



# Water decolorization using tuned ternary Deep Eutectic solvents

Andrés Asla, Óscar Martínez-Rico, Pablo Otero, Ángeles Domínguez, Begoña González\*

Department of Chemical Engineering, Universidade de Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain



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## ABSTRACT

A method to totally decolorize textile wastewaters using new extraction solvents is proposed, with the aim of vastly reducing water consumption. This technique allows for water reuse while solving one of the biggest problems of the textile industry: the generation of huge amounts of liquid residues. In these effluents, dyes are the most common present pollutants, and are toxic to both human and aquatic life, and to the environment. Full decolorization is an indispensable prerequisite to obtain a clean water that can be repurposed following circular economy principles. To decolorize aqueous streams, liquid-liquid extraction is a widely used technique, achieving both the recovery of the pollutants and the used solvent. In this context, Deep Eutectic Solvents are a promising candidate for novel optimized processes. In this work, we propose several of these agents, formed from tetrabutylammonium chloride, thymol, menthol and decanoic acid, optimized for interaction with a wide array of dye classes and processable physico-chemical properties. Across all the studied solvents, it was possible to achieve high extraction efficiency, with full decolorization for most dyes, at very low solvent to aqueous phase ratios. Furthermore, assays using synthetic effluents, containing dyes and other chemicals used to ensure a correct dyeing process, show that our solvents are good candidates to treat streams as those found in industry.

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## 1. Introduction

The textile industry is one of the main contributors to the generation of wastewater effluents, coming from several wet operations such as pretreatments, dyeing, finishing, coating, and washing. Of these, the main bulk of the emissions by volume comes from the dyeing process, which generates complex effluents containing dyes which can be toxic to aquatic life, and several auxiliaries such as alkali, salts or reducing and oxidizing agents [1,2].

The effluent will be mainly characterized by the type of fiber and the dyeing process. The main types are cellulosic fibers, protein fibers and polymeric fibers [3]. Each of these sorts of fibers is dyed with a different type of colorant that adapts best to its chemical characteristics. Hence, for a typical textile mill the dyeing

effluent will contain a complex mix of different dye molecules, with completely different structures, degradation pathways and final environmental impact [4].

Typical strategies for the control of these effluents are based on physical (filtration, coagulation, and adsorption), oxidative (advanced and chemical) or biological (enzymatic or microorganism degradation) methods [2]. However, these techniques are either destructive, with the complete mineralization of the dyestuff, or generate activated sludges that need to be treated as residues [2]. It's here where liquid-liquid techniques provide a differential value, as all the involved parts may be recovered: the dyes, the extraction solvent and the purified water [5,6]. Traditional solvents, such as volatile organic compounds (VOCs) have been used as extraction solvents for dyestuffs [7], but its use is troubled by their toxicity and safety considerations due to their low vapor pressure [8,9].

Ionic liquids (ILs) have been proposed as substitutes to VOCs due to their low vapor pressure and tunable properties [10,11]. Among them, several have proven their capabilities as extraction solvents [12,13], including for applications of dye recovery [14,15]. In any case, the application of ILs is hampered by their high cost and toxicity, which lead to the development of new greener and cheaper solvents, with more attractive characteristics while maintaining the highly tunable nature of ILs.

**Abbreviations:** VOCs, Volatile Organic Compound(s); ILs, Ionic Liquid(s); TBAC, Tetrabutylammonium Chloride; Thy, Thymol; DecA, Decanoic; Mth, Menthol; DESs, Deep Eutectic Solvent(s); HBD, Hydrogen Bond Donor; HBA, Hydrogen Bond Acceptor; LLE, Liquid-Liquid Extraction; HDESs, Hydrophobic Deep Eutectic Solvent (s); BTEAC, Benzyltrimethylammonium Chloride; MTAC, Methyltriethylammonium Chloride; NMR, Nuclear Magnetic Resonance; DSC, Differential Scanning Calorimetry; VFT, Volger-Fulcher-Tanman; TBAB, Tetrabutylammonium Bromide.

\* Corresponding author.

E-mail address: [bjp@uvigo.es](mailto:bjp@uvigo.es) (B. González).

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These new solvents, classified as Deep Eutectic Solvents (DESs), result from the combination of two or more substances with the possibility of forming strong hydrogen bond interactions; where the substances assume the roles of hydrogen bond donors (HBD) or hydrogen bond acceptors (HBA) when mixed at specific molar ratios [16,17]. These strong interactions induce a depression in the melting point of the DES, which remains liquid at temperatures far below the melting points of their single components [16,18,19]. Interestingly, when the HBA or HBD are sufficiently hydrophobic, the resulting DES is also hydrophobic (HDES) and can be directly applied for liquid–liquid extraction (LLE) [20,21]. Its stability in those applications is of the utmost importance, as to correctly leave an aqueous phase with no contamination [22].

