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Testing Thymol-Based DES for the Elimination of 11 Textile Dyes from Water

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Abstract: Textile industries release dangerous wastewater that contain dyes into the environment. Due to their toxic, carcinogenic and mutagenic nature, they must be removed before the discharge. Liquid–liquid extraction has proven to be an efficient method for the removal of these dyes. As extractants, deep eutectic solvents (DESs) have shown excellent results in recent years, as well as presenting several green properties. Therefore, four different hydrophobic DESs based on natural components were prepared thymol:decanoic acid (T:D (1:1)), thymol:DL-menthol (T:M (1:1)), thymol:DL-menthol (T:M (1:2)) and thymol:coumarin (T:C (2:1)) for the extraction of Malachite Green (MG), Brilliant Blue G (BBG), Acid Yellow 73 (AY73), Reactive Red 29 (RR29), Acid Blue 113 (AB113), Reactive Black 5 (RB5), Remazol Brilliant Blue (RBB), Direct Yellow 27 (DY27), Acid Blue 80 (AB80), Direct Blue 15 (DB15) and Acid Violet 43 (AV43) dyes from water. The operational parameters of the liquid–liquid extraction were selected in order to save time and materials, resulting in 30 min of stirring, 15 min of centrifugation and an aqueous:organic ratio of 5:1. In these conditions, the highest values of extraction obtained were 99% for MG, 89% for BBG and 94% for AY73. Based on these results, the influence of the aqueous:organic phase ratio and the number of necessary stages to achieve water decolorization was studied.

Keywords: liquid–liquid extraction; deep eutectic solvent; textile dyes

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1. Introduction

The treatment of wastewaters has become a major problem as the growing world population implies an increase in the demand for water, while water resources are becoming scarce. This environmental problem constitutes one of the main threats to the environment at a global scale [1]. Industrial activity from different sectors such as the textile, food, leather or cosmetics industries is one of the main generators of these dangerous effluents [2]. In the case of textile wastewaters, they contain dyes that give them a strong color. From the point of view of the consumer, it must be assured that dyes give clothes a bright color that is maintained over time. This requires the production of dyes that are highly stable under a wide set of conditions, which ultimately hampers their treatment and removal [3].

There are currently more than 10,000 types of dyes available on the market, and around 2.8×10^5 tons of wastewater from the textile industry are discharged every year [4]. For instance, in the leather industry, about 10–15% of the dye used during the manufacturing process ends up in the wastewater. This huge ecological impact [5] has compelled the European Union to legislate for wastewater quality, particularly regarding the regulation of the levels of color. These colorants show a low biodegradability, strong color and a high chemical and biological oxygen demand, which can cause harmful effects on aquatic ecosystems [6] and even on human health due to their carcinogenic, mutagenic and toxic nature [3].

Effluents from the textile industry that contain dyes are usually treated by means of physical, biological and chemical methods. Among the most common methods are activated carbon adsorption, biological oxidation, flocculation, coagulation, ion exchange, neutralization, electrochemical methods, microbial degradation and photocatalysis [3–5,7,8].

Methods based on microbial and enzymatic degradation processes have gained relevance lately. However, these strategies involve large processing times (ranging from 24 h to 6 days), minimal capacity to absorb contaminants and the release of metabolites sometimes even more toxic than the original dye [4].

Focusing on physical separation techniques, liquid–liquid extraction has shown high efficiency for dye removal while having a broad range of applicability [2]. It allows for the separation of compounds based on their different solubility between two immiscible liquids [9]. The selection of the extractant is relevant given that it will define the mass transfer rate of the dye and, therefore, its extraction efficiency. This technique is simple in terms of operation and offers the possibility of scaling it up [3].

Recently, a new type of solvent has been proposed and studied as extracting media for liquid–liquid extraction: deep eutectic solvents (DESs). DESs consist of two components: a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). They form a liquid mixture with a lower melting point than the starting materials, so they are liquid in a wider range of temperatures, while showing green properties such as non-toxicity, biodegradability and biocompatibility [2]. In addition, they have been recently used in metal processing, green sorption technology, nanomaterials and catalysis.

In order to test the applicability of these solvents for a diverse set of dyes, eleven different dyes were selected: Malachite Green (MG), Brilliant Blue G (BBG), Acid Yellow 73 (AY73), Reactive Red 29 (RR29), Acid Blue 113 (AB113), Reactive Black 5 (RB5), Remazol Brilliant Blue (RBB), Direct Yellow 27 (DY27), Acid Blue 80 (AB80), Direct Blue 15 (DB15) and Acid Violet 43 (AV43). MG is an organic dye derived from triphenylmethane, that in the solid state exists as green crystals with a metallic sheen. In the human body, apart from its mutagenic properties, it can cause tumor growth [10]. BBG is a derivative of triphenyl methane that is used both in the textile industry and in analytical biochemistry for protein staining [11]. AY73, also known as fluorescent disodium salt, is used as a fluorescent tracer in some medical applications, in the cosmetic industry and for detergents, soaps, silk and wool [12]. RR29 is a reactive dye with an azo chromophore group that contains a triazinyl (Procion) anchor group, used for the dyeing of cellulosic fibers [13]. AB113 is an acid dye with two azo chromophore groups (disazo) important in the dyeing of wool and polyamide [14]. RB5 is a reactive dye with two azo chromophore groups and two 2-sulfooxyethylsulfonyl anchor groups (Remazol), used for dyeing cellulosic fibers [15]. RBB is a reactive dye with an anthraquinone chromophore group, and a 2-sulfooxyethylsulfonyl (Remazol) anchor group, also used for dyeing cellulosic fibers [13]. DY27 is a direct dye containing a chromophore azo group (monoazo), a derivative of dehydrothio-p-toluidinesulfonic acid, and is used for dyeing cellulosic fibers [15]. AB80, an acid dye containing one anthraquinone chromophore group, a derivative of 1,4-diaminoanthraquinone, is used for dyeing polyamide fibers [16]. DB15 is a direct dye with two azo chromophore groups, is derived from o-dianisidine and used for dyeing cellulosic fibers. [15]. Finally, AV43 is an acid dye containing an anthraquinone chromophore group, a derivative of 1-amino-4-hydroxy-2-phenoxyanthraquinone, used for the dyeing of polyamide fibers [16]. The structures of all of these compounds are shown in Table S1.

