



# Hydrophobic deep eutectic solvents as extraction agents of nitrophenolic pollutants from aqueous systems

Olalla G. Sas<sup>a,\*</sup>, Lorena Villar<sup>a</sup>, Ángeles Domínguez<sup>a</sup>, Begoña González<sup>a</sup>,  
Eugénia A. Macedo<sup>b</sup>

<sup>a</sup> Advance Separation Processes Group, Chemical Engineering Department, Universidade de Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

<sup>b</sup> Associate Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, Porto, 4200-465, Portugal

## ARTICLE INFO

### Article history:

Received 27 October 2021

Received in revised form 30 November 2021

Accepted 2 December 2021

Available online 18 December 2021

### Keywords:

Nitrophenol

Wastewater

DES

Environment

Liquid-liquid extraction

## ABSTRACT

Nitrophenolic compounds are hazardous substances, listed as priority pollutants by World Health Organization, due to their toxicity on both the environment and human health. They are used in agriculture as insecticides and fungicides substances, and they can contaminate water reserves by filtering through the soil into groundwater. Therefore, these substances must be removed from agricultural wastewater before being discharged. In this work, several Deep Eutectic Solvents, based on menthol, thymol and organic acid, are used as separation agents in liquid-liquid extraction to remove 2-nitrophenol and 4-nitrophenol from water. The optimal extraction conditions were studied and the better extraction yields were obtained using: (1:1)  $V_{DES}:V_W$  ratio and 30 min of stirring time. All extraction experiments were carried out at 298.15 K and 30 min of centrifugation time at 6000 rpm. As the results show, these deep eutectic solvents based on menthol can be used to extract both nitrophenolic compounds, while those based on thymol can only be applied for the removal of 4-nitrophenol. All studied solvents present high extraction efficiencies, over to 90%, assuring their capability as extraction agents in aqueous systems.

© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1 Introduction

Agriculture is one of the industrial activities that consumes more water, and it is considered the main source of pollution in rivers and streams due to the presence of phenolic derivatives among the composition of herbicides, insecticides and fungicides that are commonly used to protect harvest (Diaconu et al., 2010; Mateo-Sagasta et al., 2017; Park et al., 2021). Loos et al. (2009) published an article about the presence of polar organic pollutants in different European rivers from 27 countries, finding that two of the most frequent substances were 4-nitrophenol and 2,4-dinitrophenol, which were detected in 87 and 86 of studied samples, respectively. These phenolic compounds are toxic for human life and they are severe pollutants for the environment, therefore they must be removed from wastewater in order to avoid the contamination of natural water (Boehncke et al., 2000; Chaouchi and Hamdaoui, 2014).

Different techniques can be found in literature to remove phenolic substances from aqueous or organic samples. Some of these studies are based on the adsorption of the pollutants from water (Magdy et al., 2018; Singh et al., 2018;

\* Corresponding author.

E-mail address: [olallags83@uvigo.es](mailto:olallags83@uvigo.es) (O.G. Sas).

Zhu et al., 2009), others are based on membrane sorption either from aqueous phases (Bartolomé et al., 2007) or from organic solvents forming in situ deep eutectic mixtures (Shishov et al., 2020, 2021b). Solid phase extraction (SPE) or solid-liquid extraction techniques were also applied followed by chromatographic separation coupled with different detection systems (Heberer and Stan, 1997; Padilla-Sánchez et al., 2010). Liquid-liquid extraction (LLE), is a simple, cheap and versatile technique, making it an interesting separation method for industry. To remove pollutants from aqueous samples, volatile organic compounds (VOCs) are the most commonly used extraction solvents, Cladera et al. (2000) used them to satisfactorily remove 2, 3 and 4-nitrophenol. However, due to their low vapour pressure and high toxicity, it is crucial to replace them by safer ones. Ionic Liquids (ILs) have been presented as good replacement solvents for VOCs with high extraction efficiencies in many different studies (Brinda Lakshmi et al., 2013; Fan et al., 2014; Sas et al., 2019). Nevertheless, they have some disadvantages such as high cost and toxic properties for the environment, which point out the need to explore other extraction solvents with more desirable characteristics. In this line of research, Yang et al. (2013) developed a supramolecular solvent to separate nitrophenols from aqueous samples by liquid-liquid microextraction (LLME), an effective technique when removing small initial concentrations of nitrophenols, in the range of micrograms per liter. Many studies present Deep Eutectic Solvents (DESs) as extraction agents to replace ILs, because these compounds have the same advantages as ILs and improve their disadvantages, such as toxicity and cost (Verma and Banerjee, 2018).

Information about water content and stability of hydrophobic DESs after mixing them with water is of utmost importance to apply them as extraction agents of pollutants from aqueous samples, recent works have studied the behaviour of DESs formed by quaternary ammonium salts, carboxylic acids or other natural compounds such as thymol and menthol (Dietz et al., 2019; Shishov et al., 2021a; van Osch et al., 2019, 2015).

Faraji et al. (2020) studied the use of a ternary DES, based on tetrabutylammonium bromide, octanoic acid and thymol, as extraction solvent to remove 4-nitrophenol and 2,4-dinitrophenol from water samples, using dispersive liquid-liquid micro-extraction (DLLME). Their results showed that nitrophenolic compounds were recovered with high efficiencies, 92.5 and 98.7 %, respectively, but this technique is only valid for low concentrations of nitrophenol (1–500 g/L). Higher initial concentrations of phenol were studied by Rodríguez-Llorente et al. (2020). This article gather a comparison between conventional solvents, terpenoids and DESs for the extraction of some phenolic derivatives by LLE. They concluded that the extraction of 2NP is favourable using menthol and thymol-based DESs, although the extraction yields decreases as ratio DES/aqueous phase is reduced.