Hydrophobic DES (HDES) have been successfully used as extraction solvents for several water-soluble pollutants [23,24] including dyes. Several authors have proposed microextraction procedures [22] for various pollutants, and for dye determination in aqueous samples. Aydin et al. [25] used a choline chloride (ChCl) and phenol based DESs to extract malachite green from aqueous solutions with extraction efficiencies of around 95%. Li et al [26] produced several thymol and camphor based DESs to also extract malachite green and cristal violet with extraction efficiencies between 82 and 99%. Faraji et al. [27] applied two classes of DES based on benzyltrimethylammonium chloride (BTEAC) – thymol and ChCl – thymol to extract malachite green, with the best extraction efficiencies near 100%.

Arcon et al. [28] have proposed several fatty acid based DESs combining various carboxylic acids to extract several dyes (malachite green, methyl violet and methylene blue), achieving extraction efficiencies of around 95%.

Several authors have proposed DESs containing quaternary ammonium salts, being tetrabutylammonium chloride (TBAC) and methyltrioctylammonium chloride (MTAC) the most employed [29]. Van Osch et al. [20] proposed several tetrabutylammonium salt based DES combined with decanoic acid (DecA), where TBAC – DecA presented the lowest viscosity compared to MTAC-DecA and other DES, but exhibited a high degree of leaching of the salt component to the aqueous phase, due to the increased solubility of TBAC because of its shorter alkyl chains. Florindo et al. [30] also studied the stability of the salt component upon contact with water for TBAC based DESs with different chain length carboxylic acids as HBD, where all of them showed significant leaching of the salt component to water. To increase the stability upon contact with water of a DES formed with a hydrophilic component, it has been suggested to employ a compound with a strong hydrogen bond forming capacity. Kumar et al. [31] showed that a DES formed of a hydrophilic compound such as ChCl and a strong hydrophobic HBD, such as thymol, could be stable upon contact with water at the correct molar ratio. Thymol has been identified as a strong HBD due to the presence of a hydroxyl group directly attached to the aromatic ring [32].

There are several properties of the different dye classes which point to the possibility of using TBAC based DESs to tune extraction efficiency across dye classes. In the case of acid dyes, they present sulfonate acid groups which bind to the ammonium groups on the wool fiber surface, formed from amino groups under acidic conditions [33]. For direct dyes, it is common to perform an aftertreatment step with quaternary ammonium, which binds to the sodium sulfonate groups in the dye, insolubilizing them and increasing dye fixation [34]. Finally for reactive dyes, the same sulfonate groups as in direct dyes are usually present.

A DES previously tested by the group for dye extraction [35], formed by thymol and decanoic acid in a 1:1 M proportion, is used as a starting point. Then the agent is tuned in terms of extracting abilities and physical properties. Hence, TBAC is proposed as an alternative HBA, specially selected for its strong interaction -

depicted in Figure SI 1- with several dye classes, substituting the previous decanoic acid. Coupled with Thymol as HBD, an especially strong HBD compound [32], hydrophobicity is ensured. In order to improve the physical properties of the solvents, to advantage the extraction process, two ternary DESs were prepared. The addition of menthol, and the reintroduction of decanoic acid (DecA), this time as HBDs, allows to compensate the high increase in viscosity that comes from the addition of TBAC, while maintaining its extraction capacities.

To corroborate the extraction mechanisms, several textile dyes of different classes and with different chromophores have been selected. Three acid dyes, Acid Blue 113 with two azo groups, and Acid Green 25 and Acid Blue 80, both with an anthraquinone group, one direct dye with four azo groups (Direct Black 19) and two reactive dyes, Reactive Red 29 with one azo group and Remazol Brilliant Blue with one anthraquinone group.

All DESs were contacted with water to corroborate stability, with the resulting phases studied by nuclear magnetic resonance (NMR) for component leaching. Hydrophobicity was also checked by Karl-Fischer titration. Several liquid–liquid extractions of the selected dyes were also performed to optimize the extraction procedure and to study the effect of several parameters on the extraction efficiency. The influence of the initial concentration of dye was studied for all DESs. Finally, the new tuned solvents were tested against various synthetic effluents, created to mimic those found in the dyeing processes that take place in textile industries.

## 2. Experimental procedure

### 2.1. Chemical reagents

The specifications of the chemicals used on this work are detailed in Table SI 1. Water used to prepare the aqueous solutions was Milli-Q grade. The chemical characteristics of the selected dyes are presented in Table 1 and their molecular structures in Fig. 1.

### 2.2. Formation of DESs

The DESs used in this work were prepared according to the heating and stirring method commonly described in literature [19,36]. They were prepared by weighing, in a Mettler Toledo Excellent Plus XP205 analytical balance, the required amounts of the starting compounds, in each of the ratios of interest. Later, they were heated at 343.15 K under constant stirring up to a point where both solids melted into a single liquid phase. To ensure their stability -as decompositions, gelifications or recrystallizations may occur- they were left to cool down and then to stand for 48 h.

