimony, selenium, ciprofloxacin, levofloxacin, ofloxacin, norfloxacin, enrofloxacin, methadone, steroids and benzophenone (various references in Chabib et al. 2022).

Membrane processes

DES are applied in membrane processes, at lab-scale level, namely in: manufacturing; cleaning; and as draw solution in Forward Osmosis (FO). The DES was applied as poreforming agent in polyether-sulfone membranes (PES), leading to increased water flux and slight selectivity improvement. DES was also applied to modify the polyamide layer of Reverse Osmosis (RO) membranes, with similar results. Increased water flux was also obtained when applying DES as cleaning agents, in thin-film composite polyamide membranes (Maalige et al, 2020). Furthermore, DES draw solutions for FO achieved high osmotic pressures of 365 and 317 atm, and the draw solutions were regenerated by cooling to -5 °C, requiring a low amount of energy (Mahto et al 2017).

Surface modifiers

DES are used as surface modifiers, instead of organic solvents, to enhance the surface charge and increase the adsorption capacity for various contaminants. DES was applied as functionalizing agent to carbon nanotubes, achieving increased adsorption capacity

for mercury, arsenic and lead in water (AlOmar et al, 2017). DES was also applied to metal-organic composite nanoparticles, to absorb ofloxacin and mefenamic acid; and to magnetic carbon dioxide nanoparticles, modified with Fe₃O₄ and coated with a DES, to extract mercury from water; in both cases obtaining an improved performance. A polymeric DES was developed to extract pesticides, applying a magnetic extraction process. In advanced oxidation processes (AOPs) DES has been applied to fine-tune the surface of biochar, applied as carbon-based catalyst for the degradation of micropollutants in wastewater (Ye at al., 2021). The potential of DES as catalysts in AOPs was described by Asadi et al. (2024).

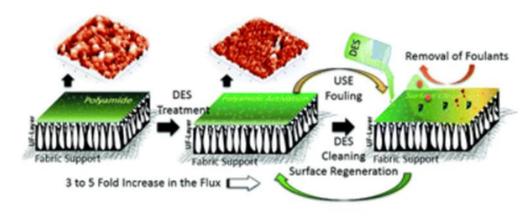


Figure 2- Use of Deep Eutectic Solvents in membrane applications to water treatment (source: Maalige et al, 2020)

More information

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Keywords

Drinking water; Deep Eutectic Solvents

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