Decolorization of synthetic textile effluents using methyltrioctylammonium-based DES

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A R T I C L E   I N F O

A B S T R A C T

In light of the escalating environmental challenges posed by the huge generation of wastewater and residues from dyeing processes, addressing water scarcity concerns has become an urgent imperative. This study proposes a sustainable and environmentally friendly solution via liquid–liquid extraction to effectively eliminate dyes from industrial effluents, producing clean and reusable water resources. Methyltrioctylammonium (N_{1888}) based deep eutectic solvents (DESs) show remarkable capabilities as extracting agents. Combined with octanoic and decanoic acids, the bromide and chloride ammonium salts were used to prepare four solvents. They were physically characterized and tested before a wide variety of colorants and synthetic effluents, including real auxiliar agents used in the textile industry. Extraction percentages across all experiments showed an average of 98.39%, reaching a maximum of 99.96% efficiency for the extraction of Reactive Black 5 from aqueous solution, which shows the potential of these solvents to mitigate the environmental impact of dyeing processes.

1. Introduction

Water consumption is the most concerning environmental problem that the textile industry must face. The European Commission has already pointed out the objectives to ensure sustainable production in this field [1]. Water is present in many stages of the manufacturing line, such as bleaching, scouring, or the cornerstone of this study: dyeing [2], resulting in the production of extensive loads of wastewaters. As these operations heavily contaminate the used water, they leave it with displaced pHs, organic matter, and plenty of other pollutants [3]. Colorants stand out for their various negative traits, as they can damage aquatic environments and human life. They cannot be directly dumped [4] due to their poor biodegradability [5].

Various methods have been commonly considered to deal with this issue, like adsorption [6,7], membrane technologies [8,9], biological methods [10], flocculation [11] or oxidation techniques [12]. However, these treatments are generally limited and end up generating more residues (e.g., sludges) or destroying the dye (and thus preventing its recovery). Also, many of them are difficult to implement, have many additional costs, and are limited to only one dye, which is rare in this sector. This problematic only stresses more the need for new pathways to clean these wastewaters.

Liquid-liquid extraction technologies offer the appeal of an easy operation, that usually works well at room temperature, and the possibility of recovering all phases [13]: the used solvent [14], the colorant [15] and the cleaned water [16]. Volatile Organic Compounds (VOCs) have been largely the main choice, until its chemical footprint was deemed too negative, in terms of toxicity towards human health [17] combined with their ample diffusivity [18], that comes with their very high vapor pressure.

Deep eutectic solvents (DESs) are substances, formed by two or more compounds, characterized for having much lower melting points than their original components, thus remaining liquid at lower temperatures [19,20]. These solvents showcase hydrogen bond interactions between its components [21], as they are normally formed by a hydrogen bond donor and a hydrogen bond acceptor. They offer a more environmentally friendly option as separation agents, typically avoiding the use of harmful substances, and leaning towards the use of more inert substances and natural products [22–24] while allowing for easy and efficient elimination of pollutants [25]. Their physical properties can be tuned by carefully choosing the compounds that form them: hydrophobicity can be obtained [26,27], which is a great advantage in liquid–liquid techniques; and viscosity can be also tuned [28], in order to reduce pumping costs and gain processability.

DESs containing ammonium salts [29] are particularly interesting for these treatments as those compounds are widely found in textile

applications. They serve as binding agents between the dyes and the fibers [30], so the interactions that take place in those operations can be harnessed to drive dyes out of wastewaters into the solvents that will be proposed here. In this case, the use of methyltrioctylammonium salts will be explored, as Van Osch et al. [26] reported those compounds as the most stable when in contact with water.