In this work, a wide selection of dyes, solvents and various operative conditions were screened in order to determine potential uses of these natural sourced solvents aiming to reduce the negative impact of the textile industry on the environment. Thymol, DL-menthol, decanoic acid and coumarin were chosen for the preparation of hydrophobic DESs with the aim of testing their ability to eliminate dyes from water. The following five DESs were prepared: thymol:decanoic acid (1:1) (T:D (1:1)), thymol:decanoic acid (2:1) (T:D (2:1)), thymol:DL-menthol (1:1) (T:M (1:1)), thymol:DL-menthol (1:2) (T:M(1:2)) and thymol:coumarin (2:1) (T:C (2:1)). After testing their stability at room temperature and in contact with water, their extractive properties were investigated. The assays conducted included studying the influence of dye concentration, the volumetric ratio between phases and the number of extraction cycles necessary for the complete decoloration of the aqueous phase.

2. Materials and Methods

2.1. Chemicals

Reagents for DES preparation: thymol (CAS 89-83-9, purity 99%) and coumarin (CAS 91-64-5, purity 99%) were purchased from Acros Organic (Geel, Belgium), DL-menthol (CAS 89-78-1, purity 98%) was purchased from Alfa Aesar (Kandel, Germany) and decanoic acid (CAS 334-48-5, purity 99%) was supplied by Thermo Scientific (Waltham, MA, USA). Dyes: RBB (CAS 2580-78-1) and BBG (CAS 6140-58-1) were purchased from Acros Organic (Geel, Belgium); AB80 (CAS 4474-24-4) was supplied by Glentham Life Sciences (Corsham, United Kingdom); DY27 (CAS 10190-68-8), DB15 (CAS 2429-74-5), RR29 (CAS 12226-09-4), AB113 (CAS 3351-05-1), RB5 (CAS 17095-24-8) and MG (CAS 2437-29-8) were purchased from Sigma Aldrich (San Luis, MO, USA); AV43 (4430-18-6) was supplied by TCI (Zwijndrecht, Bélgica) and AY73(518-47-8) was purchased from Alfa Aesar (Kandel, Germany). The structures of all chemicals are shown in Table S1 of the Supplementary Materials.

2.2. Preparation of DES

The DES were prepared by mixing the HBA and the HBD components following the methodology described in the literature [17,18]. The components were weighed in a range balance (AX-205 DeltaRange, Mettler Toledo, Columbus, OH, USA) with an uncertainty of $\pm 3 \times 10^{-4}$ g and heated to 343.15 K under magnetic stirring, using an temperature controller (ETS-D5, IKA, Staufen, Germany) with an uncertainty of ± 0.1 K. The DES is formed once a homogeneous liquid phase is obtained. Then, it is cooled down to room temperature.

To perform an extraction of the dye from an aqueous phase with a DES, it is important to know the behavior of the solvent in water. Therefore, each DES was put into contact with water in a volumetric ratio of 1:1 for 8 h and then left to settle overnight [19]. This guarantees the correct contact between phases and proves the stability of the DES in water. Moreover, in this process, the DES is saturated with water, which implies that it will not capture any more water molecules, only the desired synthetic dye in the liquid–liquid extraction of interest, and that its water content will remain constant.

To determine the amount of water that the DES has absorbed, a sample is measured with a Coulometric KF Titrator (C20, Mettler Toledo, Columbus, OH, USA) after the exposure to water. All stable formed DES were then characterized by studying their density and viscosity in temperatures ranging from 293.15 to 343.15 K. An digital vibrating tube densimeter (DSA-5000M, Anton Paar, Graz, Austria) (uncertainty of $\pm 3 \times 10^{-4}$ g cm^{-3}) and a ball viscometer (Lovis 2000/ME, Anton Paar, Graz, Austria) (uncertainty of ± 0.03 mPa s^{-1}) were used in this process. The temperature was controlled with an uncertainty of ± 0.02 K.

The density was modeled as a function of temperature via a linear regression. The viscosity was adjusted to a Vogel–Fulcher–Tammann model, whose Equation (1) is presented below.

$$\mu = \mu_0 \, e^{\frac{B}{T - T_0}} \tag{1}$$

2.3. Liquid–Liquid Extraction Procedure

In order to compare the capability of these DESs to extract each of the eleven dyes, the same operational parameters of liquid–liquid extraction were selected: 30 min of stirring, 15 min of centrifugation and an aqueous:organic phase ratio of 5:1 (*v*/*v*). Different concentrations of dye solutions were studied (50, 100, 200 and 500 mg L^{-1}) with the aim of determining the influence of dye concentration.