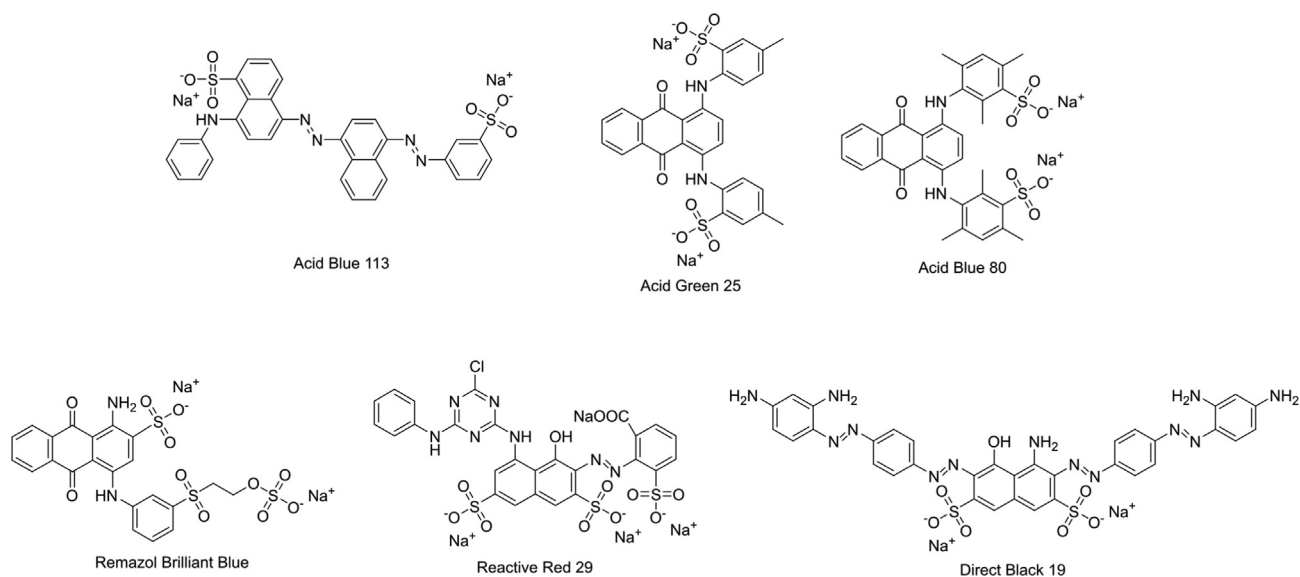
The liquid temperature range of the DESs was tested by means of differential scanning calorimetry (DSC), with a DSC Q 1000 TA instrument, measuring in hermetic aluminium capsules under an inert atmosphere ( $50 \text{ mL min}^{-1}$  of  $\text{N}_2$ ). Samples were exposed to temperatures ranging from 193.15 K to 343.15 K, where the temperature varied at  $10 \text{ K min}^{-1}$ .

### 2.3. Study of stability and hydrophobicity of the solvents. Physical properties

After letting the solvents stand for 48 h as described, their behavior upon contact with water was determined. To analyze it, binary mixtures of 50% (v/v) water and DES were prepared in 5 mL Erlenmeyer flasks and were completely mixed under stirring during 8 h in a thermostated bath at a temperature of 298.15 K, and subsequently the two phases were separated by centrifugation. Then, samples of the pure DESs, saturated DESs and of the aqueous phase were inspected with  $^1\text{H}$  NMR at 400 MHz, using a

**Table 1**  
Chemical characteristics of the studied dyes.

Dye name	Dyeing process	Chromophore group	Sodium salt	FW (g/mol)
Acid blue 113 (AB113)	Acid	Diazo	Disodium	681.7
Acid green 25 (AG25)	Acid	Anthraquinone	Disodium	622.6
Acid blue 80 (AB80)	Acid	Anthraquinone	Disodium	678.7
Remazol brilliant blue (RBB)	Reactive	Anthraquinone	Disodium	626.5
Reactive red 29 (RR29)	Reactive	Azo	Trisodium	942.1
Direct black 19 (DB19)	Direct	Tetrakisazo	Disodium	839.8



**Fig. 1.** Chemical structures of the selected dyes.

Bruker DPX 400 NMR, to check their stability. For all the solvents, the spectra of both the pure DES and saturated DES were compared to check for peak shift, also the spectrum of each aqueous phase was analyzed to detect possible leaching of the water soluble TBAC. Additionally, a Mettler Toledo C20 Coulometric KF Titrator was used to quantify the increase of water content in the DES phases and check their hydrophobicity. If a significant increase in water content was observed, the bulk DES was put in contact with water as described above for saturation before using it for further experimentation.

The density and dynamic viscosity of the solvents was determined in an operating temperature range of 298.15 K to 343.15 K using an Anton Paar DSA-5000 M digital vibrating tube densimeter (uncertainty of  $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$ ) and a Lovis 2000/ME connected to Anton Paar DSA-5000 M densimeter (uncertainty of  $\pm 0.03 \text{ mPa s}$ ). The temperature was controlled with an uncertainty of  $\pm 0.02 \text{ K}$ .

#### 2.4. Extraction procedure

Mixtures of DES and dye aqueous solution were prepared into 12 mL Erlenmeyer flasks by weighing the components and placing the vessels in a thermostatic bath at 298.15 K under stirring for the required time. Upon contact for a specified amount of time, both phases are transferred to centrifuge tubes and separated using a Hettich Universal 320 centrifuge. After separation, a sample of the aqueous phase was analyzed by spectrophotometry using a JASCO V-750 with an uncertainty of  $\pm 0.002 \text{ abs}$  from 0 to 0.5 abs and  $\pm 0.003 \text{ abs}$  from 0.5 to 1 abs, respectively. Before this analysis, a calibration curve of the dyes at their respective maximum absor-

bance wavelengths was obtained, as well as their limits of detection (LOD).

