

Review

Perspectives of Using DES-Based Systems for Solid–Liquid and Liquid–Liquid Extraction of Metals from E-Waste

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Abstract: In recent years, the linear economic model and global warming have shown that it is necessary to move toward a circular economic model. In this scenario, the recycling of waste electrical and electronic equipment (WEEE) with green processes is one of the pending tasks; thus, in the present review, advances in the solid–liquid and liquid–liquid extraction processes, processes among the most important for the recovery of metals from ores or WEEE, with green solvents such as deep eutectic solvents (DES) are presented and analyzed, identifying the present and future challenges. To date, most articles focused on one of the processes, be it solid–liquid or liquid–liquid extraction, while few reports included the entire hydrometallurgical process, which could be due to heterogeneity of the WEEE, a characteristic that influences determining the leaching kinetic and the leaching mechanisms. A deeper understanding of the phenomenon would help improve this process and the next stage of liquid–liquid extraction. This also leads to the fact that, at the liquid–liquid extraction stage, most articles considered synthetic pregnant leach solutions to evaluate each of the variables, whereas the stripping of the ions and the recycling of the DESs in continuous processes is a challenge that should be addressed in future work. From the analysis, for WEEE leaching, it was identified that acid DESs are those achieving the best extraction percentages in the leaching of copper, lithium, and cobalt, among others, where the most studied hydrogen bond acceptor (HBA) is choline chloride with an acid (e.g., citric or lactic acid) as the hydrogen bond donor (HBD). For the liquid–liquid extraction of ions is a greater variety of HBAs (e.g., lidocaine, trioctylphosphine oxide and triphenyl phosphate) and HBDs (e.g., decanoic acid, thenoyltrifluoroacetone, and benzoyltrifluoroacetone) used; however, studies on the extraction of cobalt, lithium, copper, and nickel stand out, where the pH and temperature parameters have great influence.

Keywords: deep eutectic solvents; leaching; solvent extraction; e-waste; green solvents



Citation: Dias, R.M.; da Costa, M.C.; Jimenez, Y.P. Perspectives of Using DES-Based Systems for Solid–Liquid and Liquid–Liquid Extraction of Metals from E-Waste. *Minerals* **2022**, *12*, 710. <https://doi.org/10.3390/min12060710>

Academic Editor: Chiharu Tokoro

Received: 22 April 2022

Accepted: 31 May 2022

Published: 2 June 2022

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1. Introduction

Metals are one of the most important classes of materials in modern society [1]. Over the years, they have been widely applied in many areas, including electronic devices, equipment, cell phones, batteries, and computers [2]. The growing necessity of these nonrenewable materials in such applications has led to the continuous exploitation of mineral resources, reducing the availability of these metals in nature [3]. The great demand for metals may cause an increase in their extraction and, consequently, may lead to an exhaustion of their supplies on Earth [1,4]. Some researchers have suggested that the available supply of a range of metals will run out within 50 years or less [4]. In addition, the uncontrolled use of metals and the improper disposal of electronic waste (e-waste) may cause several environmental problems, including water pollution, soil contamination, and health issues in living organisms due to metal accumulation [2].

Therefore, it is urgent to seek sustainable alternatives to recover and reuse metals in e-waste. Different techniques have been used to perform this recovery; for example, to recover high-purity alloys, the pyrometallurgical process is one of most used processes and consists of smelting the wastes after dismantling. However, this process requires high temperatures to achieve the metal separation, being an energy-intensive process. Furthermore, the generated slags often still contain metals of interest, leading to lower recovery rates than other techniques. On the other hand, with hydrometallurgical processes, higher recovery rates can be achieved with lower energy consumption, which also makes it possible to treat low-concentration aqueous solutions. However, more research is needed to reduce the environmental impact of hydrometallurgical processes [5–7]. The hydrometallurgical process for the treatment of e-wastes consists of well-defined stages. The first steps consist of dismantling and grinding the printed circuit boards (PCB), spent batteries, or other electric parts; then, plastic scraps and ferrous elements are separated with electric and magnetic separators, respectively, with the valuable metals contained mainly in the smaller fractions [8]. The metals are then released into an aqueous solution through the leaching process, where the conventional process comprises the use of acid leaching followed by leaching using cyanide, hydrogen peroxide, halides, thiosulfate, or thiourea. Li et al. [9] reported that the use of mineral acids such as hydrochloric acid has a great contribution to the life-cycle analysis of the processes. Furthermore, for e-waste recycling, Iannicelli-Zubiani et al. [10] estimated that the use of nitric acid contributed 40% to 80% to the impact of the process. Despite the fact that this process can be successfully applied to metal recovery, the use of toxic and dangerous solvents minimizes the environmental appeal and leads us to search for new strategies.

The next step is liquid–liquid extraction or solvent extraction to purify and concentrate the metals. This consists of the recovery of metal ions from the aqueous phase using an organic phase, immiscible with water [11,12]. Usually, the organic phase is made of an extracting molecule (chosen from various families such as organophosphorus compounds, quaternary amines, and malonamides) and an organic diluent (usually hydrocarbons such as kerosene) [13]. Both immiscible phases, one aqueous and one organic, are mixed to amplify the contact area and improve mass transfer; then, they are separated. After that, the organic phase, through a selective extraction process, contains the metal ion of interest, leaving the other ions in the aqueous phase depending on their different affinity to the organic phase [12]. Sometimes, modifiers are added to the organic phase, which increase the solubility of the organic extractant and metal in the organic phase. They improve the speed of phase separation and metal extraction, favoring coalescence. The most commonly used modifiers are long-chain alcohols (tridecanol) and esters [14]. Although solvent extraction is a mature and widely used technology with numerous advantages such as low operational costs, the use of organic solvents and the extraction of molecules in large quantities contribute to the environmental impact of the process, due to their volatility, types of hydrocarbon chains, etc. [15,16]. The use of organophosphate extracting molecules (and hydrocarbon solvents to a lesser degree) for the processing of rare earth minerals has been shown to have a great impact on many environmental aspects (eutrophication, acidification, climate change, land use, ecotoxicity, ozone, etc.) [17].

Recently, the use of DESs to perform the leaching step has attracted the attention of scientists as a new strategy to avoid the application of hazardous solvents and to achieve more sustainable processes [18–20]. DESs have been investigated in a wide range of areas since many of them are considered green solvents, are not environmentally toxic, present low vapor pressure, have high thermal stability, have a high ability to extract organic and inorganic compounds, and have tunable physicochemical properties [21–24]. Moreover, they are easily prepared, usually by mixing the reactants and slightly heating their mixtures [25]. Their easier preparation makes them cheaper than other alternative solvents, such as ionic liquids (ILs).

DESs are liquid mixtures prepared by mixing a combination of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) at various molar mixing ratios to form a

low-melting-point eutectic mixture. Their components are capable of establishing hydrogen bond interactions, which lead to significant negative deviations to thermodynamic ideality in the liquid state from that predicted for an ideal mixture [24,26]. Quaternary ammonium salts, mostly cholinium chloride, are the most commonly used HBA to prepare DESs because of their biodegradability and low toxicity. Regarding the HBD, different classes of compounds have been used, such as alcohols, urea, carboxylic acids, and sugars [24,27]. They can be classified into five types according to the compounds they are made from: alkylammonium halide salt + metal halide (type I), alkylammonium halide salt + metal halide hydrate (type II), alkylammonium halide salt + HBD (type III), metal halide hydrate + HBD (type IV), and HBD + HBA (type V) [28].

Additionally, some DESs are made entirely from natural products (called natural deep eutectic solvents, NADESs) [29], and their use could greatly improve the environmental aspects of process design. These new eutectic solvents have enormous potential in various fields, and some reviews can be found for some of their main applications, e.g., for carbon dioxide capture, water purification, and extraction of organic compounds [13,24,30–37]. However, the use of DESs in solid–liquid and liquid–liquid extraction for the recovery of metals from e-waste has not yet been reviewed, while these chemicals have shown promising results in various aspects of these processes. For example, DESs can solubilize metal salts and oxides, making it possible to use them for leaching metals from secondary resources to replace conventional acid leaching routes [38,39]. Additionally, the possibility to use hydrophobic DESs for the solvent extraction of metal ions from aqueous solutions was studied for the first time by Tereshatov et al. [40]. This could constitute a step toward the design of cleaner processes of leaching and solvent extraction, since it would avoid the use of large amounts of acids and hydrocarbon diluents while using low-cost chemicals, low vapor pressure, and high thermal stability, among other features. In this review, the aim is to provide an overview of recent advances in the use of DESs in solid–liquid and liquid–liquid extraction processes, specifically, for the leaching and liquid–liquid extraction of metal ions. Additionally, the advantages and disadvantages of using DESs for these processes are discussed.