Common effluents from dyeing stages can contain various sulphates, chlorides and ammonium salts [9], which could affect the behavior of the used solvent, by altering the conditions of the operation (e.g. pH) or by direct interaction. These substances are present in auxiliary products used to aid when coloring cloths: fastness-improvement agents, that help binding the colorant to the fibers [30]; crease-prevention agents, that prevent wrinkles from forming, therefore assuring a uniform color in the final product, etc. [31]. One of the aims of this work is to study cases closer to what is found in the industry: both individual and mixtures of dyes, and the presence of various combinations of the aforementioned aiding agents. In all these cases the principal objective will be the same: obtaining a decolorized water.

In order to accomplish these objectives, a series of seven dyes from different classes, types of chromophore groups and ionic charges was selected so as to explore the influence of those parameters in their interaction with the prepared separation agents. The classes represented are acid (Acid Blue 113, Acid Green 25), direct (Direct Fast Brown, Direct Blue 15, Direct Black 19) and reactive (Reactive Black 5, Reactive Red 29). Among this selection, four chromophore groups are represented: azo, diazo, tetrakisazo and anthraquinone. Also, four industrial dye mixtures of undefined composition were included to further test the correct extraction properties of the shown solvents.

The influence of their structure, their concentration in the media or the effect of their combination were studied. Operational variables were optimized (stirring time, centrifugation time, DES:Aqueous phase ratio). The influence of dye concentration was also assayed, as well as effect of the different proposed DESs on the extraction efficiency.

Two auxiliar agents from common operations in the textile industry were added to this investigation in order to create synthetic effluents and study realistic cases: Sarabid DLC is a dye leveler, used to maintain a uniform color across the dyed garment; Biavin BPA is an acrylamide-based crease-prevention agent.

Two synthetic effluents were created, using these agents and mixtures of dyes. The first mixture contained all the individual colorants of defined composition, and the second one was formed with the industrial ones. This way, the functionality of the solvents in industry-like environments is secured, and the influence of all the presented variables is determined.

The solvents combine the mentioned methyltryoctylammonium salts (as a bromide and as a chloride), as hydrogen bond acceptors (HBAs), with two carboxylic acids: octanoic and decanoic acids, as hydrogen bond donors (HBDs). This way both the influence of the anion in the salt (Br⁻ vs. Cl⁻) and the length of the alkyl chain in the acids can be studied. The ratio of each component was chosen according to bibliography [32] so as to ensure the eutectic proportion that leads to the solvent

formation. In total, four DESs were used: $N_{1888}Br$:C8 (1:2), $N_{1888}Br$:C10 (1:2), $N_{1888}Cl$:C8 (1:2) and $N_{1888}Cl$:C10 (1:2).

2. Experimental procedure

2.1. Materials and reagents

The reagents employed in this article are listed in Table S1. Milli-Q water was used to prepare the dye solutions and the synthetic effluents. As stated, the industrial materials have undisclosed compositions as they are commercial products. Additionally, characteristics of the studied dyes are available in Table 1.

2.2. DESs formation and characterization

The DESs employed in this work were synthesized according to the heating and stirring method, commonly described in literature [33–35]. After being formed, they are left to stand in order to assure its stability. Once the DESs are deemed stable and have cooled down, they are characterized. Their melting point, density, viscosity, and water content are measured.

Melting point of the DESs was determined via differential scanning calorimetry (DSC), with a DSC Q 1000 TA instrument, putting samples in hermetic aluminum capsules in an inerting system, with a nitrogen (50 mL min⁻¹) atmosphere. Experimental temperatures ranged from 193.15 K to 343.15 K, with the temperature varying at a rate of 10 K min⁻¹.