Mixtures of DES and aqueous solution were prepared and stirred at 298.15 K in a magnetic stirrer (RSM-08-10K, Phoenix, Garbsen, Germany) to ensure a proper mixture between both phases. Afterwards, the solution was centrifugated at 7000$\times$ *g* rpm with a centrifuge (Universal 320, Hettich, Tuttlingen, Germany). Following this, two different layers can be observed: an aqueous phase with the residual dye and an organic phase containing the dye extracted and the DES.

The concentration of the unextracted dye in the aqueous phase was determined by absorbance using an UV-vis spectrophotometer (V-750 UV–Vis, Jasco, Tokyo, Japan)

(uncertainty of ±0.002 abs from 0 to 0.5 abs and ±0.003 abs from 0.5 to 1 abs). The wavelength used was 617 nm for MG, 591.5 nm for BBG, 487 nm for AY73, 532 nm for RR29, 566.5 nm for AB113, 597.5 nm for RB5, 591.5 nm for RBB, 397.5 nm for DY27, 626 nm for AB80, 596 nm for DB15 and 569 nm for AV43.

Finally, the extraction efficiency (EE) can be calculated according to Equation (2):

$$EE(\%) = 100\ \frac{(C_0 - C_f)}{C_0} \quad (2)$$

where C_0 and C_f correspond to the initial and the final concentration of dye in the aqueous phase, respectively.

Depending on the obtained EE results, other ratios were tested as well as several extraction cycles following the same procedure.

3. Results and Discussion

3.1. DES Formation and Characterization

After cooling down, all DESs remained liquid. Only the mixture T:D (2:1) solidified after settling for some days, thus indicating the instability of the liquid formed and the impossibility of a DES formation with these two components in this mentioned ratio. Therefore, its use as a separation agent was discarded. The water content after saturation of the solvents is listed in Table S2, and all values are low enough to ensure immiscibility.

Characterization in terms of density and viscosity is also presented in the Supplementary Materials in Tables S3–S6 and Figures S1 and S2.

3.2. Extraction Results

Table S7 shows the extraction values tested using the operational conditions mentioned in Section 2.3. The reported values are the average of three extraction assays.

The best results were obtained for MG mainly using T:D (1:1), T:M (1:1) and T:C (2:1) and also good results were obtained using T:M (1:2). Furthermore, the EE varies slightly when the initial concentration of dye increases. Similarly, the results obtained using the four DES in the extraction of BBG are good, although lower than for MG. The EE obtained using T:M (1:1) is lower than when using the other DESs. In addition, the variation of EE with concentration is pronounced when using T:M (1:1) and T:M (1:2). In the case of AY73, the best results were achieved using T:D (1:1), while quite low EE results were obtained with the other three DES. Worse results were obtained for AV43 with a maximum EE around 33% using T:D (1:1) and 22% with T:C (2:1) for a dye concentration of 50 ppm. Using T:M (1:1), the extraction was less than 3%. The results obtained for the other dyes are lower: a maximum of 25% for the extraction of RBB with T:C (2:1) and a maximum of 23% for DY27 with T:M (1:1). Values lower than 3% using any of the four solvents were obtained for RB5 and AB80.

Figure 1 shows the results obtained for MG, BBG, AV43 and AY27 with a concentration of 100 mg L^{-1}.

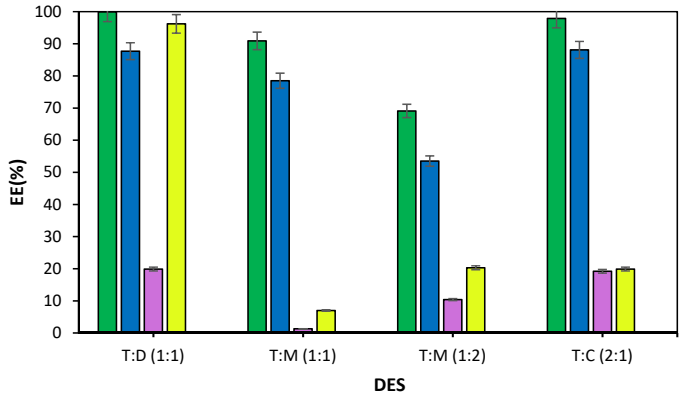

Figure 1. Extraction efficiency for each DES, starting out with a 100 mg L^{-1} dye concentration, for MG (green), BBG (blue), AV43 (violet) and AY27 (yellow).

Dyes can form hydrogen bonds with water and with DES. Consequently, their hydrogen bonds acceptor (HBA) and hydrogen bonds donor (HBD) counts should be related to the extraction efficiency, even though there are other contributing factors such as chain flexibility and aromaticity. Menthol and thymol have a hydroxy group that serves both as HBD and HBA. Decanoic acid has another -OH group with the same behavior, plus another HBA count in the oxygen atom present in the carboxyl group. Coumarin has two HBA counts in the two oxygen atoms present in the molecule, as seen in Table S1. According to that, the DES constituted by thymol and decanoic acid still has one HBD and two HBA available to form hydrogen bonds with dyes, facilitating dye extraction. This fact could explain the better results obtained with T:D (1:1). However, the formation of hydrogen bonds between the dye and water hampers the extraction, so it is expected that dyes with higher HBA and HBD counts will be more difficult to extract. The HBD counts of these dyes vary from zero for MG to four for DB15, while the HBA counts range from one for MG to twenty-four for RB5, with MG being the most easily extracted, while the EE for RB5 is lower than 5%. In general, an increase in HBA counts in the dye (mainly due to oxygen atoms) implies a decrease in EE. Figure 2 shows the EE obtained for all dyes using T:D (1:1) as a solvent, with an initial dye concentration of 100 mg L^{-1}.