2. Discussion

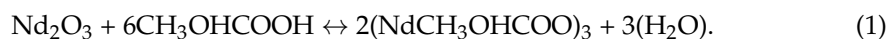
2.1. Leaching of Metals with DESs from E-Waste

Leaching is a process widely used in extractive metallurgy where ore or e-waste is treated with basic or acid solutions to dissolve the valuable metals, whereas some impurities remain insoluble. Once the pregnant leach solution (PLS) is obtained, several purification and concentration processes can be used to recover the metals, such as solvent extraction, ion exchange, and crystallization. Abbott et al. [25] reported, for the first time, the solubility of ZnO, CuO, and Fe₃O₄ in three DESs (1 ChCl:1 malonic acid, 1 ChCl:1 oxalic acid, and 1 ChCl:2 phenylpropionic acid) at 50 °C. In another work, Abbott et al. [26] studied the solubility of metal oxides in ChCl-based DESs, reporting that malonic acid-based DESs exhibited higher solubility than the corresponding liquids based on urea and ethylene glycol. One of the peculiarities of these results is that the solubility of each metal oxide depends on the DES used, which could be used to selectively leach the metals and avoid the costly separation process to purify or separate each metal from the aqueous solution. In this context, solvometallurgy, the term used to describe the extraction of metals from ores, e-waste, or other sources using nonaqueous solutions (or ones with low water content) [41], is an emerging area with several advantages compared with the hydrometallurgical process, in which DESs have a promising future. Table 1 summarizes the DESs used as leaching agents for several e-wastes, and Figure 1 shows their structures.

Table 1. Deep eutectic solvents (DESs) used for the leaching of metals from e-waste.

Materials Leached	Metals Leached/ Oxides Dissolved	DES		Noticeable Results	References
		HBA	HBD		
Used NdFeB magnets	Fe, Nd, Dy, Pr, B, Gd, Co	ChCl	Lactic acid	Leaching yield > 80% 24 h; 70 °C	[18]
Spent LIBs	Li, Co	ChCl	EG	>90% of Li and Co leached; ≥24 h; >150 °C	[39]
Spent LIBs	Co	ChCl	Citric acid	98% Co; 1 h, 40 °C, solid-liquid ratio of 20	[19]
Spent LIBs	Li, Co	ChCl	Urea	95% of Li and Co 12 h leaching at 180 °C	[20]
Spent fluorescent lamps	Y ₂ O ₃ :Eu ³⁺ (YOX), (Sr,Ca) ₁₀ (PO ₄) ₆ (Cl,F) ₂ :Sb ³⁺ ,Mn ²⁺ (HALO)	ChCl	Levulinic acid	~48% YOX, ~30%HALO; H ₂ O vol% = 30; 80 °C; L/S = 10; 70 h and 500 rpm	[42]
Cathode powder of Ni-MH spent batteries	Ni, Co	ChCl	Urea	84.1% Ni; 53.1% Co; 24 h leaching at 95 °C	[43]
Lithium-ion battery wastes	Mn, Ni, Li, Co, Cu, Al, Fe	ChCl	EG	Fresh DES: ~90% Co (24 h, 180 °C), ~85% Mn (72 h, 180 °C), 85% Cu (24 h, 90 °C). Recycled DES: 95% Co (24 h, 180 °C), 70% Mn (24 h, 180 °C), 98%Cu (24 h, 180 °C)	[44]
Spent silver oxide batteries	Ag	AcChCl	Urea	93% Ag (24 h, 70 °C)	[45]

Leaching metals from waste electrical and electronic equipment (WEEE) has been recently studied. Tran et al. [39] reported that a ChCl:EG DES can extract metals from LIB cathode materials, with leaching efficiencies of 99.3% for Co and Li. Time and temperature played an important role in the high metal extractions with high temperature leading to high leaching rates. The DES color turned blue after leaching, which was attributed to the formation of the CoCl₄²⁻ anion. Therefore, the leaching of metals seems to occur by coordination with the chloride from ChCl (HBA). Interestingly, the cobalt(III) from the battery was reduced to cobalt(II), possibly by EG (HBD), and this phenomenon seems to promote leaching. The presence of an oxygen acceptor in the eutectic solution facilitates the breaking of metal oxide bonds, which promotes digestion of the oxide [26]. Despite the high leaching yields, note that leaching kinetics is slow (minimum 24 h) and high temperatures (>150 °C) are needed, whereas leaching the same material with nitric acid only takes 2 h and lower temperatures (65 °C) to obtain similar leaching yields [46]. Riaño et al. [18] reported similar kinetics for the leaching of rare earths and other metals from NdFeB magnets. High leaching rates were obtained after 24 h of leaching at 70 °C. Leaching rates were much higher when lactic acid was used as the HBD instead of EG or urea. This high solubility of the oxides in the ChCl:lactic acid DES can be explained by the reaction of the protons in the lactic acid with the oxides to form water and the probable coordinating abilities of lactic acid and choline helping dissolution, according to the following equation:



The formation of a complex between neodymium and deprotonated lactic acid frees the metal from the oxide. Therefore, the use of an acid DES is favorable for metal leaching [47].

HBAs

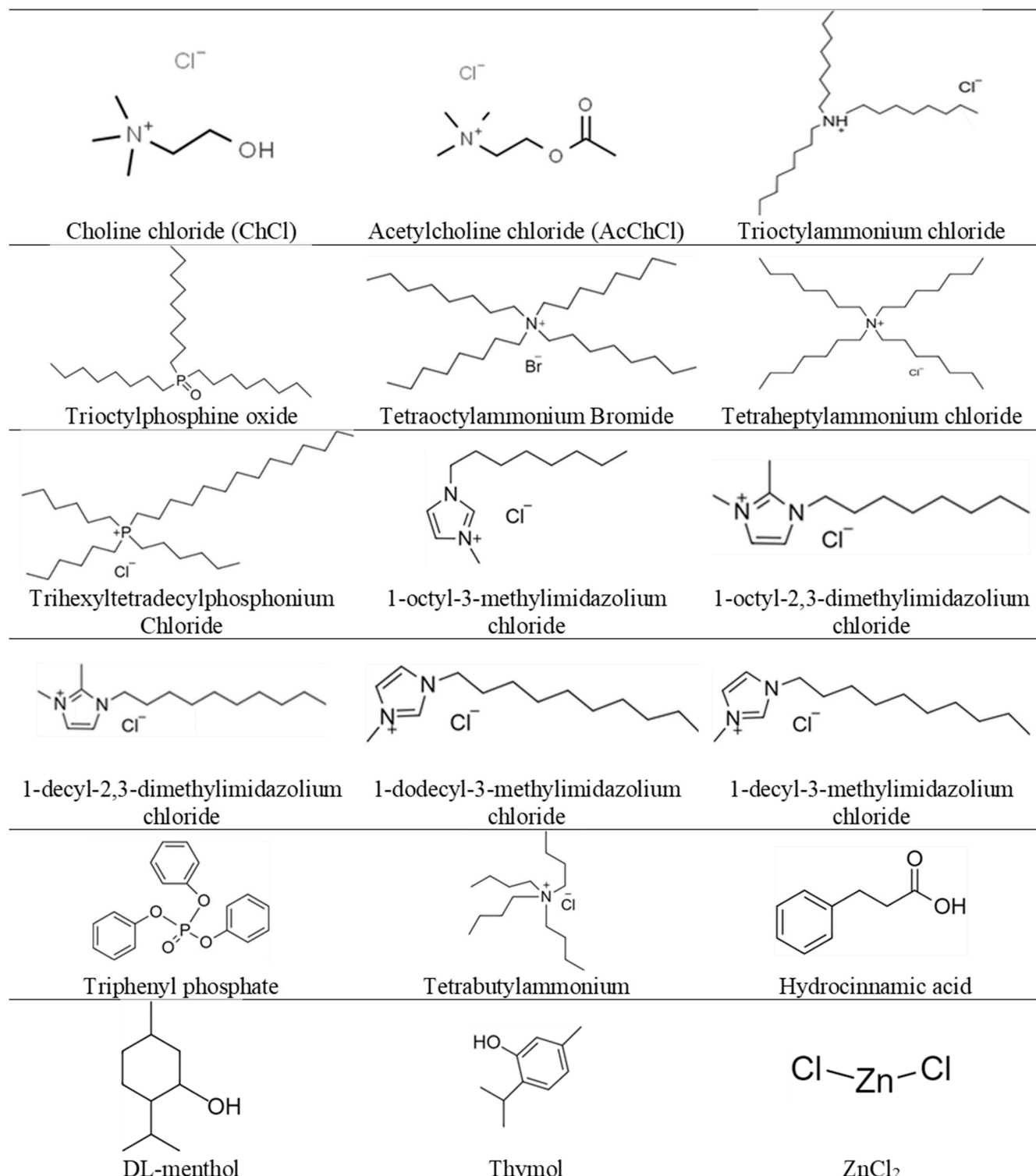


Figure 1. Cont.