The extraction efficiency of the solvent for a given equilibrium was calculated as the difference between the initial concentration ( $C_i$ ) and the final remaining concentration on the aqueous phase ( $C_f$ ), as described in equation (1).

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

#### 2.5. Creation of synthetic effluents

CHT Group, a chemical company specialized in textile and industrial solutions, was kind enough to assist this article, providing some products, such as an industrial textile dye, as well as the agents used in these processes to ensure a correct tinting process. Three agents were used in this study: Sarabid DLC, a dye leveler that helps maintaining a uniform color across the dyed garment; Biavin BPA an acrylamide based crease-prevention agent; and Rewin ACP, a post-treatment product designed to fixate the dye to the fibers and ensure the endurance of the tinting afterwards. Three tinting processes were conducted, in order to obtain two types of effluents. First a cotton fiber cloth was dyed with Tubanting Scarlet dye (also provided by CHT Group), and an aqueous solution similar to the ones used in the previous section was obtained. Then, following the instructions provided by the manufacturer, two other effluents were created. The first of them included Sarabid DLC and Biavin BPA, and the second one included Rewin ACP additionally. Therefore, an effluent with the same composition as any other industrial wastewater that used the same process was

obtained. This way, the effect of the auxiliary agents in the extraction process could be analyzed, specially distinguishing between the inclusion and absence of the fixating agent which could present quaternary ammonium salts, as stated previously in the introduction, that may interfere with the behavior of the DES. It is important to note that the full composition of this products was not disclosed by the company.

These effluents were then used for extraction essays, following the same procedure as described in the previous section.

### 3. Results and discussion

#### 3.1. Formation of DESs

The DESs were formed by the previously described heating method and were left to stand for 48 h. The abbreviations and behavior of the DESs are presented in Table 2. It was observed that TBAC:Thymol (1:1) was not correctly formed, as one of the components did not fully incorporate to the eutectic mixture. Also [TBAC:Thy] (1:6) and (1:8) were unstable after formation, where one of the components solidified. The rest of the formed solvents were stable after formation and the standing time.

The melting point and glass transition temperatures for the pure compounds and the formed DESs were analyzed by DSC, as shown in table SI 2, and show that the formed DESs all have a lower melting point than their starting pure compounds. Therefore, the formation of the DESs [Thy:DecA] (1:1), [TBAC:Thy] on molar ratios of (1:2) and (1:4), as well as [TBAC:Thy:DecA] and [TBAC:Thy:Menthol] on molar ratio (1:4:1) can be confirmed.

#### 3.2. Study of stability in water and hydrophobicity

Stability and hydrophobicity of the formed solvents was studied following the methods described in the *Experimental Procedure* section.

<sup>1</sup>H NMR spectra shows a degradation of [TBAC:Thy] (1:2) upon saturation with water, with peaks shifting for DES phases, as shown in Figure SI 3, and leaching of the salt clearly appreciable on the aqueous phase spectrum, Figure SI 8. However for [Thy:DecA] (1:1), Figures SI 2 and 7; [TBAC:Thy] (1:4), Figures SI 4 and 9; [TBAC:Thy:Menthol] (1:4:1), Figures SI 5 and 10; and [TBAC:Thy:DecA] (1:4:1), Figures SI 6 and 11; there is no significant peak shift or leaching to the aqueous phase.

The results support the use of thymol as a strong hydrophobic HBD to stabilize hydrophilic components during the formation of the DES, a similar result to that determined by Rajput et al. [31].

Hydrophobicity, studied by Karl-Fischer titration, shows that all solvents gain a significant amount of water with saturation, with quantity rising alongside the ratio of insoluble compounds (Thymol, Menthol, Decanoic Acid) to TBAC. Results are shown in Table SI 3. Therefore, for further experimentation, the saturated solvents were selected.

**Table 2**  
DES names, molar ratios, abbreviations and behaviour.

DES	Molar ratio	Abbreviation	Behavior
Thymol:Decanoic Acid	1:1	[Thy:DecA] (1:1)	Formed
Tetrabutylammonium chloride:Thymol	1:1	[TBAC:Thy] (1:1)	Not Formed
Tetrabutylammonium chloride:Thymol	1:2	[TBAC:Thy] (1:2)	Formed
Tetrabutylammonium chloride:Thymol	1:4	[TBAC:Thy] (1:4)	Formed
Tetrabutylammonium chloride:Thymol	1:6	[TBAC:Thy] (1:6)	Recrystallization
Tetrabutylammonium chloride:Thymol	1:8	[TBAC:Thy] (1:8)	Recrystallization
Tetrabutylammonium chloride: Thymol: Decanoic Acid	1:4:1	[TBAC:Thy:DecA] (1:4:1)	Formed
Tetrabutylammonium chloride: Thymol: Menthol	1:4:1	[TBAC:Thy:Menthol] (1:4:1)	Formed