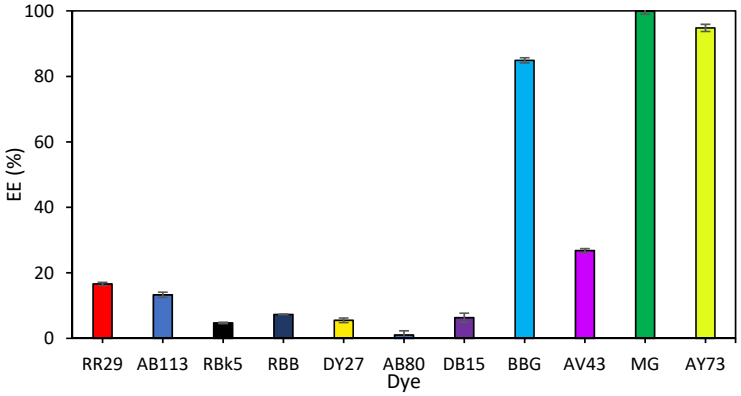

Figure 2. EE of T:D (1:1).

3.3. Influence of Aqueous:Organic Phase Ratio

In order to analyze the influence of aqueous:organic ratio, 1:1, 2:1 and 4:1 ratios were tested using dye concentrations of 100 mg L^{-1} of BBG, AY73, MG and AV43 dyes, and those solvents whose EE obtained with a 5:1 ratio was between 7% and 75%. The values obtained are reported in Table 1.

Table 1. Influence of aqueous:organic phase in EE.

DES	Ratio	T:D (1:1)	T:M (1:1)	T:M (1:2)	T:C (2:1)
BBG	1:1	-	72.9	62.8	-
	2:1	-	84.6	56.2	-
	4:1	-	76.9	54.4	-
	5:1	87.7	78.5	53.5	84.2
AY73	1:1	-	39.9	95.2	67.5
	2:1	-	22.9	63.6	40.9
	4:1	-	13.0	33.2	19.7
	5:1	94.3	7	20.3	19.9
MG	1:1	-	-	84.9	-
	2:1	-	-	77.7	-
	4:1	-	-	68.6	-
	5:1	99.9	89.3	70.0	99.6
AV43	1:1	68.8	-	-	59.0
	2:1	41.8	-	-	35.8
	4:1	28.6	-	-	21.5
	5:1	19.9	<3	<3	19.2

As it can be seen, the ratio influence is different depending on the DES. However, a general tendency can be observed: as the proportion of DES is increased, the EE grows due to the fact that the dye becomes more available to the extractant. The greatest increase is observed for AY73, varying the extraction from 20.3% to 95.2%. Increases of around 10% were obtained in the extraction of BBG with T:M (1:1) and T:M (1:2), similar to those achieved in the extraction of MG with T:M (1:2). A similar increase of EE is obtained using T:D (1:1) and T:C (2:1) to eliminate AV43, from around 19% to 68.8% and 59.0%, respectively.

3.4. Number of Cycles

For several selected DES and dye systems where one cycle extraction for an initial concentration of 100 mg L^{-1} has an acceptable value, but yielded insufficient decolorization, several extraction cycles with fresh solvent were performed on the same aqueous phase. This way, the DES consumption could be reduced. Upon each cycle, the concentration, extraction efficiency and color coordinates in the CIE L*a*b* color space determined are shown in Tables S4–S6. The color coordinates measured for tap water were L = 99.97, a = −0.02 and b = 0.13.

For each solvent, the influence of the dye is studied. For the T:D (1:1) solvent, at the 5:1 aqueous phase:DES ratio, the results are shown in Table S8. A very high EE is achieved for MG, with full color removal in one extraction cycle. Meanwhile, AY73 requires two extraction cycles for full decolorization. BBG reaches a stable concentration of 6.3 mg L^{-1} after the second extraction cycle, with the solvent being unable to achieve full decolorization of the aqueous phase. For AV43, an aqueous phase:DES ratio of 1:1 was selected, with the EE rising with the extraction cycles, achieving full decolorization after three cycles.

For the T:C (2:1) DES, the results are presented in Table S9. MG presents, once more, a very high EE, with full decolorization in a single extraction cycle. BBG presents a gradual decrease in EE, with the solvent unable to significantly reduce the concentration below 5 mg L^{-1}, which was achieved after three extraction cycles. For AV43, again with an aqueous phase:DES ratio of 1:1, the EE increases with the extraction cycles, attaining full decolorization in three cycles.

Finally, for the T:M (1:1) DES applied to the extraction of BBG, a decline of EE from a value of 72.9% to 39% can be seen, remaining constant for the second and third cycles. In the fourth cycle, a sharp decrease to a marginal extraction of 1.5% was observed, resulting in a concentration of around 10 mg L^{-1}, which remains constant for further extraction cycles, never achieving full decolorization.