In this work, six hydrophobic DESs based on menthol, thymol and decanoic acid were prepared in two different proportions, and they were used as extraction solvents to remove 2-nitrophenol (2NP) and 4-nitrophenol (4NP) from aqueous solutions. The starting compounds chosen to form the used DESs were selected with the aim of enhancing the interactions between the extraction agents and nitrophenols. Due to the aromatic structure of thymol,  $\pi$ - $\pi$  interaction with the target compounds could be favoured. Moreover, the non-aromatic compounds, menthol and decanoic acid, could link by hydrogen bonding between -OH groups. The influence of the position of the nitro group in the studied phenolic compounds will be discussed, since 2NP molecule may establish intramolecular bonds between its nitro and alcohol groups, thus not allowing interactions with the extraction agents.

Before studying the extraction capability of these extraction solvents, their behaviour in water was analysed. For that purpose, their water content and their stability in water were evaluated. Moreover, the best extraction parameters (DES-rich phase/water-rich phase ratio and stirring time) were studied and used to carry out LLE for the ternary systems {DES + nitrophenol + water}. From these results, the extraction efficiencies of the studied solvents were determined.

## 2 Experimental

### 2.1. Chemical reagents

Specifications of compounds used in this work are listed in Table 1. Water used in the whole experimental procedure was of Milli-Q quality.

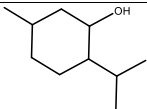
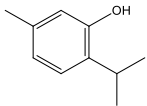
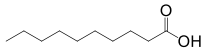
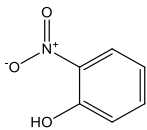
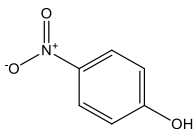
### 2.2. Methods

#### 2.2.1. Formation of DES

The DESs were obtained by weighing, stirring and heating the starting compounds in specific molar ratios, following the bibliography (Bergua et al., 2021; Florindo et al., 2018; Martins et al., 2018; van Osch et al., 2019). The six solvents prepared were: Thymol:DL-Menthol (1:1), Thymol:DL-Menthol (1:2), DL-Menthol:Decanoic acid (1:1), DL-Menthol:Decanoic acid (2:1), Thymol:Decanoic acid (1:1) and Thymol:Decanoic acid (2:1). A Mettler Toledo Excellent plus XP205 analytical balance, with an uncertainty of  $\pm 3 \cdot 10^{-4}$  g, was used for weighing and a thermostatic magnetic stirrer IKA RCT basic, with an uncertainty of  $\pm 1$  K, was used for stirring and heating (at 343.15 K) until an homogeneous liquid was achieved. Once formed, DESs were left 48 h prior to their use in order to test their stability.

The thermal behaviour of the prepared DES was studied by Differential Scanning Calorimetry technique (DSC), using a DSC Q 1000 TA Instruments. The obtained results give an indication about the range of temperatures at which solvents keep in liquid state. DSC thermograms of the formed DES, as well as of their components separately, were acquired by heating from 193.15 K to 343.15 K, with a rate of  $10 \text{ K min}^{-1}$ , under inert atmosphere ( $50 \text{ mL min}^{-1}$  of  $\text{N}_2$ ). All samples were analysed in hermetic aluminium capsules. The standard uncertainty for temperature measurements is  $\pm 1$  K.

**Table 1**  
Chemical name, structure, supplier, purity (the purities are provided by the supplier) and CAS number of compounds used in this work.

| Chemical name | Structure                                                                         | Supplier       | Purity | CAS number |
|---------------|-----------------------------------------------------------------------------------|----------------|--------|------------|
| DL-menthol    |  | Alfa Aesar     | 98%    | 89-78-1    |
| Thymol        |  | ACROS Organics | 99%    | 89-83-8    |
| Decanoic acid |  | ACROS Organics | 99%    | 334-48-5   |
| 2-nitrophenol |  | ACROS Organics | 99%    | 88-75-5    |
| 4-nitrophenol |  | Sigma Aldrich  | 99%    | 100-02-7   |

### 2.2.2. Study of stability and hydrophobicity in water of obtained DES

With the aim of using the formed DESs for extractions in aqueous samples, their stability in water and their hydrophobicity were studied. Binary mixtures of 50 (v/v) DES-water were prepared in glass cells with silicon covers and placed in a thermostatic bath with a Poly-Science digital temperature controller  $\pm 0.01$  K, coupled to a Phoenix Instrument RSM-0.3–0.1 K magnetic stirrer. Mixtures were stirred for 8 h and after that they were allowed to settle overnight. Then, water-rich phases were analysed by  $^1\text{H}$  NMR at 400 MHz, using a Bruker DPX 400 NMR, with the aim of proving their stability checking that in water phases there are no signals of DES compounds. After that, a sample of DES-rich phase was carefully separated and the water content was measured using a Mettler Toledo C20 Coulometric KF Titrator.

### 2.3. Extraction procedure

A spectrophotometric UV–Vis method was carried out using a JASCO spectrophotometer V-750 with an uncertainty of  $\pm 0.002$  abs from 0 to 0.5 abs and  $\pm 0.003$  abs from 0.5 to 1 abs, respectively. Calibration curves of both 2-nitrophenol (2NP) and 4-nitrophenol (4NP) were performed at the maximum absorbance for each compound, being 207 nm for 2NP and 317 nm for 4NP. A brief description for the preparation of nitrophenolic aqueous solutions can be found in SI section 1.