#### 3.3. Physical properties

The physical properties of the saturated solvents were determined as described in the *Experimental Procedure* section. The obtained results for density ( $\rho$ , g cm<sup>-3</sup>) and dynamic viscosity ( $\eta$ , mPa s) are presented in Tables SI 4 and 6, respectively. The density was fitted to a linear model, as shown in Equation (2). The parameters of the obtained linear equations can be found in table SI 5.

$$\rho = a + bT \quad (2)$$

$$\eta = \eta_0 e^{\frac{B}{T-T_0}} \quad (3)$$

The viscosity was adjusted using a Volger-Fulcher-Tanman (VFT) equation, which has been shown to produce good agreement for DES [29,37]. The equation takes the form presented in Equation (3), and the parameters of the obtained fittings are shown in table SI 7. Comparison between the obtained data and adjustment to the VFT equation is shown in Figure SI 13. All show good agreement to the models. It is notable the significant effect on viscosity of the TBAC, as it is much higher in all DESs that have it as a component, when compared with [Thy:DecA] (1:1). There is strong decrease in this magnitude for [TBAC:Thy:Menthol] (1:4:1), and even further for [TBAC:Thy:DecA] (1:4:1), in comparison with [TBAC:Thy] (1:4). This is explained as a result of incorporating a third component and thus reducing the ratio of TBAC in the DES. Physical properties can be tuned this way, obtaining much more processable and cheaper separation agents, that do not show any decrease in extraction efficiency.

#### 3.4. Liquid-Liquid extraction

Mixtures of DES and dye solution were prepared to study the extraction efficiency of the prepared solvents [Thy:DecA] (1:1), [TBAC:Thy] (1:4), [TBAC:Thy:DecA] and [TBAC:Thy:Menthol] (1:4:1). To analyze the influence of the dye nature, several molecules of different classes and with several chromophore groups were selected. Their characteristics are presented in Table 1 and the molecules in Fig. 1.

The process was optimized to minimize contact time (15, 30, 45, 60 min), centrifugation time (15, 30, 45, 60 min), and DES/ aqueous phase volume ratio (1/8, 1/16, 1/32, 1/48, 1/64). The optimization was performed for a selected model dye and DES system: Reactive Red 29 and [TBAC:Thy] (1:4). These optimized variables were then used to study the rest of the dye systems under different initial concentrations (50, 100, 250, 500 ppm), with the exception of the [Thy:DecA] (1:1) that presented very poor results even under more advantageous conditions.

##### 3.4.1. Study of the effect of contact time

Under maximal conditions for the centrifugation time (60 min) and DES / aqueous phase volume ratio (1/8), the stirring time was varied between 15 and 60 min in 15 min increments to study the



effect on extraction efficiency on the Reactive Red 29 at 100 ppm and [TBAC:Thy] (1:4). The aim is to minimize processing time to increase an eventual process throughput.

The results shown in Table SI 8 indicate that there is not a significant variation of extraction efficiency for the system upon the increase of contact time, indicating that equilibrium is reached before 15 min. Therefore, that contact time was selected for further experimentation, as results were around a 99% of extraction efficiency, always showing a total lack of color.

### 3.4.2. Study of the effect of centrifugation time

For the same system of Reactive Red 29 and [TBAC:Thy] (1:4), with the optimal contact time of 15 min, and the maximal DES/ aqueous phase volume ration of 1/8, centrifugation time was varied in 15 min increments between 15 and 60 min.

With the experimental results available in table SI 9, there is not a clear variation in extraction efficiency that would justify higher centrifugation times than 15 min. Therefore, that was the duration chosen for the treatment in the following experimentation, as results were around a 99% of extraction efficiency again, with total decolorization in all cases.

### 3.4.3. Study of the effect of DES / aqueous phase volume ratio

With the optimal operational times determined in the previous sections, the volumetric ratio of solvent to aqueous phase was varied to improve DES use. The studied ratios were 1/8, 1/16, 1/32, 1/48 and 1/64 for the Reactive Red 29 and [TBAC:Thy] (1:4) systems, at 15 min contact time and 15 min centrifugation time.

The results, that are available in Table SI 10, show no clear decrease in the extraction efficiency between volumetric ratios of 1/8 and 1/32, with a slight decrease for higher ratios of 1/48 and 1/64. It is important to note that even though there is a decrease in the extraction efficiency, the results at 1/64 vol ratio are still at around a 90% extraction efficiency, but they do not achieve a full decolorization of the aqueous phase. Thus, we have selected a volumetric ratio of 1/32 DES/ aqueous phase for further experimentation in this work, which keeps the consumption of solvent comparatively low while achieving exceptionally high extraction efficiencies and full decolorization of the aqueous phase. This results are comparable to the extraction efficiencies obtained by Muthuraman et al. [38], which achieved extraction percentages higher than 98% extracting textile dyes from aqueous phase using a tetrabutylammonium bromide (TBAB) salt in a dichloromethane solution, using an aqueous solution to solvent ratio of 1:1. This represents an improvement as solvent consumption is drastically reduced while maintaining high extraction efficiencies.