Density and dynamic viscosity were measured in a smaller range: from 293.15 K to 343.15 K, with an uncertainty of ± 0.02 K. Both quantifications take place simultaneously in an Anton Paar system that contains a DSA-5000 M digital vibrating tube densimeter (uncertainty of ± 3·10⁻⁴ g cm⁻³) connected to a Lovis 2000/ME ball viscometer (uncertainty of ± 3·10⁻² mPa s⁻¹). Values were then modelled: after a linear equation for density, as seen in Eq. (1); and with the Vogel-Fulcher-Tammann (VFT) law (Eq. (2) for dynamic viscosity, a model that has shown great results for DESs [36,37] and even ionic liquids [38,39].

$$\rho = bT + a \tag{1}$$

$$\eta = \eta_0 e^{\frac{B}{T-T_0}} \tag{2}$$

The behavior of the DES when in contact with water was determined. In a Bruker DPX 400 NMR, samples of the liquid–liquid equilibria (LLE) of the DESs with water (both the organic and the aqueous phases) are evaluated using ¹H Nuclear Magnetic Resonance (NMR) at 400 MHz. Any change during the LLE can be monitored in the spectrum of the organic phase. Observation of the aqueous phase reveals if any component of the solvent has leeched to water. Using a Mettler Toledo C20 Coulometric KF Titrator, the water content of the organic phase is measured after the binary LLE, in order to determine the hydrophobicity of the DES.

DES are saturated with water, by being left stirring in a water:DES

Table 1
Chemical characteristics of the studied dyes.

Dye Name	Abbreviation	Class	FW (g/mol)	Chromophore group	Sodium Salt
Acid Blue 113	AB113	Acid	681.65	Diazo	Disodium
Acid Green 25	AG25	Acid	622.57	Anthraquinone	Disodium
Direct Fast Brown M	DFB	Direct	627.53	Diazo	Disodium
Direct Blue 15	DB15	Direct	992.70	Diazo	Tetrasodium
Reactive Red 29	RR29	Reactive	942.08	Azo	Pentasodium
Direct Black 19	DBk19	Direct	839.77	Tetrakisazo	Disodium
Reactive Black 5	RBk5	Reactive	991.82	Azo	Tetrasodium
Bezaktib Blue*	BB	Mixture	–	–	–
Black Tubantin*	TBk	Mixture	–	–	–
Yellow Tubantin*	TY	Mixture	–	–	–
Tubantin Scarlet*	TS	Mixture	–	–	–

volumetric ratio of 1:1 for at least eight hours, or until titration guarantees that the water content remains constant. This is a cautionary step to ensure that the solvents will not absorb any water while performing the extraction experiments, and therefore that their psychical properties will stay constant.

2.3. Liquid-liquid extraction experiments

To conduct the liquid–liquid extraction experiments, 10 mL Erlenmeyer flasks were used. The components of the mixture of DES and dye aqueous solution were weighted in an AX-205 DeltaRange balance from Mettler Toledo (uncertainty of $\pm 3 \cdot 10^{-4}$ g). The vessels were then placed in a water bath, at 298.15 K, being stirred for different lengths of time at first, and later at the optimized value among those tested. After that, phases are transferred to centrifuge tubes and separated using a Hettich Universal 320 centrifuge at 11000 rpm, again trying different treatment durations in order to optimize processing times first.

Finally, aqueous phases were analyzed via UV–VIS spectrophotometry, in a JASCO V-750 spectrophotometer (uncertainty of $\pm$ 0.002 in abs from 0 to 0.5 and $\pm$ 0.003 in abs from 0.5 to 1, respectively). Before this analysis, the response of the instrument to different concentrations of all the dyes involved is calibrated as a linear equation, their limits of detection (LOD) were found too and were used as a threshold to consider total absence of color.

The extraction efficiency exhibited in a given experiment was calculated with Eq. (3), using the values for the initial concentration (Ci) and the final remaining concentration on the aqueous phase (Cf).

$$E(\%) = (C_i - C_f)/C_i \bullet 100 \tag{3}$$

With all the collected information, the DESs with the best performance and with the best physical properties will be chosen to be used in another series of analysis with synthetic effluents.

2.4. Creation of synthetic effluents. CIE L* a* b* color space

After studying the behavior and characteristics of the proposed solvents, the best one among them is chosen. With the objective of testing it in a variety of more realistic conditions, the mentioned industrial mixtures are introduced. At 250 mg/L, they were extracted under the optimized operational conditions obtained in the previous experimental stages. Starting with an 1:32 DES:Aqueous phase volumetric ratio, this parameter was lowered until the final aqueous phase presented color.