HBDs

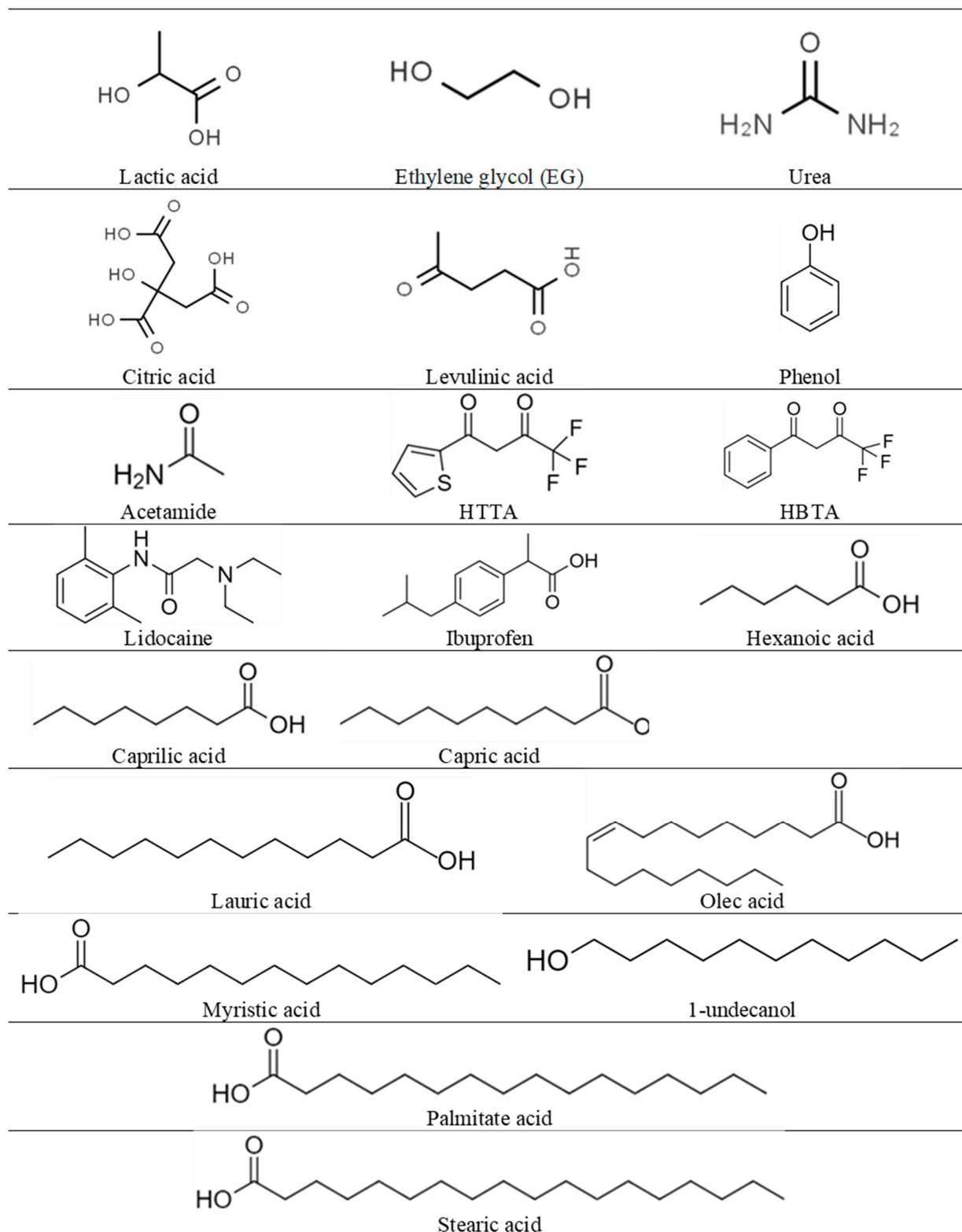


Figure 1. Structure of the hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) used in the synthesis of DESs for metal leaching and liquid–liquid extraction.

Moreover, Wang et al. [20] proposed a novel, simple, and robust experimental method to identify suitable DESs for recycling spent LIBs. According to the electrochemical principle, it could quickly determine the reduction power of DESs, obtaining interesting results such as the ChCl:urea DES for the extraction of Li and Co with efficiencies of up to 95% from used LIBs at 180 °C and a reaction time of 12 h. Kinetic experiments revealed that the solution diffusion and electron diffusion through the DES controlled the Li and Co extraction. However, Peeters et al. [19] obtained better results, reporting that, for the DES formed by ChCl and citric acid, reaching 99.6% Co extraction at room temperature and 4 h from spent LIBs is possible. One of the most interesting findings is that Cu was the most effective reducing agent for cobalt(III), thus requiring no additional reducing agents or prior separation steps. Moreover, the speciation study of the PLS revealed the prevalence of chloro complexes due to the interaction with the chloride anion from ChCl. Then, this proposed process was compared with a conventional hydrochloric acid leaching process, concluding that the most important advantage of leaching with DES is not generating gaseous chlorine. Extraction and stripping stages were also studied, and, although LIX 984 was used in the extraction stage, the final results (81% total recovery yield of Co) are promising. In the same line of Co recuperation from LIBs, Schiavi et al. [44] reported a method for the selective recovery of Co. The DES used was formed by ChCl and EG and reached around 90% Co extraction at 180 °C and 24 h, in contrast to Ni extraction that reached only 10%. Then, Co was recovered as cobalt oxalate, which was employed to produce lithium cobalt oxide cathode material. This cathode material had a discharge capacity of 150 mA·h·g⁻¹ and a capacity retention between 10 and 100 galvanostatic cycles of 83%. Subsequently, the DES was recycled and reused as feed to the process, with similar results to unused DES, which demonstrates the potential use of DESs in a complete hydrometallurgical process.

Pateli et al. [42] studied the recovery of rare-earth elements from lamp phosphor waste. They analyzed different DESs to determine the solubility of individual phosphors, among which the DES formed by ChCl and levulinic acid showed low solubility of the HALO phosphor (Sr,Ca)₁₀(PO₄)₆(Cl,F)₂:Sb³⁺,Mn²⁺ and high solubility of the YOX phosphor (Y₂O₃:Eu³⁺). This DES was also compared with pure levulinic acid, and the results showed similar leaching behaviors, indicating that the proton activity is more important than the chloride as a metal ligand. Then, the leaching process with this DES and levulinic acid was optimized and compared with the leaching with hydrochloric acid and the ionic liquid betainium bis(trifluoromethylsulfonyl)imide; the results showed that hydrochloric acid is not selective, and, despite the similar selectivity of the ionic liquid to levulinic acid, it costs more, and levulinic acid was more suitable than the DES for the selective recovery of YOX.

The analysis of these studies shows that the temperature and time of leaching with DES are critical parameters for comparison with the values used in the traditional leaching processes. One alternative to reduce the temperature and time for leaching would be the DES formed by citric, oxalic, or lactic acid; considering the physicochemical properties of the mixture is also important since diffusion mechanisms usually govern the mass transfer. Another challenge is the extraction or recovery of the ions from the DES after the leaching since most of the alternatives reported are traditional processes of solvent extraction that use commercial extractants or crystallization by precipitation with salting or drowning-out agents. Although the complementarity of these processes with DES-based processes is still attractive from an environmental point of view, the leaching mechanisms are a subject for further study even with the challenge of working with heterogeneous solids such as WEEE. A deep knowledge about leaching mechanisms would allow optimizing the process with DESs.

2.2. Liquid–Liquid Extraction of Metals with DESs from Liquid Samples

Another application of DESs concerning the recovery of metals is their use as a medium for liquid–liquid extraction purposes. Unlike the leaching process, in which WEEE is used for testing, a few reports used PLS even with synthetic solutions for the liquid–liquid

extraction process. Thus, in this section, the review is extended to the partitioning of ions from different sources. Regarding this approach, many authors have reported the ability of DESs to extract metals from samples which originally presented high contents of these materials (Table 2) [48–53]. Generally, the initial solution containing the target metal ions is mixed with a DES phase; due to them being immiscible, they form two liquid phases: a DES-rich phase, which preferentially contains the most species of metal ions, and another liquid phase, usually containing water as the major compound, which may be exhausted of metal ions. This strategy is based on the affinity of DESs for the target metal ions and on the hydrophobic nature of some DESs, aiding in the two-phase system formation [13]. Figure 1 shows the structures of the HBAs and HBDs.

