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Deep eutectic solvents in E-waste recycling: preparation, properties, and hydrometallurgical metal recovery

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Deep eutectic solvents (DESs) are promising green solvents for hydrometallurgical metal recovery, formed by heating and mixing hydrogen bond donors and acceptors in specific molar ratios, where hydrogen-bond network formation rather than chemical reactions depresses the melting point and yields a stable, tuneable liquid phase. Owing to their low volatility, high polarity, low toxicity, and ability to complex metal ions, DESs provide an attractive alternative to conventional mineral acids for leaching metals from printed circuit boards (PCBs). This review critically examines preparation routes, key physicochemical properties relevant to metal dissolution, and their mechanistic role in enhancing leaching efficiency of DESs. A structured literature-selection approach was adopted by screening publications between 2003–2024 using keywords related to preparation of DESs, metal recovery, and PCBs, focusing on studies reporting extraction efficiencies (85 to 100%), leaching mechanisms, recyclability, and solvent degradation. Across the surveyed literature, DESs such as choline chloride:ethylene glycol, choline chloride:urea, and choline chloride:oxalic acid consistently exhibit high efficiencies for copper (100%), nickel (100%), gold (≥95%), and silver (100%) recovery under mild operating conditions (40–100 °C). Emerging trends include oxidation-assisted DES leaching and integration with electrochemical recovery. However, challenges such as high viscosity, mass transfer limitations, incomplete recyclability, and potential long-term degradation remain under-reported. Overall, this review signifies the current advancements, limitations, and knowledge gaps in DES-based hydrometallurgy and highlights future directions required for scalable, circular-economy-aligned recovery of valuable metals from E-waste.

1 Introduction

One of the most rapidly increasing waste streams on a global scale that has acquired increasing attention in recent years is E-waste.[1] According to some projections, the E-waste generation might soon surpass 70 million tons per annum.[1] Printed circuit boards (PCBs) which are considered as primary devices for all the electronic gadgets are found in all EEE,[2] and constitute around 4–7% of these wastes in large quantities.[3] According to Nie *et al.* (2024), by 2050, total global E-waste generated could exceed 120 million tonnes, posing significant challenges in terms of effective disposal and management.[4,5] PCBs are complex in structure and contain both PMs as well as BMs namely gold (Au), silver (Ag), copper (Cu), zinc (Zn), aluminium (Al), and lead (Pb), in addition to various polymers, ceramics, and other materials.[6–8] Recycling E-waste is seen as an important method for maintaining metal sustainability as the demand for particular metals arises around the world. In general, the waste from electronics is considered a rich supply of metal deposits, as it includes BMs such as Pb, Sn, Zn, Al, Fe, Ni, Cu and PMs like Ag, Au, Pt, Pd and a few REEs including lanthanum (La), gadolinium (Gd), cerium (Ce), europium (Eu), and yttrium (Y).[7,9] One ton of PCB waste contains approximately 40 to 80 times the quantity of Au and 30 to 40 times the quantity of Cu compared to one ton of U.S. mined ore, as reported in ref. 10. With a Cu concentration of 10 to 50 times greater than Cu ore, abundant quantity of metals is present in comparing E-waste with ores.[11] Establishing an efficient metal recycling process from PCBs is important for ensuring the growth sustainably in the electronics industry. Traditional techniques like electrostatic separation,[12] froth flotation,[13] and the vibration gas–solid fluidized bed method[14] have been employed for segregating metallic and non-metallic components effectively. In addition, various metallurgical approaches comprising of pyrometallurgy, hydrometallurgy and bio-metallurgy are in use for efficient recovery of crucial metals.[15]

The process of pyrometallurgy separates both metal and non-metal constituents by exploiting differences in their melting and boiling points at elevated temperatures.[16,17] In a study by Chen *et al.* (2021),[18] 99.8% Sn was recovered from Cu–Sn alloys and 92.0% Cu as Cu^0 were recovered from PCBs by pyrolysis at 330 °C.[18] Similarly, research by Faraji *et al.* (2022),[19]