Figures 3 and 4 show the variation of the concentration for BBG and AV43 depending on the DES used and the cycle.

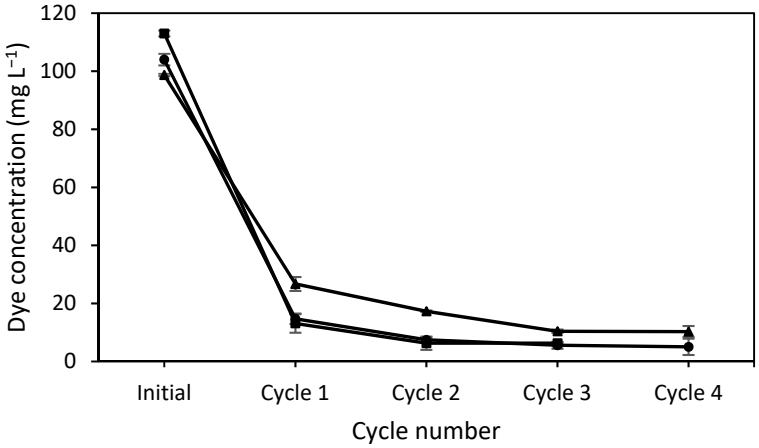

Figure 3. Variation of BBG concentration using T:D (1:1), (■), T:C (2:1), (●) and T:M (1:1), (▲).

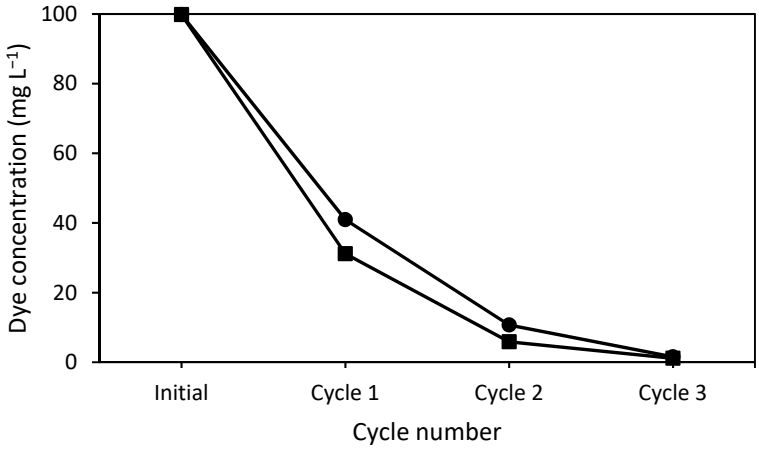

Figure 4. Variation of AV43 concentration using T:D (1:1), (■) and T:C (2:1), (●).

3.5. Comparison Study with Bibliographical Precedents

In the field of dye extraction with DESs, there are some papers using liquid–liquid extraction with different DESs for MG, while for the rest of the dyes, the literature mainly relates to adsorption or biodegradation processes. Arcon and Franco [4] reported the extraction of MG with DES formed by dodecanoic acid, combined with various carboxylic acids with an alkyl chain from 8 to 10, with >99% EE, similar to those obtained in this work using T:D (1:1) and T:C (2:1). Li et al. [20] used a thymol:camphor (1:1) DES, with TMN-10 as an emulsifier, and the percentage of extraction efficiency obtained was 99.3%. Moreover, Faraji et al. [21] showed high recovery results—97.5% of efficiency—using a thymol and benzyltrimethylammonium chloride-based DES, in a 4:1 ratio, and adding NaCl to cause the salting-out effect. Finally, Aydin et al. [22] used a choline chloride:phenol (1:4) DES, with tetrahydrofuran, in an ultrasound microextraction method and obtained more than 95% removal for MG with a ratio of 20:1. These studies, while showing positive results in terms of efficiencies, also present the use of toxic and environmentally concerning substances and functional groups, such as tetrahydrofuran or phenol.

Moreover, the most used method to study the elimination of dyes is adsorption, as in the case of MG [23,24], AB113 [25–27], RB5 [27], RBB [28], DY27 [29,30] and AB80 [31,32] or biodegradation for the elimination of AB113 [33], RB5 [34,35], DB15 [36–38] and BBG [39,40].

The extraction of RB5 using aqueous two-phase systems formed by non-ionic surfactants and choline chloride:urea (1:2) as a salting-out agent [4] reaching an extraction efficiency > 89% was reported by Fernandez [41]. An aqueous two-phase system, formed by Tween 80 or Tween 20, choline bitartrate and water, was also applied to eliminate RB5 from water [42]. The extraction efficiency of RBB from aqueous solutions reached ≥99.4% applying aqueous two-phase systems based on the ionic liquid 1,3-dibutylimidazolium dicyanamide [43].

4. Conclusions

The capability of T:D (1:1), T:M (1:1), T:M (1:2) and T:C (2:1) to extract RBB, BBG, AB80, DY27, DB15, RR29, AB113, RB5, MG, AV43 and AY73 in aqueous concentrations of 50, 100, 200 and 500 mg L^{-1} was tested. The best results were obtained for T:D (1:1) following the trend MG > AY73 > BBG > AV43 > RR29. Very good results were obtained in the extraction of MG and BBG with T:C (2:1). T:M (1:1) gives better results than T:M (1:2), and in both cases, the higher EE corresponds to the elimination of MG and BBG. None of the tested DES is adequate to eliminate RB5, RBB, DY27, AB80, AB113 and DB15.