Table 2. DESs used for the liquid–liquid extraction of metals from solutions.

Medium of Extraction	Metals Extracted	DES		Noticeable Results	Reference
		HBA	HBD		
Hydrochloric or oxalic acid medium	Indium	Tetraheptylammonium chloride, or DL-menthol	Decanoic, lauric, or oleic acids, or ibuprofen	(C ₇ H ₁₅) ₄ NCl–ibuprofen in 0.01 M oxalic acid resulted in distribution ratio ^a of 1700	[40]
HCl medium	Li(I), Co(II), Ni(II), Mn(II), and Fe(III)	Triethylmethylammonium chloride (Aliquat 336)	L-menthol	99% recovery rates for each of Fe(III), Mn(II), and Co(II), with 3:7 Aliquat	[53]
Non-buffered water	CoCl ₂ , MnCl ₂ , ZnCl ₂ , CuCl ₂ , NaCl, KCl, and LiCl Chlorides	Lidocaine	Decanoic acid	336/L-menthol molar ratio Distribution coefficient ^b close to unity for Co, Fe, Mn, Ni, Zn, Cu using Decanoic acid and Lidocaine (2:1)	[54]
Food samples	Se(IV) and Se(VI)	Choline chloride, tetrabutyl ammonium chloride, or trioctyl ammonium chloride	Phenol or decanoic acid	>97% recovery of Se(IV) can be extracted using ChCl:Phenol	[50]
Blood samples	Mercury	1-Decyl-2,3-dimethylimidazolium chloride, 1-octyl-2,3-dimethylimidazolium chloride, 1-octyl-3-methylimidazolium chloride, 1-dodecyl-3-methylimidazolium chloride, or 1-decyl-3-methylimidazolium chloride	1-Undecanol	Relative recovery of Hg from blood samples were over than 90%	[48]
Acid-digested cosmetic samples	Cd and Pb	ZnCl ₂	Acetamide	More than 97% of extraction recovery of both Pb and Cd from the standard samples	[49]
Aqueous nitric acid	Uranyl ions	Trioctylphosphine oxide (TOPO)	Phenol	Complete extraction of uranyl species	[55]
Model brine solution containing high concentration of alkali metals	Lithium	Trioctylphosphine oxide (TOPO) or triphenyl phosphate (TPP)	Thenoyltrifluoroacetone (HTTA), or Benzoyltrifluoroacetone (HBTA)	The use of HCl solution was capable of stripping > 90% of Li from the metal-loaded HTTA:TOPO	[51]
HCl medium	Platinum-group metals (PGMs) and transition metals (TMs) Cu, Fe, Cr, Ni, and Co	TOPO, thymol, or hydrocinnamic acid	TOPO, or capric acid	Distribution coefficients ^c equal to 1169, 830, and 25 for Fe ³⁺ , Pt ⁴⁺ , and Pd ²⁺ using TOPO + CA	[56]
Aqueous solutions	trace pertechnetate (^{99m} TcO ₄ ⁻)	Trihexyltetradecylphosphonium, [P _{14,666} ⁺] or Tetraoctylammonium, [N ₈₈₈₈ ⁺]	Hexanoic or decanoic	Extraction > 99% using equivolume mixtures of DES to aqueous phase containing common anions (Cl ⁻ and NO ₃ ⁻)	[52]
Aqueous solution	K ₂ Cr ₂ O ₇ , CuCl ₂ ·2H ₂ O, Cu(NO ₃) ₂ , NiCl ₂ , Ni(NO ₃) ₂ , CrCl ₃ ·6H ₂ O and K ₄ [Fe(CN) ₆]	Tetrabutylammonium chloride (TBACl)	Decanoic acid	Extraction efficiency was higher than 99%	[57]
Mildly acidic solutions	Extraction of Cu(II) and its separation from other transition metals (Co(II) and Ni(II))	Menthol or thymol	Long-chain carboxylic acids: C _n H _(2n+1) OOH (n = 8, 10, 12, 14, 16, 18)	Cu(II) extraction efficiency close to 100% was achieved using thymol + capric acid HES and 0.1 M sodium salt	[58]

^a $D = \frac{C_{\text{organic phase}}}{C_{\text{aqueous phase}}}$, where D = distribution coefficient and C = concentration; ^b $D = \frac{C_{\text{ion},0}^{aq} - C_{\text{ion},1}^{aq} \left(\frac{V_1^{aq}}{V_0^{aq}} \right)}{C_{\text{ion},0}^{aq}}$, where D = distribution coefficient, $C_{\text{ion},0}^{aq}$ and $C_{\text{ion},1}^{aq}$ are the ion concentrations before (0) extraction and after (1) extraction, and V_0^{aq} and V_1^{aq} are the volumes of the aqueous phase before and after extraction; ^c $D = \frac{C_{\text{HES phase}}}{C_{\text{aqueous phase}}}$.

To our best knowledge, the first authors who described the ability of DES to extract metals from aqueous solutions were Tereshatov et al. [40] and van Osch et al. [54], in 2016. Tereshatov et al. [40] extracted indium from hydrochloric or oxalic acid medium into quaternary ammonium and menthol-based mixtures containing carboxylic acids. The authors determined the indium distribution ratio dependency on the aqueous hydrochloric acid concentration (10 M to 4×10^{-4} M HCl), and the metal was extracted applying hydrophobic ammonium-based $(C_7H_{15})_4NCl$ -decanoic acid, $(C_7H_{15})_4NCl$ -oleic acid, or $(C_7H_{15})_4NCl$ -ibuprofen mixtures. The highest extraction was found in 6 M, and the differences in the curves' shapes were due to the indium speciation. They also studied indium extraction into menthol-based DESs from HCl aqueous solutions, and the extraction was inefficient in the range of 0.01–10.2 M HCl. However, the curve reached its maximum at 1×10^{-3} M HCl, a region in which the extraction improved significantly. Tereshatov et al. [40] also investigated the extraction of indium from oxalic acid aqueous solutions. Concerning the results, the tetraalkylammonium-based mixtures increased the indium extraction as oxalic acid concentration increased up to 0.05 M, and the $(C_7H_{15})_4NCl$ -ibuprofen showed a maximum distribution ratio of 1700 in oxalic acid medium (0.01 M). In contrast, the indium extraction ratio into the menthol-based DES was reduced when the oxalic acid concentration increased. This opposite behavior was associated with a different mechanism of indium extraction. The loading of stable indium was also investigated to determine the capacity of the organic phase. The results revealed that indium extraction into tetraalkylammonium-based and menthol-based DES was independent of metal concentration in the aqueous phase in the range of up to 1×10^{-2} M and 1×10^{-4} M, respectively. The authors concluded that the ion pair formation process was predominant in indium extraction into the tetraalkylammonium-based DES, and that the $(C_7H_{15})_4N^+]_2 [InCl_5^{2-}]$ complex was formed. The last step concerning the Tereshatov et al. [40] study was the back-extraction of indium from the $(C_7H_{15})_4NCl$ -ibuprofen and $(C_7H_{15})_4NCl$ -oleic acid mixtures in hydrochloric and oxalic acid medium. According to the results reported by the authors, Indium was successfully back-extracted from $(C_7H_{15})_4NCl$ -oleic acid into 0.2 M HCl medium; however, Indium back-extraction was unsuccessful from either mixture into oxalic acid or $(C_7H_{15})_4NCl$ -ibuprofen into HCl.