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revealed that the yield and grade of recovered Cu vary considerably depending on the specific pyrolysis conditions such as temperature, atmosphere, and processing time. Despite its advantages and efficiency in metal recovery, pyrometallurgy has several limitations in metal recovery from PCBs, including high energy requirements, emitting hazardous gases, and the risk of losing important metals due to improper extraction.[18,19]

The hydrometallurgical method of extracting metals from PCBs includes pre-treatment, selective metal leaching, leachate purification, and metal recovery from the final products.[20–22] In general, mild working conditions have been observed to allow inorganic acids to efficiently extract different metals from PCBs.[23] However, the use of leaching agents has delayed the industrialization of these technologies and caused challenges for researchers. The procedure also takes longer duration because of the slow rate of leaching. This extends the time required for generating a solution rich in metals. Oxidizing solvents including I_2, H_2O_2, $K_2Cr_2O_7$, $KMnO_4$, Cu^{2+}, and Fe^{3+} are frequently used to increase the leaching process efficiency.[24] An ammonium-ammonia solution containing 0.4 M H_2O_2 performs well in extracting 90% Ni and 100% Cu from PCBs, according to Feng *et al.* (2024). Reagent ratios can be modified to produce selective leaching of metals. However, as inorganic acids are volatile and acidic, specifically at high temperatures, and can cause secondary environmental pollution, their use poses safety issues. Additionally, alkaline, cyanide, thiosulphate, mineral acid, *etc.* serves as agents for leaching in hydrometallurgical procedures in recovering Au, Ag, Cu, Zn which are highly toxic and cause severe environmental damage that led to an exploration of alternatives which should be eco-friendly to traditional metal recovery methods.[26]

The previously listed disadvantages of the existing operating procedures need the development of more rapid and ecologically friendly methods. In this scenario, using DESs to extract metals from PCBs may have both economic and ecological benefits. DESs are an environmentally acceptable solvent due to their wide electrochemical window, low melting point, superior conductivity, and ease of preparation.[25] preparing DES for efficient metal recovery is highly effective when ChCl is incorporated as HBAs and many carboxylic acids are employed as hydrogen bond donors HBDs. ChCl is generally regarded as an environmentally benign HBA due to its low toxicity, high biodegradability, and widespread use in food, feed, and pharmaceutical applications. Although choline itself occurs naturally in biomass such as sugar beet, soybean, eggs, and animal tissues, ChCl is predominantly produced industrially *via* the quaternization of trimethylamine with ethylene oxide or hydrochloric acid. Its favourable environmental profile therefore arises primarily from its benign toxicological properties and regulatory acceptance, rather than exclusively from its feedstock origin.[26] This technique has potential applications in metal extraction and effectively dissolves metal oxides. Due to the specific molar ratios between HBAs and HBDs, the melting values of DESs are lesser in contrast to that of its constituent parts. From green chemistry prospect, DESs often exhibit less toxicity and enhanced biodegradable nature because of their naturally occurring matter.[24] In addition, the components which are required for preparing DESs are readily available and relatively inexpensive, which eliminates the need for further purification and allows for simple component mixing with 100% atom economy.[25] Due to these distinct properties of DESs, different PMs and BMs are being recovered from PCBs of computers and laptops that contains HBA (ChCl) and various HBDs such as EG, urea, LA, OA *etc.* in various molar proportions. The reason for choosing ChCl as HBA is that it acts as a strong hydrogen bonding ability, low toxicity, biodegradable in nature and more affordable. Whereas, HBDs such as urea, EG, OA, and LA have different structural functional groups and various advantages in efficient metal recovery. The DES made from ChCl : urea has demonstrated a good performance in solubilizing BMs like Cu and Zn.[26] Lower viscosity and increased conductivity are provided by the ChCl : EG DES, facilitating in better mass transfer during leaching of metals like Ni, Cu, and Zn.[27] OA not only forms strong hydrogen bonds but also functions as a chelating agent, combining metal ions to form stable complexes. OA is efficient in leaching metals like Au, Ag, Cu, Zn as it is capable to form soluble oxalate complexes.[28] LA contains both a hydroxyl (–OH) and a carboxyl (–COOH) group, making it a dual-site HBD. LA based DESs are effective in leaching metals like Cu, particularly under mild conditions, and are biodegradable.[29]