After the trials including these new dyes, the auxiliar agents Sarabid DLC and Biavin BPA were added to create mock wastewaters. Therefore, aqueous phases with similar compositions as industrial sewerage derived from dyeing stages were obtained. This way, the effect of the auxiliar agents in the extraction process can be analyzed. It is important to note that the full composition of these products was not disclosed by the company. Sarabid DLC was added at 1 g·L⁻¹ and Biavin BPA at 0.5 g·L⁻¹, following manufacturer instructions. Dyes were mixed in equal parts for these solutions. Given that there were seven commercial dyes, incorporating their 250 mg/L, a mixture with a concentration of 35.7 mg/L was obtained. This first preparation was named "Synthetic Effluent 1". In the case of the industrial dyes, their individual final concentration was of 62.5 mg/L and was named "Synthetic Effluent 2". This procedure assures a final total dye concentration of 250 mg/L.

The extraction procedure remains the same as the one followed in the preceding section. The only difference comes when observing the results for the experiments where various dyes were mixed, as it is not possible to choose an optimal wavelength, because the UV–Vis spectra show various peaks coming from the different colors overlapping. Therefore, a color space that employs data from all wavelengths was chosen.

CIE 1976 L*a*b* was defined by ISO 11664–4:2008 [40], and provides three coordinates to define the tone and quantity of color:

- 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).
- b* the hue from yellow to blue, again in a scale of −128 (blue) to 128 (yellow).

As the goal is to attain fully decolorized water, the values obtained in the experiments were compared against those coming from uncontaminated water. Theoretically, the CIE L*a*b* coordinates for a transparent liquid would be L*=100, a*=0 and b*=0.

3. Results and discussion

3.1. DESs formation and characterization

The stability of the DES was first observed to assure its correct formation. All prepared DESs resulted stable after letting them rest and cool down. DSC determined the melting points of the solvents and their original components. Results can be consulted in Table S2. The prepared solvents always show a descent in their melting point with respect to their components. No glass transitions or any other phase alterations were discovered in this assay.

¹H NMR confirmed the stability of the solvents. Figs. S1–S4 display the results of the NMR analysis of the organic phases, assigning each signal to the corresponding proton. They do not show any change after reaching liquid–liquid equilibria with water, as identified peaks remain the same, with no changes in the chemical shift. In Fig. S5 an example of the same analysis, but for the aqueous phase, can be observed. Only the peak corresponding to the water signal appears, indicating no leaching of components to the aqueous phase. Only one graph was included as the other three were the same as the one shown. Finally, water content for the DESs after the binary LLE with water are displayed in Table S3. The bromide salt-based DES absorb more water than their chloride counterparts. Decanoic acid-based DES also absorb more water than the ones prepared with octanoic acid. Final water content in decreasing order goes as: $[N_{1888}Br:C10\ (1:2)] > [N_{1888}Br:C8\ (1:2)] > [N_{1888}Cl:C10\ (1:2)] > [N_{1888}Cl:C8\ (1:2)]$.

Density values for the saturated DESs can be observed in Table S4, the parameters of the linear adjustment in Table S5 and the graphical representation in Fig. S6. Similarly, for viscosity, values are included in Table S6, parameters for the VFT adjustment in Table S7 and the graphic representation in Fig. S7. All these thermophysical magnitudes that were measured reproduce accurately the ones reported in the literature [32,41,42]. To the best of our knowledge, there is only published thermophysical data in the same temperature range considered in this study for $N_{1888}Br:C10\ (1:2)$ [43]. A graphical comparison can be seen in Figs. S11 and S12. There was only data at room temperature for some of the other solvents, which are also compared in Table S8.