### 3.4.4. Liquid-Liquid Extraction: Effects of the DES

First, it is important to note the studies carried out with the [Thy:DecA] (1:1) solvent, as it was proven that it did not achieve efficiencies anywhere near to the rest of the DESs that had TBAC as a component. The maximum extraction percentage obtained with this solvent was of only 16.56%, for the Reactive Red 29 dye, starting out with 50 ppm, as it is shown in the Table 3, below.

**Table 3**

. Extraction efficiency (%) of [thy:deca] (1:1) for the removal of various dyes at four initial concentrations in the previously optimized conditions.

Dye	Initial dye concentration (mg L <sup>-1</sup> )			
	50	100	250	500
Acid Blue 113	13.4	6.54	4.43	3.51
Acid Green 25	0.00	0.00	0.00	0.00
Acid Blue 80	0.00	1.12	0.58	0.00
Reactive red 29	16.6	7.27	7.24	7.44
Remazol Brilliant Blue	7.27	2.13	2.16	0.90
Direct Black 19	7.79	7.58	6.45	6.76

All of these experiments were performed using a DES/ aqueous phase ratio of 1:1, which is 32 times more solvent consumption than what the remainder of the solvents studied in this article needed to obtain total decolorization in most of cases.

The performances of the other three DES employed for the LLE experiments: [TBAC:Thy] (1:4), [TBAC:Thy:Menthol] (1:4:1) and [TBAC:Thy:DecA] (1:4:1) show much higher efficiencies. These results are presented in the next section, where they are discussed along with the influence of the type of dye and its concentration. This structure for the presentation of the data was chosen to avoid repeating data throughout the analysis.

### 3.4.5. Liquid-Liquid Extraction: Effects of the dye

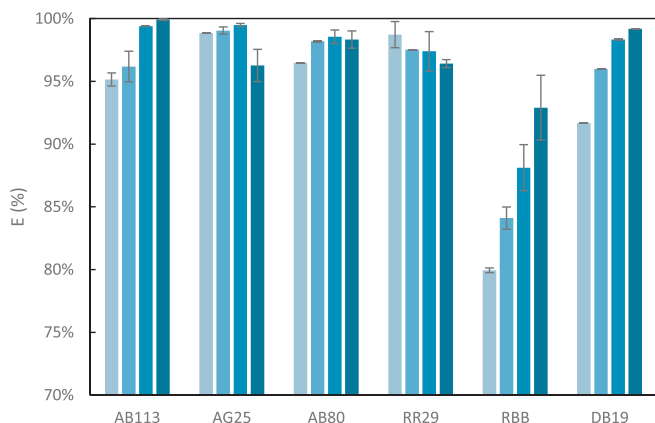
Under the optimized operational conditions, a study of the effect of the initial concentration for all dyes is carried out for each of the solvents at different initial concentrations (50, 100, 250 and 500 ppm). For the binary solvent [TBAC:Thy] (1:4), the results are presented in Fig. 2.

The data shows good performances for all dye classes, with extraction efficiencies well above 90% except for Remazol Brilliant Blue, where extraction efficiencies at low initial concentration fall to around 80%.

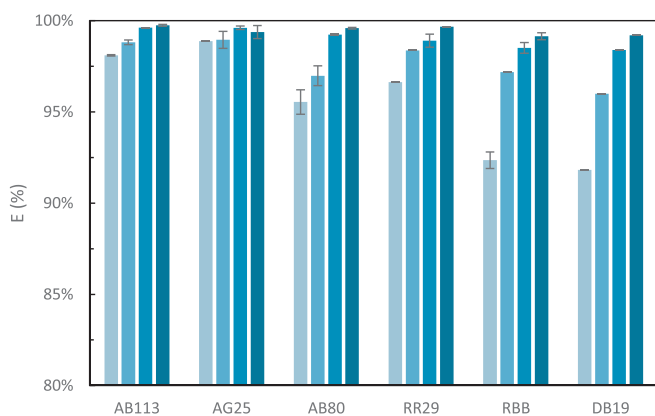
Based on the data, two classes of dye appear, depending on the strength of the solvation interactions with water. AB113, RBB and DB19 all show a clear increase on extraction efficiency as initial concentration rises, while AG25, AB80 and RR29 do not show a clear variation in extraction efficiency with changing initial concentrations.

In these results, a sharp increase of the extraction percentages, in comparison with those obtained with the [Thy:DecA] (1:1) DES, is appreciated. The presence of TBAC is the difference from previous experiments, so it can be expected to be crucial for the extraction mechanism. Given that the improvement comes for all dyes, it is important to draw some conclusion about what they have in common. Since the sulfonate auxochrome groups are present in all of them, independently from their class, we can assume that the ammonium groups present in the dyes and the auxochromes interact (Figure SI 1), therefore improving extraction efficiency.