Van Osch et al. [54] developed another pioneer study, in which they demonstrated for the first time the possibility of using hydrophobic DES to remove metal ions from non-buffered water. The DESs applied were prepared with decanoic acid (DA) and lidocaine (Lid) in 2:1, 3:1, and 4:1 molar ratios. The metals tested were cobalt ($CoCl_2$), manganese ($MnCl_2$), zinc ($ZnCl_2$), copper ($CuCl_2$), sodium (NaCl), potassium (KCl), and lithium (LiCl) as chlorides. The distribution coefficients of the metal ions over the water and the DES phases were determined, showing that most metal cations (Co, Fe, Mn, Ni, Zn, and Cu) were extracted with high efficiencies (distribution coefficients close to the maximum). The experiments with only single metal salts in the water phase showed high distribution coefficient values for cationic metal ions, except for K^+ , due to the preference of fatty acids to bind with transition metals and not with alkali metals. The authors mentioned small precipitations in the water phase after extraction of Fe^{2+} , due to the higher pH that induces its precipitation [54]. The DES phase formed a gel/solid like phase after Mn^{2+} extraction, which resulted from the interaction of the Mn^{2+} with DES compounds. The extraction of K^+ was more efficient with DESs prepared with higher DA contents. This effect might be explained by the increase in the hydrophobic behavior of the DES as DA proportions increase. Overall, extraction of transition metals (Co, Fe, Mn, Ni, Zn, and Cu) exhibited high distribution coefficient values, while alkali metal ions (Na, Li, and K) showed low distribution coefficients. Regarding the extraction of chloride, the distribution coefficients were small, which may be explained by the interaction of the protonated Lid with chloride anions: during the interactions, Lid hydrochloride was formed, which is more water-soluble than Lid. The DES/water mass ratio was varied to investigate its influence on the distribution coefficient of Co^{2+} . The results showed that, even for low DES/water

mass ratios (<0.1), distribution coefficient values were ≥ 0.796 . The authors demonstrated that regenerating the DES used for extraction using sodium oxalate ($0.1\text{ M Na}_2\text{C}_2\text{O}_4$) was feasible; however, efficient use was only possible for the DESs with a higher DA-to-Lid ratio (3:1 and 4:1).

In 2017, Panhwar et al. [50] reported a study in which they five 5 DESs using choline chloride (ChCl), phenol (Ph), trioctyl ammonium chloride (TOACl), and tetrabutyl ammonium chloride (TBACl) at different molar ratio, and tested them for separation and enrichment of selenium species (Se(IV) and Se(VI)) from food samples. The DES were prepared using ChCl:Ph at three molar ratios equal to 1:1, 1:2, and 1:3, while TBACl:DA and TOACl:DA were prepared at a molar ratio equal to 1:2. For the extraction, an ultrasound-assisted liquid-phase microextraction (UALPME) based on DES was tested. The UALPME-DES method was applied to determine total Se in food samples: cow milk, mixed fruit juice, orange juice, grapefruit, sheep milk, yogurt, honey, egg, canned fish, and edible mushroom. Many factors were considered to achieve the optimized conditions. According to the results, pyrolysis temperature was $1100\text{ }^\circ\text{C}$, whereas the atomization temperature to determine the Se(IV) concentration was $2250\text{ }^\circ\text{C}$. The optimum signal integration acquired showed at 3.5 s. They chose the DES based on their ability for Se extraction from standard sample solutions. The best DES results showed more than 97% recovery of Se(IV) extracted when ChCl:Ph was applied, and the molar ratio of 1:3 was the most effective for the optimum extraction of Se(IV). The volume of selected DES was checked in the range of 0.2–1 mL, and 0.5 mL was selected since the quantitative recovery of Se(IV) was obtained at this condition. The effect of 3,3'-diaminobenzidine (DAB) concentration on the extraction recovery of the Se-DAB complex was investigated in the concentration range of $0.002\text{--}0.005\text{ mol}\cdot\text{L}^{-1}$ for the extraction of Se(IV). The extraction recovery of the Se(IV) ion increased with the increase in DAB concentration up to $0.004\text{ mol}\cdot\text{L}^{-1}$, and became constant with increments of DAB. Therefore, the best result was achieved at $0.004\text{ mol}\cdot\text{L}^{-1}$ DAB. Different sonication times were applied to investigate the impact of this factor for Se(IV) extraction purposes. The time of sonication was investigated in the range of 2–5 min at $30\text{--}60\text{ }^\circ\text{C}$, with the highest extraction recovery of Se(IV) at $45\text{ }^\circ\text{C}$ and 3 min. Furthermore, 10–50 mL of sample volume was selected to evaluate the impact of sample volume on Se(IV) recovery. The results showed that the recovery of Se(IV) was quantitative with 25 mL of sample volume; therefore, this volume was selected for subsequent experimental work. The interference of cations and anions with the selective recovery of Se(IV) was carried out by addition of dissimilar cations and anions in the samples. The results indicated that these ions did not interfere with the measurement of Se ions; therefore, the method developed was selectively suitable for Se(IV) extraction. According to the authors, the method developed provided an efficient and innovative method for preconcentration and speciation of Se(IV) and Se(VI) combined with electrothermal atomic absorption spectrometry (ETAAS). The experimental procedure was considered simple and cheap, and it used nontoxic solvents (DESs). The UALPME-DES presented parameters compatible with other methods reported in the literature such as short extraction time, high selectivity, good reproducibility, and accuracy.

Akramipour et al. [48] developed a method using vortex-assisted dispersive liquid-liquid microextraction based on freezing the DES (VADLLME-FDES) to determine inorganic and total mercury in blood samples. The researchers investigated different parameters to optimize the experimental conditions for the mercury determination: molar ratio of HBA and HBD, the DES and its volume, pH of the medium, effect of salt addition, vortex time, temperature, and chelating agent concentration. Initially, the authors tested five ionic liquids of imidazolium chloride as HBAs: 1-decyl-2,3-dimethylimidazolium chloride ([DDMIM]Cl), 1-octyl-2,3-dimethylimidazolium chloride ([ODMIM]Cl), 1-octyl-3-methylimidazolium chloride ([OMIM]Cl), 1-dodecyl-3-methylimidazolium chloride ([C12MIM]Cl), and 1-decyl-3-methylimidazolium chloride ([DMIM]Cl), mixed with 1-undecanol in a molar ratio of 1:2 to select the most appropriate extractant for VADLLME-FDES. According to their results, the [DMIM]Cl exhibited a better analytical signal for Hg^{2+} than other DESs tested and was chosen as HBA for the molar ratio assays. The [DMIM]Cl was mixed with 1-undecanol

in different molar ratios (1:1, 1:2, 1:3, 2:5, and 3:7), and the analytical signal for Hg^{2+} was analyzed. All extraction solvents, except for the 1:1 molar ratio, had a positive effect on the extraction of Hg^{2+} from blood samples, while the 1:2 molar ratio exhibited better extraction efficiency compared with the other DESs. They also investigated the effect of the volume of DES on extraction efficiency, testing volumes from 35 to 85 μL , at 10 μL intervals, for extraction of $5.0 \mu\text{g}\cdot\text{L}^{-1} \text{Hg}^{2+}$ in 10 mL of ultrapure water. The analytical signal was enhanced by increasing the volume of DES from 35 to 55 μL and remained almost constant when it exceeded 55 μL . The volume of 55 μL was selected for its high analytical signal and good repeatability. The authors applied diethyldithiophosphoric acid (DDTP) as the chelating agent since it can form stable complexes with several metals, even in acidic medium. Since this chelating ability is dependent on the pH of the aqueous solution, the pH effect was investigated, with a higher analytical signal of Hg^{2+} shown for the pH range of 1–3. The recovery of Hg^{2+} was achieved by adding NaCl to the mixture to break the emulsion. The amount of NaCl added ranged from 50 to 550 mg at 100 mg intervals. The recovery of Hg^{2+} achieved a maximum at 350 mg and then decreased with the addition of more salt, probably, according to Akramipour et al. [48], due to the distribution coefficient of the desired analytes in the DES decreasing since the ionic strength of the solution increased. The DES was completely dispersed in the aqueous sample by mixing with a vortex, which enhanced the extraction process and the durability of the two unmixable phases in demulsification. The analytical signal of the Hg^{2+} increased with increasing vortex time from 0 to 3 min and became constant with increasing times. The temperature factor is related to mass transfer and the contact surface of the extractant and the solution; therefore, the authors tested the range of 30–70 °C at 10 °C intervals, and they obtained the best performance of the Hg^{2+} absorbance signal at 50 °C since higher temperatures aid the Hg^{2+} and DES dissolution in water. Lastly, the concentration of DDTP was investigated in the range of 0.02–0.40 % (v/v), which revealed that the analytical signal of Hg^{2+} increased upon increasing the concentration of DDTP up to 0.15 % (v/v). After investigating all these parameters, Akramipour et al. [48] proposed the following method for extraction and quantification of Hg^{2+} in solutions using [DMIM]Cl: an aliquot of 10 mL of ultrapure water containing $5 \mu\text{g}\cdot\text{L}^{-1} \text{Hg}^{2+}$ was mixed with 55 μL of DES and 15 μL of DDTP. This solution was kept at 50 °C, and 350 mg of NaCl was added to this solution. The mixture was put in a vortex agitator for 3 min. The mixture was centrifuged for 4 min at 5000 rpm to be separated into phases. Fine droplets of DES stayed afloat at the top of the tube. The DES was solidified using an ice bath after 5 min and separated. A sample of 25 μL of the extractant was injected into the graphite furnace atomic absorption spectrometry (GFAA). The mentioned method was validated with the monitoring of the mercury in blood samples, and the results indicated that VADLLME-FDES is a sensitive, fast, simple, and reproducible technique. The relative recovery of Hg from blood samples applying the proposed methodology was over 90%.