The most interesting ones were shown by $N_{1888}Cl:C8\ (1:2)$, as its viscosity is the lowest among the studied solvents. For the working temperature of 298.15 K, the dynamic viscosity of $N_{1888}Cl:C8\ (1:2)$ is 51 % lower than its bromide counterpart, and 48 % than when decanoic is the HBD with the same salt. When it comes to density, it is only the second lowest one behind $N_{1888}Cl:C10\ (1:2)$, but their data is very similar and, in both cases, almost 10 % lower than the density of water. The chloride anion influences both density and viscosity, giving lower values than when bromide is present. Similarly, when looking at the alkyl chain length, a longer chain gives the DES a lower density, but a higher viscosity. These values guarantee a sufficient difference in order to separate the organic and the aqueous phases by centrifugation after the extractions take place.

3.2. Optimization of the operative variables

The first experimental phase was centered into reducing processing

times. These experiments were conducted with a selected dye and DES system: Reactive Red 29 and $N_{1888}Cl:C10$ (1:2). For stirring time, it was found that the extraction process is very fast, as the maximum efficiency was reached in only five minutes, and even in quadruple times the extraction percentage did not increase, as seen in Table S9. Same results were achieved after trying different centrifugation times, which are available in Table S10. Consequently, following experiments were performed using five minutes for each operation. Efficiency in these trials was always around 97 %.

3.3. Optimization of the DES:Aqueous phase ratio

With the objective of minimizing the use of solvent, its proportion was optimized. Starting out with a DES:Aqueous phase volumetric ratio of 1:8, based on previous studies, this ratio was lowered for each dye, until the point where color was observed. The selected DES for these assays was once again $N_{1888}Cl:C10$ (1:2). Extraction efficiencies are available in Table S11. In Table 2, the results are visually represented, and as seen the chosen solvent does not behave equally for every dye. Reactive dyes like RR29 and RBk5 showed the worst results, presenting color when the studied ratio was lowered to 1:32. On the other hand, the acid ones were extracted more efficiently, and started showing color after extraction when the ratio reached 1:64. Direct dyes present a more diverse behavior. As the DB15 experiment with a ratio 1:32 presented slight coloration that became more intense as the ratio was further lowered; DBk19 was the one which presented the strongest interaction with the solvent, only remaining in the final aqueous phase at ratio 1:72; DFB did at 1:64. This implies that dye class is not really the defining feature when it comes to the behavior in these trials.

As far as the number of sodium groups in the dye molecule is concerned, a more direct correlation can be drawn. Dyes with four or five sodium units (RR29, DB15, RBk5) were less likely to interact with the organic phase, while the ones that only had two (DFB, AB113, AG25, DBk19) were better extracted with less proportion of solvent.

The lowest ratio where the final aqueous phase showed no color was the one chosen as optimal for the extraction of each colorant, and consequently used in the next experimental phase. This way, DES:Aqueous phase volumetric ratio was always equal to or lower than 1:16.

3.4. Influence of the dye concentration

After optimizing the process for each dye, the treatment was then tested for various dye concentrations between 50 mg/L and 500 mg/L, and for all the presented solvents. It was found that all the tested DESs worked almost exactly the same, and the changes in the efficiency values are negligible. The extraction percentages obtained with the DESs $N_{1888}Br:C8$ (1:2), $N_{1888}Br:C10$ (1:2) and $N_{1888}Cl:C10$ (1:2), are available in the supplementary information, in Tables SI12 to 15. Here, the results for the solvent $N_{1888}Cl:C8$ (1:2) are displayed, in Fig. 1. These results are rather successful as the lowest value presented is 93.77 % for Direct Fast Brown at 50 mg/L, and generally are well above 95 %, always attaining full decolorization.

Final concentration for almost every experiment was under the limits of detection, so their quantified values are essentially the same in the set of data for each dye. In Fig. 2, an example comparing extraction percentages of RR29 for these series of experiments using each dye can be observed. As explained, all solvents produce the same final result.