In this context, the present review comprehensively explores the preparation routes, physicochemical properties, and functional applications of DESs with a focus on their role in hydrometallurgical recovery of metals from PCBs. It further highlights their environmental compatibility, techno-economic feasibility, and integration within circular economy frameworks. By comparing DES-based systems with conventional and emerging metal recovery techniques, this review emphasizes how DESs contribute to sustainable resource management and position E-waste as a viable secondary source for critical and PMs.

2 Literature review and bibliometric analysis

To evaluate the existing literature on the application of DESs for metal extraction, a systematic literature review was conducted. Relevant publications were retrieved from the Scopus database using targeted keyword combinations (I) printed circuit boards and Deep eutectic solvents; and (II) E-waste, metal recovery, and deep eutectic solvents. Bibliometric analysis was performed using VOSviewer software to assess publication trends, keyword co-occurrence, and author networks. The Scopus platform provided comprehensive metadata, including titles, abstracts, authors, and keywords. Specifically, 15 articles were identified using the first keyword set, while 16 articles were retrieved using the second set. The bibliometric mapping highlights the growing research interest in DES-based metal recovery from e-waste and helps identify emerging research directions and existing knowledge gaps. The results of this analysis are presented in Fig. 1, which illustrates the distribution and frequency of publications associated with the selected keywords.