Ternary mixtures of DES – nitrophenol – water were prepared as indicated in SI section 2, and stirred at controlled temperature (298.15 K) in a thermostatic bath in order to allow contact between both aqueous and DES-rich phases. Then, both phases of the mixture were separated by 30 min of centrifugation at 6000 rpm in a Hettich Universal 320 Centrifuge. Finally, samples from aqueous phases were analysed and the extraction capability of DESs ( $E$ ) was calculated by the difference between the initial concentration ( $C_i$ ) and the final concentration that remains in the aqueous phase after the extraction procedure ( $C_f$ ), as follows:

$$E(\%) = \left( \frac{C_i - C_f}{C_i} \right) \cdot 100 \quad (1)$$

Moreover, other important parameters that can influence the extraction process, are stirring time and volume ratio of the two phases. These parameters were evaluated in order to find the best values that allow to reach the maximum extraction capability of DESs and the obtained results are discussed in the following section.

**Table 2**DES name, molar ratio, abbreviation and water content ( $\text{mg L}^{-1}$ ) after their formation (pure) and after equilibrium with water (hydrated).

| DES name              | Molar ratio | Abbreviation    | Water content ( $\text{mg L}^{-1}$ )<br>pure solvents | Water content ( $\text{mg L}^{-1}$ )<br>hydrated solvents |
|-----------------------|-------------|-----------------|-------------------------------------------------------|-----------------------------------------------------------|
| Thymol:Menthol        | 1:1         | [Thy:Mth] (1:1) | $218.1 \pm 5.3$                                       | $19\,336 \pm 127$                                         |
| Thymol:Menthol        | 1:2         | [Thy:Mth] (1:2) | $207.2 \pm 2.4$                                       | $16\,343 \pm 211$                                         |
| Thymol:Decanoic acid  | 1:1         | [Thy:C10] (1:1) | $539.4 \pm 7.0$                                       | $35\,421 \pm 424$                                         |
| Thymol:Decanoic acid  | 2:1         | [Thy:C10] (2:1) | $473.8 \pm 8.7$                                       | $38\,113 \pm 167$                                         |
| Menthol:Decanoic acid | 1:1         | [Mth:C10] (1:1) | $490.6 \pm 1.4$                                       | $21\,551 \pm 258$                                         |
| Menthol:Decanoic acid | 2:1         | [Mth:C10] (2:1) | $399.0 \pm 9.9$                                       | $21\,658 \pm 196$                                         |

### 3 Results and discussion

#### 3.1. Formation of DES

In order to know the thermal behaviour, the obtained solvents were analysed by DSC and the melting temperatures, as well as glass transition temperatures, are presented in Table SI 1. These results enable us to observe the deeper glass transition/melting point of DESs when compared to the starting compounds. Furthermore, it is possible to establish a wide range of working temperatures at which these solvents remain in liquid state, allowing to work with them at room temperature, and being those based on thymol and menthol the ones that present the widest range of temperatures.

#### 3.2. Stability and hydrophobicity in water of DES

In order to study the stability of the obtained solvents and to check that there is no solubilization of HBD and HBA in water, water phases were analysed by  $^1\text{H}$  NMR. The results verify the stability of all solvents in water, due to the fact that no signal, neither of DESs nor of starting compounds, were found in aqueous phase spectra. As example, the obtained spectrum for water-rich phase of [Thymol:Decanoic acid] (1:1) can be consulted in supplementary information (Figure SI 1).

Water content of DES-rich phases was measured after the equilibrium with water in order to study their hydrophobicity. These values ( $\text{mg L}^{-1}$ ) were compared with those measured immediately after the formation of DESs, and results are presented in Table 2, together with name, molar ratio and abbreviation of solvents used in this work. These data vary between 207.2 to 539.4  $\text{mg L}^{-1}$  when pure solvents are compared, being low values for all studied solvents. However, after their mixture with water all DESs absorbed a significant amount of water, resulting those based on menthol in the most hydrophobic ones, capturing the least water amount. When these values are compared with those obtained by van Osch et al. (2019) for the same solvents, similar results are found between them. Furthermore, the results from this work are significantly lower in water content than those measured for other hydrophobic DES, before and after their mixture with water (van Osch et al., 2015).

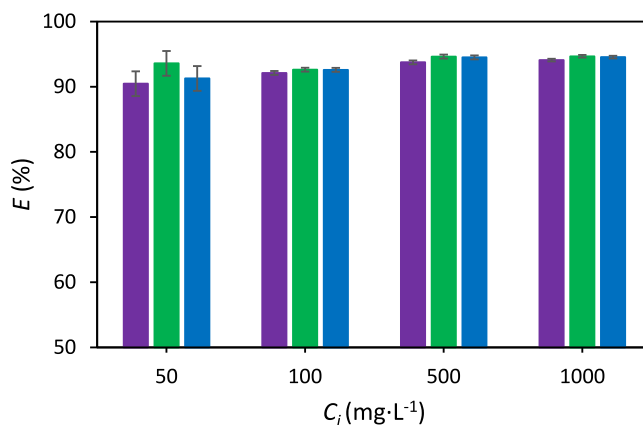
Moreover, hydrophobicity of hydrated DESs was studied in a range of temperatures from 298.15 K to 343.15 K. This study showed that saturated DESs do not follow the usual behaviour expected for this kind of solvents, on the contrary, their water content remains stable despite increasing the temperature (Table SI 2). Therefore, hydrated DESs show a constant behaviour that allows to work with them at different temperatures without changing their behaviour in aqueous systems.