The distinction in extraction efficiencies among the displayed data are explained exclusively because of the initial concentration. As the final concentration is essentially constant for each dye, Equation (3) produces increasing extraction percentages in each series. All in all, the targeted pollutant was eliminated in every case beyond the limits defined by the method.

3.4.1. Study of the synthetic effluents and dye mixtures

First, when industrial dyes were added, they were extracted individually, using once again the optimized parameters obtained in the previous section: stirring, centrifugation time and $N_{1888}Cl:C8$ (1:2). The first DES:Aqueous phase volumetric ratio considered was 1:16, as all commercial dyes were fully extracted at this value, and then in was lowered to 1:32. Results for these two ratios are found in tables SI16-SI17 respectively. At ratio 1:16, decolorization was obtained for all dyes, with efficiencies between 98.6 % and 99.47 %. In the second series at ratio 1:32, dyes showed color and efficiency dropped, so it was not further lowered. A graphical comparison is displayed in Fig. 3.

Next, the mixture of all commercial dyes was tested, with the addition of Sarabid DLC and Biavin BPA: it was named Synthetic effluent 1. Total decolorization was achieved, in a 1:16 DES:Aqueous phase volumetric ratio, same as with each colorant individually. The ratio of DES was lowered to test the limits of the operation, but the effluents started to show color at 1:32 as expected, just as RR29 did when extracted individually. Then, the CIE L* a* b* values approached the initial ones. These results are presented in Table 3. Reference values of the CIE L* a* b* system for Milli-Q and tap water are presented for comparative purposes.

Moreover, the industrial dyes were tested again, and the selected solvent $N_{1888}Cl:C8$ (1:2) was successful in extracting them. The combination of all mixtures of industrial dyes with the auxiliar agents Sarabid DLC and Biavin BPA was named Synthetic effluent 2. The ratio which obtained total decolorization was again 1:16, and more color was observed progressively as the DES proportion was reduced. These results can be observed in Table 4. Obtained values are in agreement with previous outcomes, as they are in the same range of necessary ratio of solvent, and are considered a success given that the operation is able to maintain its efficiency in the wide array of studied situations.

Table 2

Final color visualization for the extraction for the initial selection of dyes, with $N_{1888}Cl:C10$ (1:2), at various DES:Aqueous phase volumetric ratios. Green indicates total absence of color, yellow a slight hue and red denotes a colored solution.

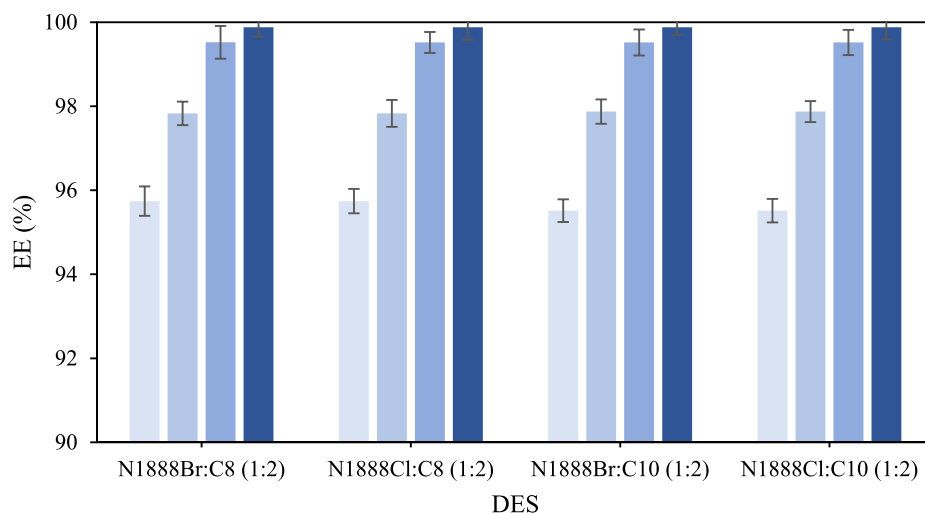|	DES:Aqueous phase volumetric ratio						Number of sodium groups
	1:8	1:16	1:32	1:48	1:64	1:72	
RR29	green	green	red	red	red	red	5
DFB	green	green	green	green	red	red	2
AB113	green	green	green	green	green	red	2
AG25	green	green	green	green	green	red	2
DBk19	green	green	green	green	green	yellow	2
DB15	green	green	yellow	red	red	red	4
RBk5	green	green	red	red	red	red	4