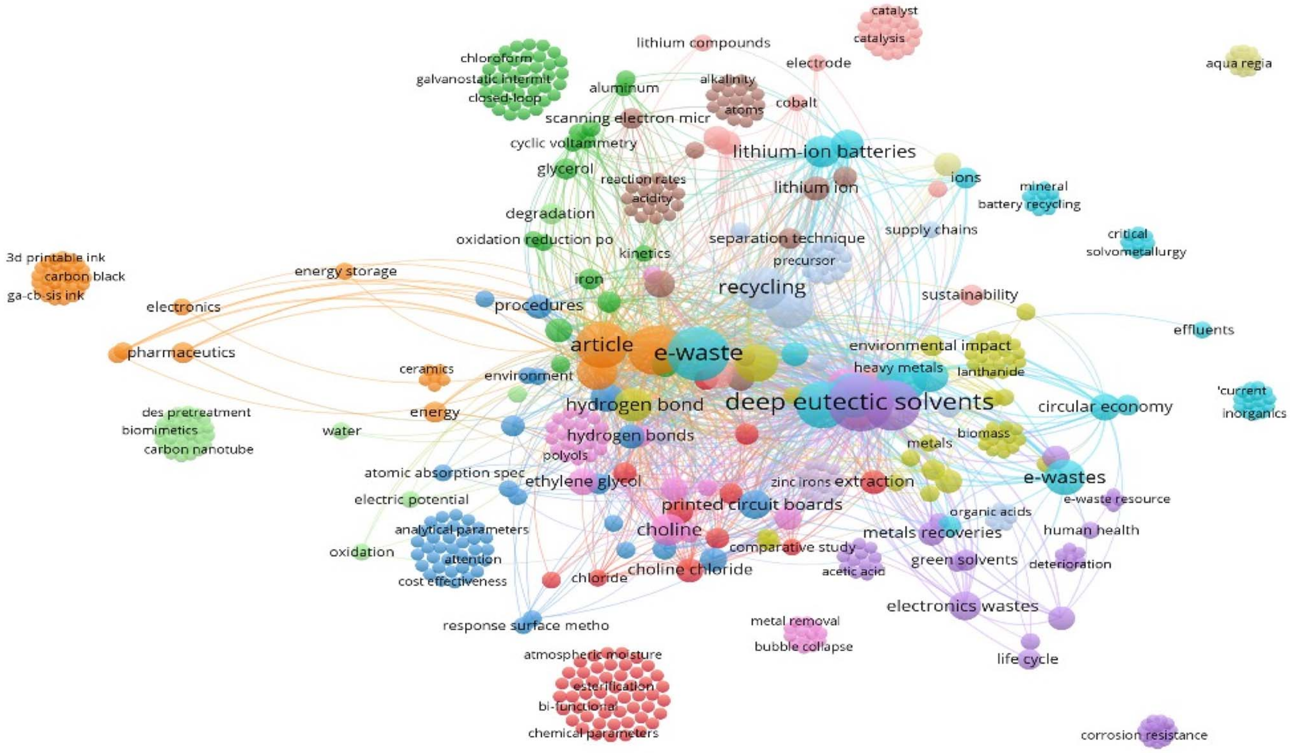

Fig. 1 Major keywords like E-waste, deep eutectic solvents *etc* plotted in VOS viewer.

Early studies on DESs established their potential as green alternatives to ionic liquids due to their low melting points, negligible vapour pressure, non-flammability, and strong hydrogen-bond networks, which collectively provide excellent solvation capabilities for a wide range of metal species.[24–27] Various preparation techniques, including heating–stirring, mechanochemical grinding, microwave irradiation, and ultrasonic methods, have been explored to produce DESs with high purity while minimising energy consumption. Furthermore, the development of NADES, composed of organic acids, sugars, and amino acids, has significantly enhanced the environmental compatibility and biodegradability of these solvent systems.[28,29]

The applicability of DESs in hydrometallurgical metal recovery has been demonstrated in numerous studies. Commonly investigated systems such as ChCl : EG, ChCl : OA, and ChCl : urea have shown high efficiency in leaching base and precious metals, including Cu, Ni, Co, Au, Ag, Li, and Mn, from printed circuit boards and spent lithium-ion batteries through the formation of stable metal–ligand complexes.[26–29] The tuneable acidity, viscosity, and coordination environment of DESs enable selective dissolution of target metals, allowing multi-metal recovery with minimal interference from co-existing components. Under mild operating conditions (40–100 °C), leaching efficiencies exceeding 90% for Cu, Ni, and Co, along with near-quantitative dissolution of Au, have been reported, often facilitated by oxidising agents such as H_2O_2 and I_2.[25,28]

Comparative assessments with conventional hydrometallurgical processes indicate that DES-based systems substantially reduce secondary effluent generation, energy consumption, and overall carbon footprint. Reductions of more than 80% in CO_2 emissions and solvent recyclability exceeding 85% have been reported, highlighting the sustainability advantages of DES-based approaches.[15–19] However, several limitations remain, including high viscosity, reduced mass-transfer rates, incomplete mechanistic understanding of metal dissolution pathways, and a lack of large-scale industrial demonstrations.[20–24]

Recent research has increasingly focused on emerging strategies such as task-specific DESs, closed-loop solvent regeneration, integration of DES leaching with electrowinning, and data-driven or AI-assisted solvent design.[17–22] These advancements underscore the growing need for scalable, selective, and environmentally responsible hydrometallurgical processes. DESs have established themselves as a versatile and promising solvent platform for sustainable metal recovery from complex PCB waste streams.[24–28]

3 DES preparation and properties

3.1 What is deep eutectic solvent?

According to Smith *et al.* (2014), "DESs are mixtures of two or more components that form a eutectic with a melting point much lower than either of the individual components, often based on hydrogen bond interactions between a hydrogen bond donor and a hydrogen bond acceptor".[30] Based on their low melting point and toxicity, superior solubility and reduced ecological effect, DESs have high metal recovery potential from

Table 1 Common hydrogen bond acceptors (HBAs) used in DES preparation[33,34]