EE can be improved by decreasing the volumetric ratio of the aqueous and organic phase, even though the results are quite different depending on the dye and the DES. Using T:C (2:1) in a ratio of 1:1, the EE increases from 19.9 to 67.5 for AY73 and from 19.2 to 59.0 for AV43. For AY73, in the case of T:M (1:2), the efficiency rose from 20.3 to 95.2 when reducing the ratio from 5:1 to 1:1. The other remarkable effect is the increment of EE from 19.9 to

68.8 in the extraction of AV43 with T:D (1:1). Even though some of the results achieved showed limitations for these solvents, it has been demonstrated that they are capable of substituting some of the toxic agents and environmentally impactful techniques reviewed in Section 3.4. Finally, according to the results of the color coordinates in the CIE L*a*b* color space obtained, water decolorization was achieved for MG in one cycle using T:D (1:1) or T:C (2:1), for AY73 in two cycles using T:D (1:1) and for AV43 in three cycles using T:D (1:1) or T:C (2:1).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations9120442/s1, Figure S1: Density measured values for: T:D(1:1), (■); T:M(1:1), (▲); T:M(1:2), (♦) and T:C(2:1), (•); and linear regression (dashed lines) for the stable DESs; Figure S2: Kinetic Viscosity measured values for: T:D(1:1), (■); T:M(1:1), (▲); T:M(1:2), (♦) and T:C(2:1), (•); and VFT modelling (dashed lines) for the stable DESs; Table S1: Structures of chemicals.; Table S2: Water content of the DES after saturation expressed as mass fraction; Table S3: Density of the stable DES after hydration, at temperatures ranging from 293.15 K to 343.15 K. Results are expressed as g cm^{-3}; Table S4: Rate of change (g cm^{-3} K^{-1}), y-intercept (g cm^{-3}) and coefficient of determination for the linear adjustement of the density data; Table S5: Kinetic viscosity of the stable DES after hydration, at temperatures ranging from 293.15 K to 343.5 K. Results are expressed as mPa·s; Table S6: Parameters for the adjustement of the kinetic viscosity data to a Volger-Fulcher-Tammann equation (VFT equation); Table S7: Extraction efficiencies for all DESs and dyes under consideration at 50, 100, 200 and 500 mg L^{-1}, in aqueous:organic ratio of 1:1; Table S8: Cycle number, initial concentration C0, final concentration Cf, extraction efficiency (%) and colour coordinates from the CIE 1976 L*a*b* system, for the extraction with T:D (1:1) for BBG, AY and MG at aqueous:organic ratio of 5:1, and AV aqueous:organic ratio of 1:1; Table S9: Cycle number, initial concentration C0, final con-centration Cf, extraction efficiency (%) and colour coordinates from the CIE 1976 L*a*b* system, for the extraction with T:Cu (1:1) for BBG and MG at aqueous:organic ratio of 5:1, and AV at aque-ous:organic ratio of 1:1; Table S10: Cycle number, initial concentration C0, final concentration Cf, extraction efficiency (%) and colour coordinates from the CIE 1976 L*a*b* system, for the extraction with DES T:M (1:1) for BBG at DES:aqueous phase ratio 1:5.

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Data Availability Statement: The data presented in this study are available in the manuscript and Supplementary Materials.

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References

1. Konsowa, A.H.; Abd El-Rahman, H.B.; Moustafa, M.A. Removal of azo dye acid orange 7 using aerobic membrane bioreactor. *Alex. Eng. J.* **2011**, *50*, 117–125. [CrossRef]
2. Kaur, P.; Rajani, N.; Kumawat, P.; Singh, N.; Kushwaha, J.P. Performance and mechanism of dye extraction from aqueous solution using synthesized deep eutectic solvents. *Colloids Surf. Physicochem. Eng. Asp.* **2018**, *539*, 85–91. [CrossRef]
3. Muthuraman, G. Extractive removal of astacryl blue BG and astacryl golden yellow dyes from aqueous solutions by liquid-liquid extraction. *Desalination* **2011**, *277*, 308–312. [CrossRef]
4. Arcon, D.P.; Franco, F.C. All-fatty acid hydrophobic deep eutectic solvents towards a simple and efficient microextraction method of toxic industrial dyes. *J. Mol. Liq.* **2020**, *318*, 114220. [CrossRef]
5. Vijayaraghavan, R.; Vedaraman, N.; Surianarayanan, M.; MacFarlane, D.R. Extraction and recovery of azo dyes into an ionic liquid. *Talanta* **2006**, *69*, 1059–1062. [CrossRef]