Fig. 1. Extraction efficiencies (%) for the extraction of the selection of commercial dyes, using N₁₈₈₈Cl:C8 (1:2), in the optimized ratio values, for the four studied concentrations of 50 (▢) 100 (▢), 250 (▢) and 500 (▢) mg/L.
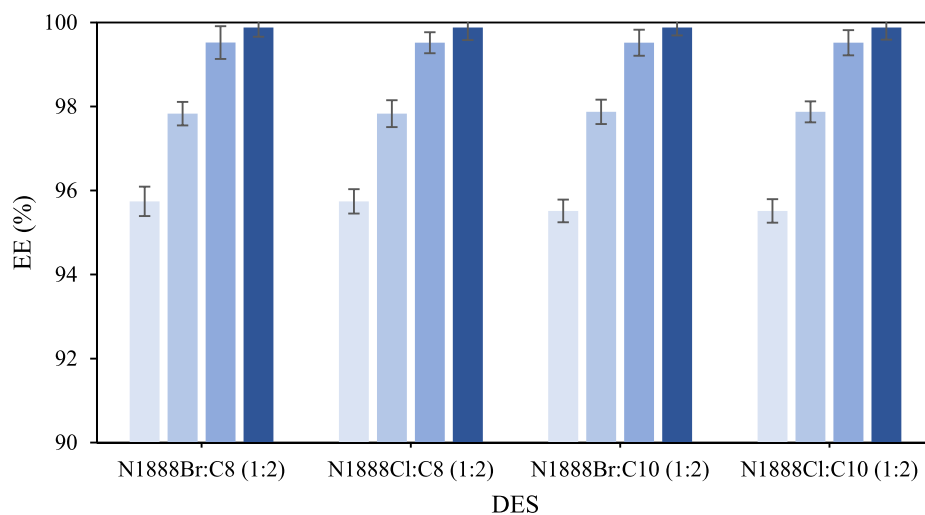

Fig. 2. EE (%) for RR29 extraction with each DES, at 1:16 DES:Aqueous phase volumetric ratio, with initial concentrations of 50 (▢) 100 (▢), 250 (▢) and 500 (▢) mg/L.

4. Conclusions

- Methyltrioctylammonium based DESs are very effective when it comes to extracting dyestuff from aqueous solutions. It is not affected by the presence of most auxiliary agents in the industry, only the binding agent refrained the solvent from working, and these agents will typically not appear in the same effluent as they are used in a separate stage in the process.

- They are able to extract all groups and classes of colorants, and mixtures of them. It also works well with industrial dyes. The lowest extraction efficiency achieved across all instances was 92 %, but presenting total absence of color. Total decolorization was observed for the mixtures and the synthetic effluents.

- The consumption of solvent is very low, allowing to reduce residue volume until one sixteenth of the original volume in the worst case, but reaching a minimum aqueous phase:DES ratio of 72 for some dye classes. In mixtures, the proportion did not have to be increased additionally: it was chosen among the optimized values for individual pigments.

- The extraction percentages remain unchanged among the selection of solvents; both the anion present in the salt and the alkyl chain length seem to only affect physical properties. Physical properties were in fact the deciding factor when it came to determining the best solvent of the ones studied: N₁₈₈₈Cl:C8 (1:2) showed mostly the same performance as its companions, while displaying both lower viscosity (51 %) and density (5 %) than its bromide counterpart.