#### 3.3. Study of the extraction parameters

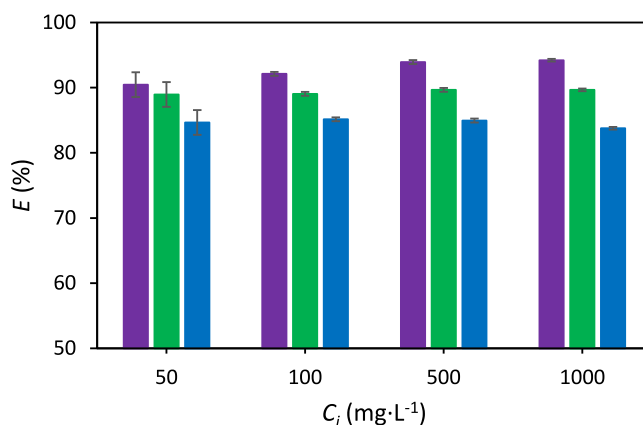
Before the use of these solvents to extract phenolic pollutants from water, the parameters which have influence in the extraction process were established with the aim of obtaining the best extraction efficiencies. For that, stirring time and phase volume ratio  $V_{\text{DES}}:V_{\text{w}}$  were studied using {[Thy:Mth](1:1) + 4NP + water} system at different initial concentrations. The 4NP was selected due to its high presence in pesticides and fungicides substances used in agriculture.

##### 3.3.1. Study of the influence of stirring time

This parameter is essential in order to achieve the correct contact between the immiscible phases (DES and water) and therefore the extraction process of phenolic compound from water to DES phase takes place. Three stirring times were studied, 30 min, 1 h and 2 h to remove 4NP from initial concentrations of 50, 100, 500 and 1000  $\text{mg L}^{-1}$ . From the experimental (Fig. 1) it is possible to conclude that, in general, the influence of the stirring time is small, due to the fact that all extraction results are higher than 90 %. Henceforth, in order to reduce the time of the process and the energy consumption, 30 min was selected.



**Fig 1** Extraction efficiency ( $E$ ) versus initial concentration ( $C_i$ ) for 4NP, using [Thy:Mth] (1:1) as extraction solvent, at different initial concentrations and for different stirring times: (—) 30 min; (—) 1 h and (—) 2 h. This experiment was conducted with 1:1 ratio  $V_{DES}:V_w$ .



**Fig 2** Extraction efficiency ( $E$ ) versus initial concentration ( $C_i$ ) of 4NP, using [Thy:Mth] (1:1) as extraction solvent, at different initial concentrations and for different volume ratios of DES-phase and water-phase: (—) (1:1); (—) (1:2) and (—) (1:3).

### 3.3.2. Study of the influence of phase volume ratio $V_{DES}:V_w$

Optimizing this parameter allows to know the lower amount of extraction solvent which produces high extraction efficiencies, in order to reduce the consumption of DES. For this study, three  $V_{DES}:V_w$  ratios were tested: (1:1), (1:2) and (1:3). As it is possible to observe in Fig. 2, (1:1) volume ratio present better results than the other two studied ratios, being more noticeable at the lowest initial concentration, obtaining extraction efficiencies higher than 85%. These higher extraction efficiencies justify the choice of this ratio for the extraction process, although the higher solvent consumption.

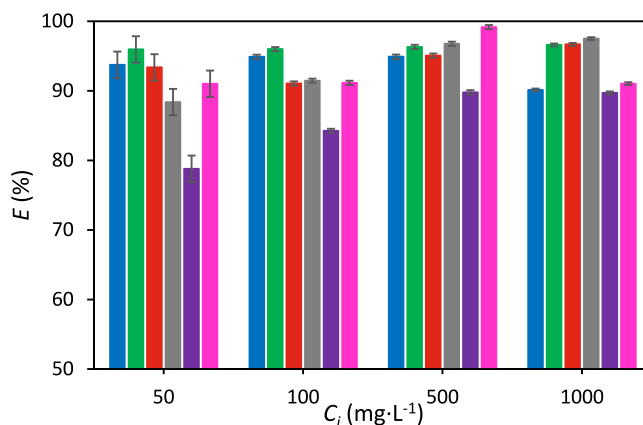
Moreover, Fig. 2 shows a growing trend of the extraction capability as initial concentration of 4NP increases at the selected volume ratio, which denotes that DES does not become saturated and its binding sites are enough for all the studied initial concentrations.

To sum up, the parameters used in this work to study the extraction capability of the eight obtained DESs were: (1:1)  $V_{DES}:V_w$  ratio, 30 min of stirring time and 30 min of centrifugation at 6000 rpm. All experiments were performed at 298.15 K.

### 3.4. Liquid–liquid extraction of 2NP and 4NP from aqueous solutions

In order to evaluate the extraction ability of obtained DESs to remove two phenolic compounds (2NP and 4NP) from water, ternary systems {DES + nitrophenol + water} were prepared and a liquid–liquid extraction was carried out using the extraction parameters reported in the previous section.