Kazi et al. [49] studied the extraction efficiency of DES for organometallic complexes of Cd and Pb with ammonium pyrrolidine dithiocarbamate (APDC) in acid-digested cosmetic samples using ultrasound energy. The authors optimized seven variables for the developed method: ultrasonication time, volume, pH, ratio of metal salt and acetamide volume, conventional shaking time, and volume of DES and tetrahydrofuran (THF). The DES was prepared by heating zinc chloride and acetamide ($\text{ZnCl}_2:\text{AC}$) in different molar ratios (1:2, 1:3, or 1:4). To investigate the seven variables concerning the extraction of Cd and Pb in a complex matrix of acid-digested cosmetic samples, they used the Plackett–Burman Design (PBD). According to the statistical tests, ultrasound energy-assisted shaking time (US), volume of DES (DV), and pH were statistically significant at the 95% confidence level, while the volume of THF, ratio of DES components, and concentration of complexing reagent did not have significant effects. These three statistically significant factors were optimized, and US, DV, and pH parameters at 6 min, 350 μL , and 6.0, respectively, resulted in more than 97% extraction recovery of both Pb and Cd from the standard samples. The last step in this study was the determination of Pb and Cd contents in lipstick and eye shadows

from different brands using the ultrasound-assisted microextraction method based on DES (UA μ E-DES). For these tests, firstly, the cosmetic samples (lipstick and eye shadows) were digested in acidic medium, with 15 samples of lipstick and 15 samples of eye shadow submitted to extraction assays using UA μ E-DES. The lipstick samples contained Pb and Cd in the range of 15.3–21.8 μ g/g and 16.3–22.6 μ g/g on a wet basis, respectively, with six brands of lipsticks having a higher Pb concentration than the international standard, which is a maximum level of 20.0 μ g/g for cosmetic products. Regarding the eye shadow, Pb and Cd were in the range of 50.5–120.0 μ g/g and 16.7–45.3 μ g/g, respectively. Furthermore, dark-colored eye shadow contained higher levels of Pb and Cd, suggesting that the heavy-metal content varies with the type of pigment used in eye shadows. The resulting data showed that Pb and Cd in the cosmetic samples studied were above the limits allowed by the different agencies.

Recently, the use of hydrophobic DESs to extract metals via a liquid–liquid extraction approach has been attracting the attention of some researchers [51,52,55,56,58], and trioctylphosphine oxide (TOPO)-based DESs have been the most studied systems [51,55,56]. Gilmore et al. [55] evaluated the use of a hydrophobic eutectic solvent based on TOPO and phenol for the removal of uranyl ions ($[\text{UO}_2]^{2+}$) from aqueous nitric acid. The extractions assays were performed using 1 cm³ of DES and 1 cm³ of uranyl-containing feeds with uranyl nitrate concentrations of 250 and 2350 ppm in nitric acid (0.01–3 M) and using UV/Vis spectroscopy to determine the final concentration of uranyl. The use of TOPO:phenol as the liquid extract reduced uranyl concentrations in the raffinate phase, and uranyl species were completely extracted under the conditions analyzed, demonstrating the excellent extraction potential of the TOPO:phenol system. These results were comparable to conventional TOPO-based extraction systems, and, according to the authors, the high uranyl extraction efficiency is related to the presence of TOPO in the extracting phase [55]. Furthermore, the phenol seemed to have no role in the uranyl extraction, instead acting solely as the liquefaction component of the TOPO-rich eutectic. The use of TOPO-based DES could significantly reduce the volumes of solvents needed since TOPO:phenol is hydrophobic and TOPO concentration in the extracting phase was elevated, which could aid the extraction process. The authors also called attention to the fact that TOPO:phenol presents potential problems such as corrosivity and toxicity. In this sense, more chemical and environmentally compatible HDB components should be tested, for example, vanillin and menthol.

Hanada and Goto [51] studied the use of a hydrophobic DES based on betadiketones and neutral extractants for the separation of lithium (Li) from a model brine solution containing a high concentration of alkali metals. The authors used thenoyltrifluoroacetone (HTTA) and benzoyltrifluoroacetone (HBTA) as HBDs, as well as TOPO and triphenyl phosphate (TPP) as HBA in different molar ratios. The synergy of Li extraction using HTTA and TOPO involved one molecule of HTTA and two molecules of TOPO interacting with one Li ion to form a $\text{Li}[\text{TTA}]^- [\text{TOPO}]_2$ complex; therefore, the ideal ratio of the extracts was 1:2 (HTTA:TOPO). This was the proportion used to prepare all eutectic mixtures. According to the authors' results, the extraction of Li ions was negligible when a single extract system was used (pure HTTA, HBTA, TOPO, or TPP) [51]. A conventional solvent extraction system control was made using synergistic extracts dissolved in Toluene, and showed a large improvement in Li extraction when HTTA:TOPO and HBTA:TOPO were used as extractants. However, TPP-based systems showed little to no synergy for Li extraction. The TOPO-based DES extraction phase showed significant synergy for Li extraction when not diluted in toluene. According to the authors, the extracted complex was stable, and the DES and the aqueous phase achieved satisfactory phase separation, without precipitation in liquid phase. The use of TPP-based eutectic solvents showed lower efficiency and synergy for extraction of Li ions when compared with TOPO-based DES. Liquid–liquid extraction of Li, Na, and K ions using TOPO-based DES or HTTA:TTP eutectic solvents was performed to investigate the ability of these systems for Li separation. The results showed that HTTA:TOPO preferentially extracts the Li over Na and K, preferably when HTTA and TOPO are diluted in toluene. The use of HCl solution stripped more than 90% of Li from

the metal-loaded HTTA:TOPO. The extraction of Li using HTTA:TPP was inefficient despite being selective, and the difference in the extraction capabilities of HTTA:TOPO-based DES and HTTA:TPP-based DES for Li was due to the donor natures of TOPO and TPP, since TOPO is a harder electron donor than TPP. The extraction performance of HBTA:TOPO for Li, Na, and K was comparable to HTTA:TOPO, due to similar complexation abilities of the HBDs. Lastly, the authors tested the reusability of the HTTA:TOPO in repeated Li extraction and stripping experiments, revealing negligible degradation of the DES for at least five cycles. The DES was highly stable and would be acceptable for long-term use in Li separation. The last step was the test of the HTTA:TOPO for the selective recovery of Li from a model brine solution. The results proved that the DES could extract nearly twice the value reported for the conventional solvent extraction system, and it could be applied to the separation of Li from salt-lake brine containing a high concentration of Li [51].