- To summarize, a group of solvents with high capacities for drawing dyes from textile wastewaters was found, being able to reduce vastly the residue volume and process different colorants or even mixtures of them. This treatment presents a very manageable and competitive option for a concerning problem and would not imply any atmospheric emissions or the use of environmentally hazardous substances.
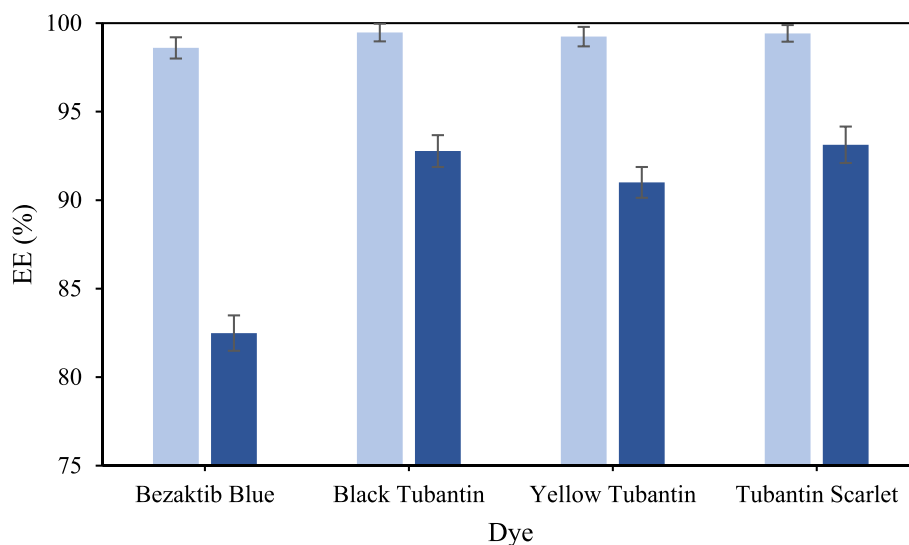
Fig. 3. EE (%) for the extraction of the selection of industrial dyes, with $N_{1888}Cl:C8$ (1:2), starting at 250 mg/L at DES:Aqueous phase volumetric ratios of 1:16 (▢) and 1:32 (▪).

Table 3
CIE L* a* b* values and defining parameters for reference waters, initial Synthetic effluent 1 and final aqueous phases of the extractions with $N_{1888}Cl:C8$ (1:2).

	Ratio	L*	a*	b*
Milli-Q water	–	99,99	0,00	0,00
Tap water	–	99,97	−0,02	0,13
Synthetic effluent 1	–	27.45	−3.87	2.96
Extraction experiments	1:16	99.70	0.10	0.07
	1:32	89.83	−0.02	−0.30
	1:48	78.10	−0.23	−0.89
	1:64	50.90	−3.62	−3.70
	1:72	32.37	−0.17	−5.76

Table 4
CIE L* a* b* values and defining parameters for reference waters, initial Synthetic effluent 2 and final aqueous phases of the extractions with $N_{1888}Cl:C8$ (1:2).

	Ratio	L*	a*	b*
Milli-Q water	–	99,99	0,00	0,00
Tap water	–	99,97	−0,02	0,13
Synthetic effluent 2	–	0.32	0.55	0.18
Extraction experiments	1:16	98.39	−0.13	1.29
	1:32	90.50	−0.02	1.23
	1:48	78.75	0.17	1.60
	1:64	14.28	1.85	3.06
	1:72	9.06	2.47	2.97

CRediT authorship contribution statement

Óscar Martínez-Rico: Investigation, Validation, Formal analysis, Writing – original draft. **Andrés Asla:** Investigation, Validation, Formal analysis, Writing – original draft. **Begoña González:** Supervision, Funding acquisition, Project administration, Resources. **Ángeles Domínguez:** Supervision, Conceptualization, Funding acquisition, Resources.

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.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2023.109600.

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