HBA	Key properties	DES use	Typical applications in metal recovery
Choline chloride (ChCl)	Low toxicity, biodegradable, inexpensive	Strong H-bond acceptor, forms stable DES with many HBDs	Cu, Zn, Ni, Au, Ag leaching
Betaine	Zwitterionic, biodegradable	Enhances polarity and acidity control	Selective extraction of transition metals
Tetramethylammonium chloride (TMAC)	High thermal stability	Produces DES with low viscosity	Extraction of Cu, Co
Tetrabutylammonium bromide (TBAB)	Hydrophobic, stable at high temp	Enables formation of hydrophobic DES	Recovery of Pd, Pt from acidic media
Imidazolium salts	Wide electrochemical window	Strong solvation of metal complexes	Precious metal leaching (Au, Pd, Pt)

PCBs. Because of its fewer negative effect on environment, it can reduce secondary pollution during the recycling process and replace waste generated by conventional metallurgical procedures.[30,31] Because of its better solubility, it consumes less energy and release more energy into the environment during pyrometallurgical operations. It also minimizes the environmental effect during the recycling process.[32] Unlike usual conventional solvents, DESs demonstrates the chemical and thermal stability characteristic of liquids which are ionic (ILs) and had attained great interest over the past 2 decades because of its controlled polarity and ease of preparation.[33,34] In Fig. 4 and Fig. 5, a few typical HBAs and HBDs are depicted. Common HBAs and HBDs are tabulated below in Tables 1 and 2.

Metals and metal salts are efficient in the recovering metals from solutions because of their efficient solubility and conductivity in DES, which has been found as research advances. The following two elements are primarily involved in the mechanics of DES-metal interactions as shown in Fig. 2.

1. In line with reference Yuan *et al.* (2022), protons from donors initially interact with the active hydroxyl (–OH) sites on

Table 2 Common hydrogen bond donors (HBDs) used in DES preparation[33,34]

HBD	Functional groups	Key advantages	Metals recovered
Urea	$-NH_2$ groups	Strong H-bond donor, increases polarity	Cu, Zn
Ethylene glycol	–OH groups	Reduces viscosity, improves mass transfer	Ni, Cu, Zn
Oxalic acid	–COOH groups (2 sites)	Chelating ability, forms soluble oxalate complexes	Au, Ag, Cu
Lactic acid	–OH and –COOH	Dual-function donor, increases acidity	Cu, Co
Glycerol	Three –OH groups	Highly biodegradable, reduces solvent volatility	Base metal dissolution
Citric acid	Three –COOH groups	Strong complexation ability	Rare earths, Cu

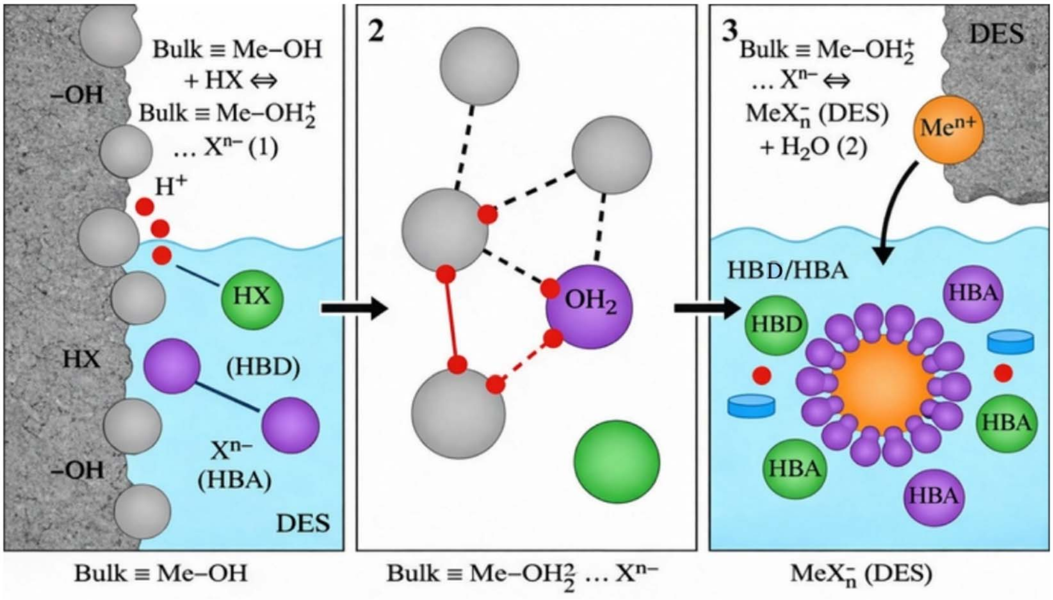

Fig. 2 Proton activity and DES chelating capacity drive metal dissolution and increased metal solubility in DES[52]

hydrated metal oxides in DESs, forming an intermediate species characterized by protonated oxide groups.