The results showed that for the extraction of 2NP with solvents based on thymol ([Thy:Mth] (1:1), [Thy:Mth] (1:2), [Thy:C10] (1:1) and [Thy:C10] (2:1)) the obtained absorbances were not consistent. In order to go deeper with this evidence, water-rich samples after extraction procedure were analysed by HPLC-DAD. In the obtained chromatograms it was possible to observe a new peak that is not consistent with any peak of studied analytes, so that these solvents



**Fig 3** Extraction efficiencies vs. initial concentrations for the systems [DES + 4NP + water]: (—) [Thy:Mth] (1:1); (—) [Thy:Mth] (1:2); (—) [Thy:C10] (1:1); (—) [Thy:C10] (2:1); (—) [Mth:C10] (1:1) and (—) [Mth:C10] (2:1).

were not used in this work for the extraction of 2 NP. As an example, Figure SI 2 shows the obtained chromatogram for the extraction of 2NP using [Thy:Mth] (1:1). These results are not in agreement with those obtained by Rodríguez-Llorente et al. (2020) for the extraction of 2NP using thymol-based DESs. They reported high extraction yields for the extraction of 2NP by LLE with Thymol:Menthol solvent, using CG-FID as quantification technique for aqueous phase. With this separation technique they may only focus on 2NP signal but the new peak stated in this work (Figure SI 2) should be taken into account, as it could denote the formation of a new third component lowering the final concentration of nitrophenol measured, that may lead to no-real extraction yields.

For the extraction systems with 4NP, the results are shown in Fig. 3. It is possible to observe that all extraction efficiencies are high, superior to 90 for most of the studied initial concentrations of 4NP, except for [Mth:C10] (1:1) which present extraction efficiencies higher than 85.

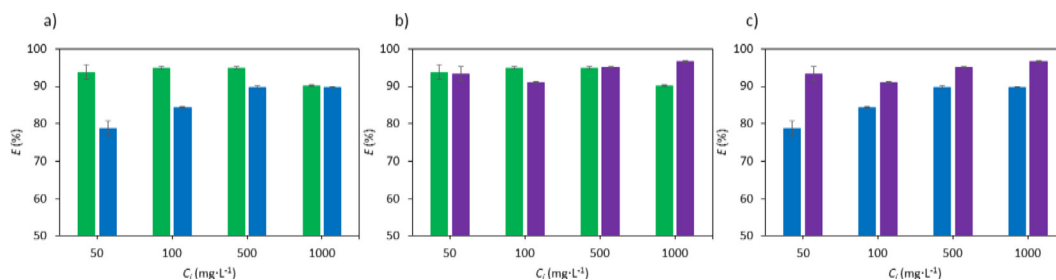
As far as the authors knowledge, it is barely found bibliography about liquid-liquid extraction (LLE) of nitrophenolic compounds from water using DESs as extraction agents. However, the extraction of nitrophenolic compounds from aqueous matrices by LLE using other extraction solvents, VOCs, was reported in 1997 by Chee et al. (1997). In this work, there were listed some references for the extraction of both 4NP and 2NP with recovery percentages of 40 and 57, respectively.

To compare the suitability of the studied solvents for the extraction of nitrophenolic compounds from water, the results presented will be discussed as follows: the influence of the compounds which were used to form the extraction solvents, the influence of the molar ratio of the starting compounds and the influence of the nitro group position in phenolic compound structure on the extraction efficiency.

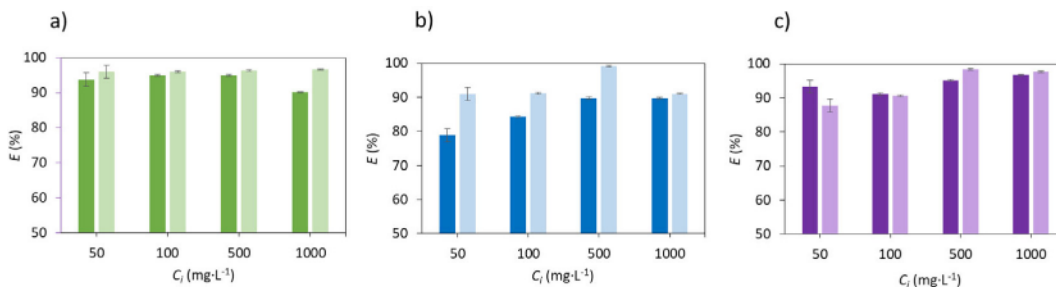
### 3.4.1. Influence of the extraction agent

**3.4.1.1. Study of the starting compounds.** Fig. 4 shows a comparison between the extraction efficiency of DESs depending on the starting compounds used. When thymol-based DESs were used (Fig. 4a), better results were achieved in the presence of menthol, being more noticeable at low initial concentrations of 4NP. When menthol-based DESs were used (Fig. 4b), similar extraction efficiencies were reached either with thymol or decanoic acid. When decanoic acid-based DESs were used (Fig. 4c), higher yields are obtained if this starting compound is combined with menthol. Consequently, the presence of non-aromatic cyclic compound (menthol) increases the extraction efficiency of the formed DESs for the extraction of 4NP. This behaviour could be explained with the Kamlet-Taft parameters ( $\alpha$ ,  $\beta$  and  $\pi^*$ ) for menthol and thymol-based solvents studied by Martins et al. (2018). Menthol has a large  $\beta$  value that represents a high capacity to accept hydrogen bonding, while thymol is not a good hydrogen bond acceptor, this fact benefit the linkage of the target compound with menthol. Moreover, although  $\pi^*$  parameter (that refers to the polarizability of the solvent) is higher in thymol-based solvents because of the aromatic ring of thymol molecule, co-planarity of molecules is required in order to establish  $\pi$ - $\pi$  interaction.