6. Shindhal, T.; Rakholiya, P.; Varjani, S.; Pandey, A.; Ngo, H.H.; Guo, W.; Ng, H.Y.; Taherzadeh, M.J. A critical review on advances in the practices and perspectives for the treatment of dye industry wastewater. *Bioengineered* **2021**, *12*, 70–87. [CrossRef]
7. Lawal, I.A.; Dolla, T.H.; Pruessner, K.; Ndungu, P. Synthesis and characterization of deep eutectic solvent functionalized CNT/$ZnCo_2O_4$ nanostructure: Kinetics, isotherm and regenerative studies on Eosin Y adsorption. *J. Environ. Chem. Eng.* **2019**, *7*, 102877. [CrossRef]
8. El-Khalafy, S.H.; Hassanein, M.T.; Abd-Elal, M.F.; Atia, A.A. Oxidation of azo dye Orange II with hydrogen peroxide catalyzed by 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinato-cobalt(II)tetraiodide in aqueous solution. *J. Saudi Chem. Soc.* **2020**, *24*, 520–526. [CrossRef]
9. Rovina, K.; Siddiquee, S.; Shaarani, S.M. Extraction, analytical and advanced methods for detection of Allura Red AC (E129) in food and beverages products. *Front. Microbiol.* **2016**, *7*, 798. [CrossRef]
10. Ren, Q.; Kong, C.; Chen, Z.; Zhou, J.; Li, W.; Li, D.; Cui, Z.; Xue, Y.; Lu, Y. Ultrasonic assisted electrochemical degradation of malachite green in wastewater. *Microchem. J.* **2021**, *164*, 106059. [CrossRef]
11. Brunelle, E.; Le, A.M.; Huynh, C.; Wingfield, K.; Halámková, L.; Agudelo, J.; Halámek, J. Coomassie Brilliant Blue G-250 Dye: An Application for Forensic Fingerprint Analysis. *Anal. Chem.* **2017**, *89*, 4314–4319. [CrossRef] [PubMed]
12. Iqbal, J.; Wattoo, F.H.; Wattoo, M.H.S.; Malik, R.; Tirmizi, S.A.; Imran, M.; Ghangro, A.B. Adsorption of acid yellow dye on flakes of chitosan prepared from fishery wastes. *Arab. J. Chem.* **2011**, *4*, 389–395. [CrossRef]
13. Zhang, S.; Tappe, H.; Helmling, W.; Mischke, P.; Rebsamen, K.; Reiher, U.; Russ, W.L.; Schläfer, L.; Vermehren, P. Reactive Dyes. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2005; ISBN 978-352-730-673-2.
14. Hunger, K.; Mischke, P.; Rieper, W.; Zhang, S. Azo Dyes, 2. Anionic Dyes. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2005; ISBN 978-352-730-673-2.
15. Hunger, K.; Mischke, P.; Rieper, W.; Zhang, S. Azo Dyes, 3. Direct (Substantive) Dyes. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2005; ISBN 978-352-730-673-2.
16. Bien, H.-S.; Stawitz, J.; Wunderlich, K. Anthraquinone Dyes and Intermediates. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2005; ISBN 978-352-730-673-2.
17. Martins, M.A.R.; 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. Tunable Hydrophobic Eutectic Solvents Based on Terpenes and Monocarboxylic Acids. *ACS Sustain. Chem. Eng.* **2018**, *6*, 8836–8846. [CrossRef]
18. van den Bruinhorst, A.; Raes, S.; Maesara, S.A.; Kroon, M.C.; Esteves, A.C.C.; Meuldijk, J. Hydrophobic eutectic mixtures as volatile fatty acid extractants. *Sep. Purif. Technol.* **2019**, *216*, 147–157. [CrossRef]
19. Sas, O.G.; Sánchez, P.B.; González, B.; Domínguez, Á. Removal of phenolic pollutants from wastewater streams using ionic liquids. *Sep. Purif. Technol.* **2020**, *236*, 116310. [CrossRef]
20. Li, Y.; Li, X.; Tang, S.; Yang, Y. Emulsification liquid–liquid micro-extraction based on natural deep eutectic solvent for (triarylmethane) dyes determination. *Chem. Pap.* **2020**, *74*, 3617–3626. [CrossRef]
21. Faraji, M.; Adeli, M.; Noormohammadi, F. Deep eutectic solvent-based dispersive liquid-liquid micro-extraction for extraction of malachite green and crystal violet in water samples prior their determination using high performance liquid chromatography. *Int. J. Environ. Anal. Chem.* **2020**, *102*, 681–689. [CrossRef]
22. Aydin, F.; Yilmaz, E.; Soylak, M. A simple and novel deep eutectic solvent based ultrasound-assisted emulsification liquid phase microextraction method for malachite green in farmed and ornamental aquarium fish water samples. *Microchem. J.* **2017**, *132*, 280–285. [CrossRef]
23. Sadiq, A.C.; Olasupo, A.; Rahim, N.Y.; Ngah, W.S.W.; Suah, F.B.M. Comparative removal of malachite green dye from aqueous solution using deep eutectic solvents modified magnetic chitosan nanoparticles and modified protonated chitosan beads. *J. Environ. Chem. Eng.* **2021**, *9*, 106281. [CrossRef]
24. Sadiq, A.C.; Rahim, N.Y.; Suah, F.B.M. Adsorption and desorption of malachite green by using chitosan-deep eutectic solvents beads. *Int. J. Biol. Macromol.* **2020**, *164*, 3965–3973. [CrossRef]
25. Lawal, I.A.; Klink, M.; Ndungu, P. Deep eutectic solvent as an efficient modifier of low-cost adsorbent for the removal of pharmaceuticals and dye. *Environ. Res.* **2019**, *179*, 108837. [CrossRef] [PubMed]
26. Lee, L.Y.; Chin, D.Z.B.; Lee, X.J.; Chemmangattuvalappil, N.; Gan, S. Evaluation of *Abelmoschus esculentus* (lady's finger) seed as a novel biosorbent for the removal of Acid Blue 113 dye from aqueous solutions. *Process. Saf. Environ. Prot.* **2015**, *94*, 329–338. [CrossRef]
27. Shirzad-Siboni, M.; Jafari, S.J.; Giahi, O.; Kim, I.; Lee, S.M.; Yang, J.K. Removal of acid blue 113 and reactive black 5 dye from aqueous solutions by activated red mud. *J. Ind. Eng. Chem.* **2014**, *20*, 1432–1437. [CrossRef]
28. Zhang, H.; Xing, L.; Liang, H.; Ren, J.; Ding, W.; Wang, Q.; Geng, Z.; Xu, C. Efficient removal of Remazol Brilliant Blue R from water by a cellulose-based activated carbon. *Int. J. Biol. Macromol.* **2022**, *207*, 254–262. [CrossRef] [PubMed]
29. Sirajudheen, P.; Poovathumkuzhi, N.C.; Vigneshwaran, S.; Chelaveettil, B.M.; Meenakshi, S. Applications of chitin and chitosan based biomaterials for the adsorptive removal of textile dyes from water: A comprehensive review. *Carbohydr. Polym.* **2021**, *273*, 118604. [CrossRef] [PubMed]
30. Mo, J.H.; Lee, Y.H.; Kim, J.; Jeong, J.Y.; Jegal, J. Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse. *Dye Pigment.* **2008**, *76*, 429–434. [CrossRef]