Recently, Schaeffer et al. [56] investigated the potential of nonionic hydrophobic eutectic solvents (HESs) as selective extraction solvents for the recovery and separation of platinum-group metals (PGMs) and transition metals (TMs) Cu, Fe, Cr, Ni, and Co in HCl medium. The authors analyzed the stability of novel HES under acidic conditions, as well as the price and toxicity of their constituents; on the basis of the results, they chose three HESs: thymol (Th):TOPO, TOPO:capric acid (CA), and hydrocinnamic acid (HA):CA. Furthermore, they studied the influence of metal type, HCl concentration, nature, and composition of HES on the extraction ability. According to the results obtained, HA:CA HES showed the greatest affinity for Fe^{3+} in the absence of HCl and the highest extraction of Cu^{2+} in the same conditions [56]. Increasing the acidity of the aqueous solution decreased the extraction of all studied metals for the HA:CA HES, with no extraction observed when HCl concentration was higher than 1 M. The TOPO:CA and HA:CA HESs exhibited the following order of metal extraction: $\text{Fe}^{3+} \gg \text{Cu}^{2+} \gg \text{Cr}^{3+} > \text{Co}^{2+} \approx \text{Ni}^{2+}$. The authors attributed the absence of PGM extraction in the HA:CA system to the unfavorable electrostatic interactions among the anionic palatinate, palladate chloro-complexes, and the carboxylate ligands [56]. TOPO:CA in 2 M HCl solution showed distribution coefficients of 1169, 830, and 25 for Fe^{3+} , Pt^{4+} , and Pd^{2+} , respectively. The authors also observed the formation of metal-carboxylate complexes and the release of acidic protons to the aqueous phase. The formation of these complexes may have increased the loss of the carboxylic acid component under neutral or alkaline conditions and could have restricted the applicable range of the HESs tested [56]. Regarding the TOPO-based HESs, they presented good to excellent extraction of the PGMs Pt^{4+} and Pd^{2+} at any HCl concentration tested, as well as for Fe^{3+} when the HCl concentration is higher than 2 M. The metal extraction affinity of the TOPO-based HES followed the sequence $\text{Pt}^{4+} > \text{Pd}^{2+} > \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} \approx \text{Cu}^{2+} \gg \text{Ni}^{2+} \approx \text{Cr}^{3+}$, and TOPO played a dominant role in the extraction of the metals [56]. The authors also observed that the distribution curve of palladium in TOPO-based HESs presented a concave shape with a minimum at 0.5 M HCl, and it increased thereafter with the rise in HCl concentration. This behavior was consistent with the charge in palladium coordination [59,60]. Moreover, the authors investigated the influence of the HES structure on metal extraction: the differences in the distribution coefficient were attributed to variations in intermolecular interactions between the HES components [56]. The authors performed molecular dynamics analysis to confirm the dominant nature of the TOPO-thymol H-bond interaction compared with thymol-thymol aggregation in TOPO-based HESs, and they supplemented the analysis using gas-phase density functional theory (DFT). Lastly, the authors revealed the possibility of recovering the HES after its use as the medium for metal extraction by applying a conventional stripping step or using the HES phase as a sacrificial template for Pd nanoparticle synthesis based on the ability of TOPO to act as a capping agent [61].

Some authors have also reported the ability of carboxylic-based DES to extract metals from aqueous solutions [52,57,58]. Phelps et al. [52] tested three hydrophobic DES prepared with trihexyltetradecylphosphonium, $[\text{P}_{14,666}^+]$, or tetraoctylammonium, $[\text{N}_{888}^+]$, as HBAs and hexanoic (He) or decanoic (De) acids as HBD combined in a 1:2 molar ratio to extract trace pertechnetate ($^{99\text{m}}\text{TcO}_4^-$) from aqueous solutions. Firstly, the authors mixed

TcO_4^- with aqueous solutions of hydrophobic DES and several anion matrices spiked with radiotracer levels of $^{99\text{m}}\text{TcO}_4^-$ (0.15 M Cl^- , NO_3^- , H_2PO_4^- , SO_4^{2-} , I^- , or ReO_4^- at pH 5 or HCO_3^- at pH 8) until the equilibrium condition; then, the phases were centrifuged and separated, while the content of $^{99\text{m}}\text{TcO}_4^-$ was determined in each phase [57]. A quantitative extraction was demonstrated (over 99%) using equivolume mixtures of DES to aqueous phase containing common anions, such as Cl^- and NO_3^- . The authors also tested a 1:50 volume ratio of DES to aqueous phase, and they concluded that the presence of HCO_3^- , Cl^- , H_2PO_4^- , and SO_4^{2-} maintained a quantitative extraction of $^{99\text{m}}\text{TcO}_4^-$ not impeding its extraction [57]. On the other hand, ReO_4^- and I^- suppressed $^{99\text{m}}\text{TcO}_4^-$ extraction when exceeding a 1:5 (*v/v*) or 1:10 (*v/v*) ratio, respectively, and this behavior is explained by more favorable hard-soft/acid-base (HSAB) electrostatic interactions. The authors performed assays to understand the kinetics of $^{99\text{m}}\text{TcO}_4^-$ extraction and observed that trace $^{99\text{m}}\text{TcO}_4^-$ was more rapidly extracted from slightly acidic aqueous media compared with basic solutions. In both cases, the extraction was completed within 1 h. The authors attempted to recycle the DES using organic cosolvents, acids, bases, reducing agents, or agents with high ionic strength; however, none of those could completely remove $^{99\text{m}}\text{Tc}$ from DES previously used for $^{99\text{m}}\text{TcO}_4^-$ extraction from water, with residual $^{99\text{m}}\text{Tc}$ contents within the DES phase of 35–95%. A maximum back-extraction efficiency of 57–69% for Tc(VII)O_4^- removal was achieved using aqueous solutions at pH 5 containing citrate and tin(II) chloride (SnCl_2) as reducing agents. According to the authors, the results indicated that at least partial reduction of the technetium from the DES was possible. A viable alternative for removing sequestered TcO_4^- could be the electrochemical deposition of Tc(0) from Tc(VII) . Another possibility for reductive Tc stripping involves using metallic zinc in the presence of formic acid to serve as a reducing agent with $^{99\text{m}}\text{Tc}$ recovered as a Zn(II) hydroxide and hydrous Tc(IV) oxide coprecipitate [57]. The authors concluded that the DES tested exhibited large distribution ratios which are highly competitive with known extraction systems, being an excellent medium for extraction and separation of trace $^{99\text{m}}\text{TcO}_4^-$ from water in the presence of a variety of competing anions within 5–60 min at 25 °C. The efficiency of extraction depends on the nature of the competing anions, the choice of HBD component, and the pH of the media.

Ruggeri et al. [57] prepared a hydrophobic DES using tetrabutylammonium chloride (TBACl) and decanoic acid (DA) in a 1:2 molar ratio, which was applied as the extractant in liquid–liquid extractions at room temperature. Aqueous solutions containing a salt of the metallic cation under investigation were mixed with the DES in a 1:1 volume ratio, and the solution was then left to rest until phase separation. The species adopted for the extraction experiments were $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{K}_4[\text{Fe}(\text{CN})_6]$. According to the results, the Cr(VI) extraction depended on the pH in the aqueous medium. The Cr(VI) ions were quantitatively transferred to the DES rich phase when unbuffered solutions with pH of 4.1 and 4.5 and concentrations of 5 and 50 mM, respectively, were used. On the other hand, partial extraction was achieved when 0.1 M NaOH solutions were used. When 500 mM Cr(VI) solution (unbuffered pH 5.6) was used for liquid–liquid extraction purposes, part of the DES formed a separate liquid phase at the bottom of the system (higher density), and the extraction efficiency was higher than 99%. The success in the extractions, according to Ruggeri et al. [57], was due to the high affinity of TBA to Cr(VI). The TBA and chromate establish a strong ion pair at low pH, whereas its stability is weak under basic conditions, which was proven in 0.1 M NaOH extractions. The authors also observed spontaneous reduction of Cr(VI) to Cr(III) by the DES components [57]. Regarding the results with other metallic species, Cu(II), Ni(II), and Cr(III) were dissolved in an unbuffered aqueous solution at different concentrations: 50 and 500 mM. For the Cu(II) assays, jellification occurred at 50 mM, whereas minimal quantity was extracted at the 500 mM concentration level. Jellification also occurred for NiCl_2 at 50 mM, and the efficiency of extraction was negligible when NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, and CrCl_3 were used. The Ni(II) and Cr(III) concentrations were quantified by inductively coupled plasma mass spectrometry (ICP-MS) and did not exceed around 0.1 mM in DES. Overall,

the use of this DES to extract Cu(II), Ni(II), and Cr(III) was inefficient. Furthermore, the authors concluded that using buffered solutions for the extraction of metals studied was problematic [57]; regarding phosphate buffer, Cu(II), Ni(II), and Cr(III) phosphates were poorly soluble, and hydroxides precipitated in alkaline conditions. The results showed a selective extraction of Cr(VI) species from aqueous phase, and the maximum concentration of this metal in DES was quite high.