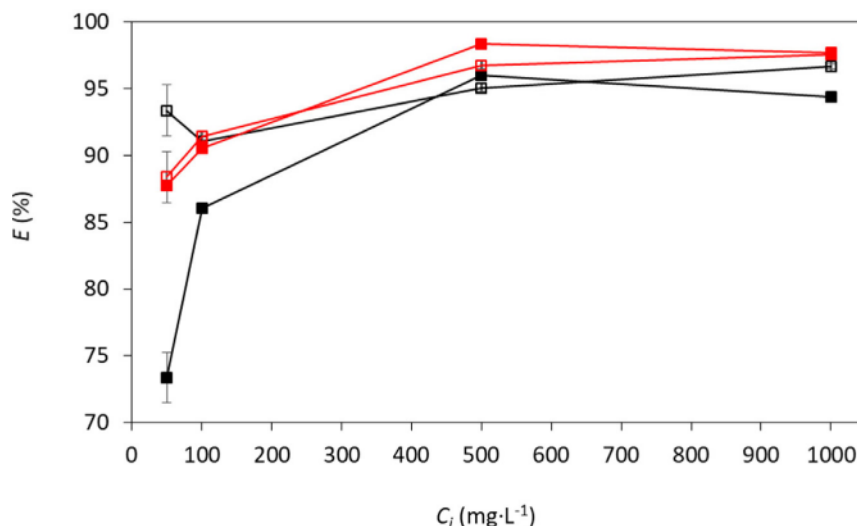
**3.4.1.2. Study of molar ratio.** Fig. 5 shows a comparison between the molar proportion of starting compounds used for the formation of DES. When molar ratio of menthol increases in [Thy:Mth] solvent (Fig. 5a), extraction capability of DES grows slightly. Regarding the presence of thymol in [Thy:C10] DES (Fig. 5b), extraction efficiency increases as molar ratio also increases. As for the increment of menthol proportion in [Mth:C10] extraction agent (Fig. 5c), ratio (2:1) showed better results at high initial concentration of 4NP. Therefore, increasing the molar proportion of cyclic over lineal structures increases the extraction capability of the studied DESs. Moreover, the higher non-aromatic ratio, the higher extraction efficiency.



**Fig 4** Extraction efficiencies vs. initial concentrations for the systems {DES + 4NP + water}: (—) [Thy:Mth] (1:1); (—) [Thy:C10] (1:1) and (—) [Mth:C10] (1:1). Comparison between thymol-based DES (a), menthol-based DES (b) and decanoic acid-based DES (c).



**Fig 5** Extraction efficiencies vs. initial concentrations for the systems {DES + 4NP + water}: (—) [Thy:Mth] (1:1); (—) [Thy:Mth] (1:2); (—) [Thy:C10] (1:1); (—) [Thy:C10] (2:1); (—) [Mth:C10] (1:1) and (—) [Mth:C10] (2:1). Comparison between influence of menthol molar ratio in [Thy:Mth] (a), thymol molar ratio in [Thy:C10] (b) and menthol molar ratio in [Mth:C10] (c).



**Fig 6** Extraction efficiencies vs. initial concentration of 4NP (empty squares) and 2NP (filled squares), using menthol-based DESs: (—) [Mth:C10] (1:1) and (—) [Mth:C10] (2:1).

### 3.4.2. Influence of nitrophenolic compound.

From Fig. 6 it is possible to observe that menthol-based DESs are suitable candidates for the removal of both 4NP and 2NP from water, reaching extraction efficiencies higher than 70 . Although at high initial concentrations of nitrophenolic compound similar results were obtained, at low initial concentrations 4NP extraction yields were promoted up to 97 . The better extraction results for 4NP can be associated with the position of nitro and alcohol groups in this molecule, that allows the possibility to link with the extraction solvent by hydrogen bonding. Furthermore, the formation of intramolecular bonds between nitro and alcohol groups in 2NP molecule, could be the cause of the lower extraction efficiencies obtained for this target compound (Kovacs et al., 2000).

Comparing the results obtained for the extraction of 2NP, the observed behaviour corroborates that increasing menthol proportion enhances the extraction capability of studied DESs.

#### 4 Conclusions

In this work, the preparation of six DESs based on thymol, menthol and decanoic acid with the aim of removing two nitrophenolic compounds from water, are reported. The thermal behaviour of the extraction solvents was studied by DSC analysis and their stability in water, as well as their hydrophobicity, were analysed by means of  $^1\text{H}$  NMR and KF titrator, respectively.

The influence of the stirring time and volume ratio of DES:aqueous phase on the extraction yields was studied. Experimental results confirmed that 30 min of contact between phases are enough to achieve good extraction efficiencies, and volume ratio (1:1) was selected as the most suitable between the studied proportions.

The six formed DESs were satisfactorily applied for the extraction of 4NP with high extraction efficiencies, while two of the six studied DESs, those based on [Mth:C10], showed significant extraction capability for removing 2NP. Furthermore, it was confirmed that the presence of menthol as starting compound of DESs promotes an increase in the extraction efficiency for the removal of both 2NP and 4NP.

In conclusion, the best extraction agent is [Mth:C10] (2:1) for both nitrophenolic compounds and regarding to the extraction of 4 NP, [Thy:Mth] (1:2) presents the best results.