31. Toumi, K.H.; Bergaoui, M.; Khalfaoui, M.; Benguerba, Y.; Erto, A.; Dotto, G.L.; Amrane, A.; Nacef, S.; Ernst, B. Computational study of acid blue 80 dye adsorption on low cost agricultural Algerian olive cake waste: Statistical mechanics and molecular dynamic simulations. *J. Mol. Liq.* **2018**, *271*, 40–50. [CrossRef]
32. Luo, X.; Zhang, Z.; Zhou, P.Y.; Ma, G.; Lei, Z. Synergic adsorption of acid blue 80 and heavy metal ions (Cu^{2+}/Ni^{2+}) onto activated carbon and its mechanisms. *J. Ind. Eng. Chem.* **2015**, *27*, 164–174. [CrossRef]
33. Khehra, M.S.; Saini, H.S.; Sharma, D.K.; Chadha, B.S.; Chimni, S.S. Decolorization of various azo dyes by bacterial consortium. *Dye Pigment.* **2005**, *67*, 55–61. [CrossRef]
34. Alkas, T.R.; Ediati, R.; Ersam, T.; Purnomo, A.S. Reactive Black 5 decolorization using immobilized Brown-rot fungus *Gloeophyllum trabeum*. *Mater. Today Proc.* **2022**, *65*, 2934–2939. [CrossRef]
35. Srivastava, A.; Kumar Dangi, L.; Kumar, S.; Rani, R. Microbial decolorization of Reactive Black 5 dye by Bacillus albus DD1 isolated from textile water effluent: Kinetic, thermodynamics & decolorization mechanism. *Helyon* **2022**, *8*, e08834. [CrossRef]
36. Pazarlioglu, N.K.; Urek, R.O.; Ergun, F. Biodecolourization of Direct Blue 15 by immobilized *Phanerochaete chrysosporium*. *Process. Biochem.* **2005**, *40*, 1923–1929. [CrossRef]
37. Saroj, S.; Kumar, K.; Pareek, N.; Prasad, R.; Singh, R.P. Biodegradation of azo dyes Acid Red 183, Direct Blue 15 and Direct Red 75 by the isolate *Penicillium oxalicum* SAR-3. *Chemosphere* **2014**, *107*, 240–248. [CrossRef] [PubMed]
38. Zhuo, R.; Fan, F. A comprehensive insight into the application of white rot fungi and their lignocellulolytic enzymes in the removal of organic pollutants. *Sci. Total Environ.* **2021**, *778*, 146132. [CrossRef]
39. Jadhav, S.U.; Jadhav, M.U.; Kagalkar, A.N.; Govindwar, S.P. Decolorization of Brilliant Blue G dye mediated by degradation of the microbial consortium of *Galactomyces geotrichum* and *Bacillus* sp. *J. Chin. Inst. Chem. Eng.* **2008**, *39*, 563–570. [CrossRef]
40. Khambhaty, Y.; Mody, K.; Basha, S. Efficient removal of Brilliant Blue G (BBG) from aqueous solutions by marine *Aspergillus wentii*: Kinetics, equilibrium and process design. *Ecol. Eng.* **2012**, *41*, 74–83. [CrossRef]
41. Fernández, A.; Deive, F.J.; Rodríguez, A.; Álvarez, M.S. Towards the use of eco-friendly solvents as adjuvants in remediation processes. *J. Mol. Liq.* **2020**, *305*, 112824. [CrossRef]
42. Escudero, N.; Deive, F.J.; Sanromán, M.A.; Álvarez, M.S.; Rodríguez, A. Design of eco-friendly aqueous two-phase systems for the efficient extraction of industrial finishing dyes. *J. Mol. Liq.* **2019**, *284*, 625–632. [CrossRef]
43. Dimitrijević, A.; Jocić, A.; Zec, N.; Tot, A.; Papović, S.; Gadžurić, S.; Vranes, M.; Trtic-Petrovic, T. Improved single-step extraction performance of aqueous biphasic systems using novel symmetric ionic liquids for the decolorisation of toxic dye effluents. *J. Ind. Eng. Chem.* **2019**, *76*, 500–507. [CrossRef]