Schaeffer et al. [58] evaluated an HES based on menthol or thymol combined with carboxylic acids for the extraction of Cu(II) and its separation from other transition metals (Co(II) and Ni(II)) in mildly acidic solutions. The authors investigated the influence of some factors on the ability of the HES for extraction purposes such as the carboxylic acid chain length at a fixed composition, change in composition for a given carboxylic acid, pH, Cu(II) concentration, and salt additive selection. According to the results, the extraction decreased as the carboxylic acid alkyl chain was increased in both menthol- and thymol-based HESs. The same behavior was observed when decreasing the carboxylic acid molar fraction in the HES with increasing carboxylic acid chain length. The presence of capric acid aided the Cu(II) extraction until reaching a plateau (0.6–0.8 molar fraction), and increasing the carboxylic acid content did not increase extraction yield [58]. According to the authors, only a fraction of acid may be involved in metal extraction due to the formation of dimers in solutions [58]. Moreover, pure capric acid exhibited the highest ability for Cu(II) extraction, while pure menthol or thymol dissolved in cyclohexane or xylene, respectively, failed to extract any metal. UV/Vis analysis showed that the Cu(II) was extracted in the form of a Cu–capric acid complex. Regarding the other factors analyzed, temperature had no important influence on Cu(II) extraction. Extraction was negligible below pH 3 for both HESs tested and increased to a maximum at pH 5.2. A further increase in pH was prevented by Cu(II) hydrolysis. The loading of Cu(II) was also evaluated to investigate the capacity of the HES phase to extract copper ions. Extraction of Cu(II) into the HES was high until 0.0075 M after which its efficiency sharply decreased. The addition of a salt showed an important impact on the loading of the HES phase. The extraction efficiency increased 10% by adding 0.1 M Na₂SO₄ due to a salting out phenomenon. Replacing Na₂SO₄ with its nitrate and chloride counterparts did not meaningfully improve Cu(II) extraction; however, adding 0.1 M of sodium acetate, sodium malate, or sodium salicylate allowed quantitative Cu(II) extraction. Cu(II) extraction efficiency close to 100% was achieved using the thymol + capric acid HES and 0.1 M sodium salt. The authors measured the water content in pure HES and in HES after Cu(II) extraction showing an increase from 0.15 wt.% to 2.50 wt.% after extraction. No measurable loss of any of the HESs to the aqueous phase was observed. The HESs were recyclable over five extractions, and the stripping cycles showed no appreciable loss in the extraction efficiency. Lastly, the partitioning of first-row transition metals (0.01 M) was studied. According to the results, Cu(II) and Fe(III) could be extracted, whilst extraction of Mg(II), Ca(II), Cr(III), Mn(II), Co(II), and Ni(II) was negligible at the tested conditions [58]. The authors concluded that terpene-based HESs display the selectivity of traditional solvent extraction whilst eliminating the need for organic diluent.

Lastly, Milevskii et al. [53] studied a process based on Aliquat 336 and L-menthol to form a hydrophobic deep eutectic solvent (HDES) for the extraction of Li(I), Co(II), Ni(II), Mn(II), and Fe(III), elements present lithium-ion batteries. At the beginning, the solid–liquid equilibrium phase diagram of the Aliquat 336 and L-menthol mixture was analyzed to determine the hydrogen bond donor and hydrogen bond acceptor molar ratios corresponding to eutectic points. Additionally, the physicochemical properties such as density, refractive index, and viscosity of the HDESs were determined. Then, the authors determined that the most convenient molar ratio for the experimental tests was 3:7 Aliquat 336/L-menthol; once this molar ratio was established, 1 mol/L HCl was added to the metal solution, and then HCl up to 3 mol/L and LiCl up to 5 mol/L were added. Through this procedure, 99% recovery rates for Fe(III), Mn(II), and Co(II) were achieved. Moreover, the stripping of each metal was studied until two cycles, 1 mol/L NaH₂PO₄ and 0.5 mol/L H₃PO₄ were used as stripping agents for Fe(III) and 0.01 mol/L HCl was

used for Mn(II) and Co(II); in all cases, 99.9% stripping efficiency was obtained. However, for the second cycle, the extraction efficiency of Mn(II) and Co(II) dropped to 21.9% and 85.1%, respectively, whereas the extraction efficiency of Fe(III) remained at 99.9%. The authors proposed that Ni(II) could be separated via precipitation, leading to a concentrated hydrochloric solution of Li(I), but no further details were presented.

As demonstrated by the papers cited before, the studies concerning the liquid–liquid extraction of metals applying DESs as solvent media are recent in the literature, and information about the phenomena involving this topic is still lacking. At this point, we can affirm that the nature and the structure of the HBA and the HBD have a direct impact on the ability to extract the metals from another solution. Initially, the studies reported the use of choline chloride as the HBA to perform the extraction of metals using liquid–liquid extraction of metals [40,50]; however, more recently, many authors have applied TOPO-based eutectic solvents and carboxylic acids as HBDs to produce DESs and achieve this separation [51,52,55–58]. Another notable trend is the use of hydrophobic DESs. This class seems to be preferred when liquid–liquid extraction of metals is the objective, due to their ability to form two-phase systems and establish strong interactions with metals [51,52,55,56,58]. The pH is another factor playing a major role in extracting metals from solutions via liquid–liquid extraction. The pH is related to precipitation and metal complex formation, which depends on the nature of the metal evaluated; therefore, the impact of this parameter must be addressed in this kind of study. Lastly, a challenge that some authors addressed is the fact that the DES-rich phase must be recovered after the metal extraction to achieve an economical and feasible process [51,52,58]. Despite some promising results, further investigation concerning the recycling and reuse of DESs after extraction is still needed, and different approaches must be considered and tested.

3. Perspectives of the Application of DESs in the Extraction of Metals

Figure 2 shows the limitations and advantages of the application of DESs in the solid–liquid and liquid–liquid processes.

Limitations	Advantages
<ul style="list-style-type: none">• Long leaching times• High viscosity• High purity is required• Hygroscopicity• Significantly low or high pH• Limited regeneration and reuse• Limited selectivity	<ul style="list-style-type: none">• Possibility of modifying its structure and properties• Biodegradability• Low emissions• Low cost• Low inflammability• High availability• Wide polarity range

Figure 2. Limitations and advantages of the application of DESs in the solid–liquid and liquid–liquid processes.

On the basis of these limitations and advantages and the articles previously analyzed, Forthcoming studies and developments utilizing DESs may focus on the following areas: (I) synthesis of new DES and NADES solvents with different polarities and their use in the development of new extraction techniques for selective extractions; (II) improvement of the yield and selectivity of the various extraction techniques to help the execution of the extraction and separation procedure on a laboratory scale; (III) kinetics and mechanisms of extraction; (IV) design of continuous processes with real or industrial solutions; (V) scale-up of the processes from laboratory to pilot or industrial scale; (VI) complementation the proposed processes with life-cycle assessments (LCAs).

4. Conclusions

DESs considered as green solvents have application potential in separation processes such as the solid–liquid and liquid–liquid extraction of ions from WEEE. Although most articles focused on studying the processes separately, future studies must consider all stages of a hydrometallurgical process. A thorough characterization of WEEE is important for further planning of leaching tests and for selecting the most suitable DESs; this will also allow a more accurate determination of leaching kinetics and leaching mechanisms. With a better understanding of the leaching process and of the liquid–liquid extraction, optimizing this latest process will be possible. Moreover, after the extraction and stripping of ions, recycling the DESs in continuous processes is a challenge that future studies should address. Lastly, the toxicity and LCA of the DESs and their processes should be evaluated.

Author Contributions: Conceptualization, R.M.D., M.C.d.C. and Y.P.J.; methodology, R.M.D., M.C.d.C. and Y.P.J.; software, R.M.D., M.C.d.C. and Y.P.J.; validation, R.M.D., M.C.d.C. and Y.P.J.; formal analysis, R.M.D., M.C.d.C. and Y.P.J.; investigation, R.M.D., M.C.d.C. and Y.P.J.; resources, R.M.D., M.C.d.C. and Y.P.J.; data curation, R.M.D., M.C.d.C. and Y.P.J.; writing—original draft preparation, R.M.D., M.C.d.C. and Y.P.J.; writing—review and editing, R.M.D., M.C.d.C. and Y.P.J.; visualization, R.M.D., M.C.d.C. and Y.P.J.; supervision, R.M.D., M.C.d.C. and Y.P.J.; project administration, R.M.D., M.C.d.C. and Y.P.J.; funding acquisition, R.M.D., M.C.d.C. and Y.P.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Coordination for the Improvement of Higher Education Personnel—Brasil (CAPES)—Finance Code 001, the National Council for Scientific and Technological Development (CNPq—306666/2020-0 and 163506/2020-5), the Fund for the Support of Education, Research and Extension (FAEPEX/UNICAMP) and ANID-Chile FONDECYT Project N° 1221428.

Acknowledgments: Mariana C. da Costa and Rafael M. Dias would like to thank the Coordination for the Improvement of Higher Education Personnel—Brasil (CAPES)—Finance Code 001, the National Council for Scientific and Technological Development (CNPq—306666/2020-0 and 163506/2020-5), and the Fund for the Support of Education, Research and Extension (FAEPEX/UNICAMP) for the financial support. Yecid P. Jimenez thanks ANID-Chile for financing this research through FONDECYT Project N° 1221428, and also to the Universidad de Antofagasta. The authors also thank the Espaço da Escrita—Pró-Reitoria de Pesquisa—UNICAMP—for the language services provided.

Conflicts of Interest: The authors declare no conflict of interest.

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