#### CRediT authorship contribution statement

**Olalla G Sas:** Investigation, Writing – original draft. **Lorena Villar:** Investigation, Writing – original draft. **Ángeles Domínguez:** Supervision, Visualization, Writing – review & editing. **Begoña González:** Supervision, Visualization, Writing – review & editing, Project administration. **Eugénia A Macedo:** Supervision, Visualization, Writing – review & editing, Project administration.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by Comisión Interministerial de Ciencia y Tecnología (Spain) (CTM2013-46093-P) and Xunta de Galicia, Spain (GPC-ED431B 2020/08). This work was financially supported by: Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM, Portugal - funded by national funds through FCT/MCTES, Portugal (PIDDAC). Authors would like to thank the use of RIAIDT-USC analytical facilities of Universidade de Santiago de Compostela and CACTI facilities of Universidade de Vigo. L. Villar is grateful to Universidade de Vigo, Spain for her predoctoral grant (00VI 131H 641.02). Begoña González is grateful to Ministerio de Ciencia, Innovación y Universidades (Spain) for her grant (PRX 19/00372).

#### Appendix A Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2021.102170>.

#### References

- Baritolomé, L., Lezamiz, J., Etxebarria, N., Zuloaga, O., Jönsson, J.Å., 2007. Determination of trace levels of dinitrophenolic compounds by microporous membrane liquid–liquid extraction in environmental water samples. *J. Sep. Sci.* 30, 2144–2152. <http://dx.doi.org/10.1002/JSSC.200600509>.
- Bergua, F., Castro, M., Muñoz-Embid, J., Lafuente, C., Artal, M., 2021. Hydrophobic eutectic solvents: Thermophysical study and application in removal of pharmaceutical products from water. *Chem. Eng. J.* 411, 128472. <http://dx.doi.org/10.1016/j.cj.2021.128472>.
- Boehncke, A., Koennecker, G., Mangelsdorf, I., Wibbertmann, A., 2000. Mononitrophenols. World Health Organization, Geneva.
- Brinda Lakshmi, A., Balasubramanian, A., Venkatesan, S., 2013. Extraction of phenol and chlorophenols using ionic liquid [Bmim]+[BF4]- Dissolved in tributyl phosphate. *CLEAN – Soil Air Water* 41, 349–355. <http://dx.doi.org/10.1002/CLEN.201100632>.
- Chaochi, S., Hamdaoui, O., 2014. Extraction of priority pollutant 4-nitrophenol from water by emulsion liquid membrane: Emulsion stability, effect of operational conditions and membrane reuse. *J. Dispers. Sci. Technol.* 35, 1278–1288. <http://dx.doi.org/10.1080/01932691.2013.844704>.
- Chee, K.-K., Wong, M.-K., Lee, H.-K., 1997. Membrane solid-phase extraction with closed vessel microwave elution for the determination of phenolic compounds in aqueous matrices. *Mikrochim. Acta* 126, 97–104.
- Cladera, A., Miró, M., Estela, J.M., Cerdà, V., 2000. Multicomponent sequential injection analysis determination of nitro-phenols in waters by on-line liquid-liquid extraction and preconcentration. *Anal. Chim. Acta* 421, 155–166. [http://dx.doi.org/10.1016/S0003-2670\(00\)01035-7](http://dx.doi.org/10.1016/S0003-2670(00)01035-7).
- Diaconu, I., Girdea, R., Cristea, C., Nechifor, G., Ruse, E., Totu, E.E., 2010. Removal and recovery of some phenolic pollutants using liquid membranes environmental applications of composite and liquid membranes view project aqueous systems treatment using membranes and membrane reactors view project. *Rom. Biotechnol. Lett.* 15, 5702–5708.