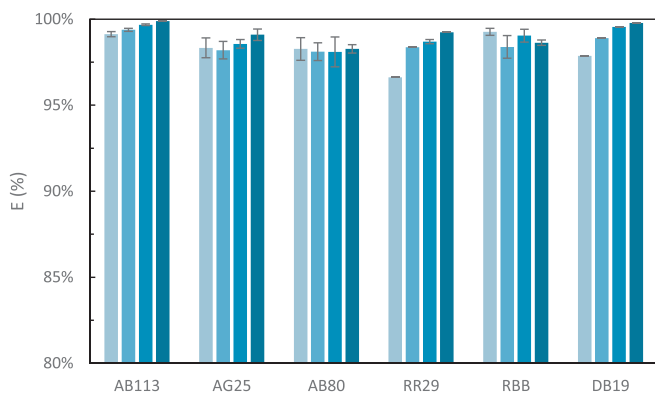
For the ternary DES prepared, [TBAC:Thy:Menthol] (1:4:1) and [TBAC:Thy:DecA] (1:4:1), the results are presented in Fig. 3 and Fig. 4 respectively. With the inclusion of Menthol, the solvent shows an increase in extraction efficiency for most of the selected dyes. Moreover, the effect of solvation strength becomes apparent for all dyes, with increasing extraction efficiency with increased initial concentration. The increase in extraction efficiency, and thus of DES – Dye interaction could be explained by the sharp decrease in viscosity observed by the addition of a ternary solvent. It could also be partly explained by the increase on HBA strength of the solvent by the addition of menthol as a third component. Menthol is a strong hydrogen bond donor acceptor, as shown by Martins et al. [18], and can interact with the amino group present on the dyes. For [TBAC:Thy:Menthol] (1:4:1), full decolorization was achieved except for RBB at 50 and 100 ppm, and AG 25 at 50 ppm.



**Fig. 2.** Extraction efficiencies for the selected dyes, under initial concentrations of 50 (■), 100 (■), 250 (■) and 500 ppm (■) with DES [TBAC:Thy] (1:4) at DES / aqueous phase volume ratio of 1/32.



**Fig. 3.** Extraction efficiencies for the selected dyes, under initial concentrations of 50 (■), 100 (■), 250 (■) and 500 ppm (■) with DES [TBAC:Thy:Menthol] (1:4:1) at DES / aqueous phase volume ratio of 1/32.



**Fig. 4.** Extraction efficiencies for the selected dyes, under initial concentrations of 50 (■), 100 (■), 250 (■) and 500 ppm (■) with DES [TBAC:Thy:DecA] (1:4:1) at DES / aqueous phase volume ratio of 1/32.

When adding decanoic acid, an even sharper decrease of the viscosity can be observed, and again this decrease in viscosity also leads to an increase in extraction efficiency for all dyes, as presented in Fig. 4. The increase in extraction efficiency also decreases the effect of solvation when comparing across initial concentrations for all dyes, with comparable extraction efficiencies across the complete range.

The addition of a long chain carboxylic acid to a tetrabutylammonium based DES increases both HBD and HBA strength as shown by Kundu et al. [39]. The long alkyl chain also increases the hydrophobicity of the solvent and the opportunity for nonpolar Van de Waals interactions. For [TBAC:Thy:DecA] (1:4:1), full decolorization is achieved.

### 3.4.6. Liquid-Liquid Extraction: Mixed dyes

First, to evaluate the effect of several dye classes being present on an effluent, a solution was prepared, with a total dye concentration of 250 ppm, with all the pigments present in the previous study being included at a concentration of around 42 ppm. The resulting aqueous phase was extracted with the binary and ternary solvents following the same optimized procedure as described in prior sections.

Since the peak wavelengths for several of the dyes overlap, it was not possible to determine by spectroscopy the concentration of a single dye in aqueous phase. It was however possible to perform a full wavelength spectroscopy scan of the aqueous phase to extract the color coordinates. The color space used was CIE 1976  $L^* a^* b^*$  as defined by ISO 11664-4:2008 [40], where  $L^*$  represents the lightness of the color in a scale of 0 (black) to 100 (diffuse white),  $a^*$  represents the hue between red and green, in a scale of  $-128$  (green) to  $128$  (red) and  $b^*$  the hue from yellow to blue, again in a scale of  $-128$  (blue) to  $128$  (yellow).

The aim is to produce a completely decolorized aqueous phase, which would present CIE  $L^* a^* b^*$  coordinates similar to those presented by tap water or Milli-Q water, represented in Table 4, where a value of  $L^*$  close to 100 and values of  $a^*$  and  $b^*$  close to 0 show absence of color.

The CIE  $L^* a^* b^*$  color coordinate values for the aqueous phases obtained before and after extraction are presented in Table 5. There is full decolorization of the aqueous phase for all the DESs except for the [Thy:DecA] (1:1), which had already shown poor efficiencies, corroborated visually and by the colorimetric assay, where there is a slight variation in color coordinates that was not distinguishable visually. This shows that competing solvated dyes enhance extraction for all solvents. This confirms [TBAC:Thy:DecA] (1:4:1) as the best solvent studied, as it already presented both the best performance against individual dyes and the best physical properties among all studied DESs.

### 3.4.7. Liquid-Liquid Extraction: Synthetic effluent

In this final experimental section, [TBAC:Thy:DecA] (1:4:1) efficacy will be assayed against a synthetic wastewater, created to mimic those generated after dyeing processes in textile industry. As explained in the experimental procedure, experiments were carried out both using only the dye itself and including also auxiliary agents typically used in these processes. The selected DES achieved notable efficiencies either way, always higher than 94%, as shown in Table 6. Only a descent of nearly 5% in the case where the fixing agent was added, is appreciated. The most probable cause is the common presence, as stated previously, of quaternary ammonium salts in these products. These salts could interfere with the normal behavior of the DES, rendering lower efficiencies.