- Dietz, C.H.J.T., Erve, A., Kroon, M.C., van Sint Annaland, M., Gallucci, F., Held, C., 2019. Thermodynamic properties of hydrophobic deep eutectic solvents and solubility of water and HMF in them: Measurements and PC-SAFT modeling. *Fluid Phase Equilib.* 489, 75–82. <http://dx.doi.org/10.1016/J.FLUID.2019.02.010>.
- Fan, Y., Li, Y., Dong, X., Hu, G., Hua, S., Miao, J., Zhou, D., 2014. Extraction of phenols from water with functionalized ionic liquids. *Ind. Eng. Chem. Res.* 53, 20024–20031. <http://dx.doi.org/10.1021/IE503432N>.
- Faraji, M., Noormohammadi, F., Adeli, M., 2020. Preparation of a ternary deep eutectic solvent as extraction solvent for dispersive liquid-liquid microextraction of nitrophenols in water samples. *J. Environ. Chem. Eng.* 8, 103948. <http://dx.doi.org/10.1016/J.JECE.2020.103948>.
- Florindo, C., Romero, L., Rintoul, I., Branco, L.C., Marrucho, I.M., 2018. From phase change materials to green solvents: Hydrophobic low viscous fatty acid-based deep eutectic solvents. *ACS Sustain. Chem. Eng.* 6, 3888–3895. <http://dx.doi.org/10.1021/ACSSUSCHEMENG.7B04235>.
- Heberer, T., Stan, H.J., 1997. Detection of more than 50 substituted phenols as their t-butyltrimethylsilyl derivatives using gas chromatography-mass spectrometry. *Anal. Chim. Acta* 341, 21–34. [http://dx.doi.org/10.1016/S0003-2670\(96\)00557-0](http://dx.doi.org/10.1016/S0003-2670(96)00557-0).
- Kovacs, A., Keresztury, G., Izvekov, V., 2000. Intramolecular hydrogen-bonding in 2-nitroresorcinol. A combined FT-IR, FT-Raman and computational study. *Chem. Phys.* 253, 193–204.
- Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. *Environ. Pollut.* 157, 561–568. <http://dx.doi.org/10.1016/J.ENVPOL.2008.09.020>.
- Magdy, Y.M., Altaher, H., ElQada, E., 2018. Removal of three nitrophenols from aqueous solutions by adsorption onto char ash: equilibrium and kinetic modeling. *Appl. Water Sci.* 8, 1–15. <http://dx.doi.org/10.1007/S13201-018-0666-1>.
- Martins, M., Crespo, E.A., Pontes, P.V.A., Silva, L.P., Bülow, M., Maximo, G.J., Batista, E.A.C., Held, C., Pinho, S.P., Coutinho, J.A.P., 2018. Tunable hydrophobic eutectic solvents based on terpenes and monocarboxylic acids. *ACS Sustain. Chem. Eng.* 6, 8836–8846. <http://dx.doi.org/10.1021/acssuschemeng.8b01203>.
- Mateo-Sagasta, J., Marjani Zadeh, S., Turrall, H., 2017. Water pollution from agriculture: a global review. Rome.
- Padilla-Sánchez, J.A., Plaza-Bolaños, P., Romero-González, R., Garrido-Frenich, A., Martínez Vidal, J.L., 2010. Application of a quick, easy, cheap, effective, rugged and safe-based method for the simultaneous extraction of chlorophenols, alkylphenols, nitrophenols and cresols in agricultural soils, analyzed by using gas chromatography–triple quadrupole-mass spectrometry/mass spectrometry. *J. Chromatogr. A* 1217, 5724–5731. <http://dx.doi.org/10.1016/J.CHROMA.2010.07.004>.
- Park, J.M., Kim, C.M., Jhung, S.H., 2021. Melamine/polyaniline-derived carbons with record-high adsorption capacities for effective removal of phenolic compounds from water. *Chem. Eng. J.* 420, 127627. <http://dx.doi.org/10.1016/J.CEJ.2020.127627>.
- Rodríguez-Llorente, D., Cañada-Barcala, A., Muñoz, C., Pascual-Muñoz, G., Navarro, P., Santiago, R., Águeda, V.I., Álvarez-Torrellas, S., García, J., Larriba, M., 2020. Separation of phenols from aqueous streams using terpenoids and hydrophobic eutectic solvents. *Sep. Purif. Technol.* 251, 117379. <http://dx.doi.org/10.1016/J.SEPPUR.2020.117379>.
- Sas, O.G., Domínguez, I., Domínguez, Á., González, B., 2019. Using bis(trifluoromethylsulfonyl)imide based ionic liquids to extract phenolic compounds. *J. Chem. Thermodyn.* 131, 159–167. <http://dx.doi.org/10.1016/J.JCT.2018.11.002>.
- Shishov, A., Dubrovsky, I., Kirichenko, S., Bulatov, A., 2021a. Behavior of quaternary ammonium salts and terpenoids-based deep eutectic solvents in aqueous phase. *J. Mol. Liq.* 117987. <http://dx.doi.org/10.1016/J.MOLLIQ.2021.117987>.
- Shishov, A., Gagarionova, S., Bulatov, A., 2020. Deep eutectic mixture membrane-based microextraction: HPLC-FLD determination of phenols in smoked food samples. *Food Chem.* 314, 126097. <http://dx.doi.org/10.1016/J.FOODCHEM.2019.126097>.
- Shishov, A., Volodina, N., Gagarionova, S., Shilovskikh, V., Bulatov, A., 2021b. A rotating disk sorptive extraction based on hydrophilic deep eutectic solvent formation. *Anal. Chim. Acta* 1141, 163–172. <http://dx.doi.org/10.1016/J.ACA.2020.10.020>.
- Singh, N.B., Nagpal, G., Agrawal, S., Rachna, 2018. Water purification by using Adsorbents: A review. *Environ. Technol. Innov.* 11, 187–240. <http://dx.doi.org/10.1016/J.ETI.2018.05.006>.
- van Osch, D., Dietz, C., van Spronsen, J., Kroon, M.C., Gallucci, F., van Sint Annaland, M., Tuinier, R., 2019. A search for natural hydrophobic deep eutectic solvents based on natural components. *ACS Sustain. Chem. Eng.* 7, 2933–2942. <http://dx.doi.org/10.1021/ACSSUSCHEMENG.8B03520>.
- van Osch, D., Zubeir, L.F., Bruinhorst, A., van den Rocha, M.A.A., Kroon, M.C., 2015. Hydrophobic deep eutectic solvents as water-immiscible extractants. *Green Chem.* 17, 4518–4521. <http://dx.doi.org/10.1039/C5GC01451D>.
- Verma, R., Banerjee, T., 2018. Liquid–liquid extraction of lower alcohols using menthol-based hydrophobic deep eutectic solvent: Experiments and COSMO-SAC predictions. *Ind. Eng. Chem. Res.* 57, 3371–3381. <http://dx.doi.org/10.1021/ACS.IECR.7B05270>.
- Yang, Q., Chen, X., Jiang, X., 2013. Liquid–liquid microextraction of nitrophenols using supramolecular solvent and their determination by HPLC with UV detection. *Chromatogr.* 76, 1641–1647. <http://dx.doi.org/10.1007/S10337-013-2554-Z>, 2013, 7623.
- Zhu, S., Niu, W., Li, H., Han, S., Xu, G., 2009. Single-walled carbon nanohorn as new solid-phase extraction adsorbent for determination of 4-nitrophenol in water sample. *Talanta* 79, 1441–1445. <http://dx.doi.org/10.1016/J.TALANTA.2009.06.011>.