**Table 4**

CIE 1976  $L^* a^* b^*$  color coordinates values for Milli-Q and Tap Water measured by full wavelength spectroscopy scan.

	$L^*$	$a^*$	$b^*$
Milli-Q Water	99.99	0.00	0.00
Tap Water	99.97	-0.02	0.13

**Table 5**

CIE 1976 L\* a\* b\* color coordinates values for the initial mixed effluent, and the aqueous phases extracted with [TBAC:Thy] (1:4), [TBAC:Thy:DecA] (1:4:1) and [TBAC:Thy:Mth] (1:4:1).

Aqueous Phase	L*	a*	b*
Synthetic Mixed Effluent	2.8	17.37	-34.85
[Thy:DecA] (1:1)	2.8	9.49	-21.05
[TBAC:Thy] (1:4)	99.33	-0.02	0.41
[TBAC:Thy:DecA] (1:4:1)	98.31	-0.08	0.66
[TBAC:Thy:Mth] (1:4:1)	98.95	-0.03	0.30

**Table 6**

Extraction efficiencies (%) for the different industrial Scarlet Tubantin dye based systems, with DES [TBAC:Thy:DecA] (1:4:1) at DES / aqueous phase volume ratio of 1/32.

Dye System	E (%)
Scarlet Tubantin	99.81
Scarlet Tubantin + Sarabid DLC + Biavin BPA	98.51
Scarlet Tubantin + Sarabid DLC + Biavin BPA + Rewin ACP	94.17

#### 4. Conclusions

In this work, eight DES, seven of them based on tetrabutylammonium chloride and molecular components Thymol, Menthol and Decanoic Acid have been formed under varying molar ratios. There was confirmed stability for five of the solvents [Thy:DecA] (1:1), [TBAC:Thy] (1:2) and (1:4), [TBAC:Thy:Menthol] (1:4:1) and [TBAC:Thy:DecA] (1:4:1) and confirmed hydrophobicity for four of them, excluding [TBAC:Thy] (1:2) which showed significant leaching of TBAC to the aqueous phase. This improved hydrophobicity, shown after increasing thymol ratio, confirms this component as an excellent hydrophobic HBD to stabilize water soluble HBA such as ammonium salts (Choline Chloride, Tetrabutylammonium Chloride).

The formed HDES which have the ammonium salt as a component show a strong interaction with the most used textile dye classes (Acid, Reactive and Direct), with extraction efficiencies over 80% for all dye and solvent systems studied, over a wide range of initial conditions. This confirms the proposed mechanisms of interaction for TBAC with the sodium sulfonate auxochrome groups present on the dyes, specially taking into account the low extraction efficiencies attained by the [Thy:DecA] (1:1) DES.

It is also shown that the addition of a ternary component to the solvent enhances processability of the solvent by sharply reducing viscosity which in turn leads to a further increase in extraction efficiencies, achieving results over 95% for all dye classes and concentrations for the solvent [TBAC:Thy:DecA] (1:4:1), while maintaining a low processable viscosity. For this solvent, full decolorization was accomplished for most dyes, depending on initial concentration: AB 113 up to 500 ppm, for AG25 up to 100 ppm, AB80 up to 250 ppm, RR29 up to 100 ppm, RBB up to 250 ppm and DB19 up to 500 ppm.

Working with a DES/aqueous phase volume ratio so low as 1:32 implies a very low consumption of the separation agent, while reducing the generation of residue after the treatment of the wastewater. This results in a highly efficient way to obtain great quantities of clean water, with total absence of color. Both the low processing times and lack of need for additional extraction stages are great features of this newly presented treatment.

Additionally, the reutilization of this water in textile industries is accomplished, reducing water consumption in the process, and thus promoting the principles of circular economy. Atmospheric emissions associated to traditional extraction agents are also avoided as DES present a practically null vapor pressure.

The DES [TBAC:Thy:DecA] (1:4:1), when tested with synthetic effluents, containing various dyes or auxiliary agents, showed extraction efficiencies that remained almost as high as in the previous assays conducted with individual pigments. Only the fixating agent seemed to affect the behavior of the solvent, and even then, the efficiency only dropped 5%, still prevailing well above 90%.

Summarizing, water decolorization was achieved via an optimized and efficient process that can drastically cut down waste generation and atmospheric emissions. Tailored solvents that interact directly with target pollutants, with tunable physical properties, seem to be in the right direction when it comes to separation technologies.

#### CRediT authorship contribution statement

**Andrés Asla:** Methodology, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Óscar Martínez-Rico:** Methodology, Validation, Investigation, Writing – review & editing. **Pablo Otero:** Conceptualization, Investigation, Formal analysis, Writing – original draft, Resources. **Ángeles Domínguez:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **Begoña González:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

#### Data availability

Data will be made available on request.

#### 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.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2023.121832>.

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