$$\text{Bulk} \equiv \text{Me–OH} + \text{HX}^{n-} \leftrightarrow \text{Bulk} \equiv \text{Me– OH}_2^{+} \ldots\ldots \text{X}^{n-} \rightarrow (1)$$

Given the context where Bulk ≡ Me–OH represents a hydrated metal oxide with an active hydroxyl site (Me = metal, OH = hydroxyl group) and HX represents the HBD in DES.

2. If the combination of metal and ligand is more stable than the metal–OH complex, the proton disrupts the metal-oxide link.[36,37] Metal complex would be stabilized as a dissolved ion when the deprotonated HBD ligand takes the place of the active OH site. By forming a metal–ligand complex in a mixed solvent environment through hydrogen bonding, the metal ions in the DES may become more soluble.

$$\text{Bulk} \equiv \text{Me– OH}_2^{+}\ldots\ldots \text{X}^{n-} \leftrightarrow \text{MeX}^{n-}{}_{(\text{DES})} + \text{H}_2\text{O} \qquad (2)$$

In conclusion, proton activity and DESs chelating capacity are crucial for the breakdown of metals in DES. The metal dissolution mechanism in DES-based hydrometallurgy is governed primarily by proton-assisted surface activation and subsequent stabilization of metal cations through coordination with DES components. HBDs act as proton sources that protonate surface hydroxyl groups on hydrated metal oxides, weakening metal oxygen bonds and facilitating metal detachment. Importantly, HBDs do not inherently generate free radicals or directly oxidize metallic atoms. Oxidation of metallic species ($\text{Me}^0 \rightarrow \text{Me}^{n+}$) occurs only in the presence of an external oxidizing agent, such as dissolved oxygen, hydrogen peroxide, iodine, or ferric ions, which are often deliberately introduced to enhance leaching kinetics. The released metal cations are subsequently stabilized in the DES phase *via* complexation with chloride ions, carboxylate groups, or polyol ligands, thereby preventing re-precipitation and promoting dissolution.

3.2 Characteristics of DESs

The preparation of DES is comparatively simple and involves heating and mixing the hydrogen bond acceptor and hydrogen bond donor at temperatures typically between 40 and 100 °C until a homogeneous liquid is formed through the establishment of an extended hydrogen-bond network.[38] The components of DES often regulate its chemical properties because of its design purpose. To accomplish the design goal, DES made by various HBAs and HBDs are often altered to some degree while maintaining the original material structure.[39] The diverse physical properties of DESs affects its recovery abilities in different ways throughout the metallurgical process. Through their effects on the mass transfer rate, its density, viscosity and other physical characteristics have a major influence on how well it performs in the metal recovery process. Water content, DES proportion, and other parameters must be adjusted to control the various physical characteristics of DESs for efficient metal recovery.[40]

3.2.1 Viscosity. The high viscosity of DES significantly makes its use more challenging.[41] Weak intermolecular hydrogen bonding networks inside DESs are caused by low viscosity, which in turn reduces metal dissolving. Phase separation and mass transfer can be significantly affected by high viscosity. A summary of some DES viscosity values at standard atmospheric pressure is provided in Table 3 below. The physical characteristics of ChCl : acetoacetate Lev in 1 : 2 DES were thoroughly examined by Mjalli and Mousa (2017), using suitable experimental confirmation. Variations in temperature, water content, and pressure had a major effect on DESs physical properties. Study by Mjalli and Mousa (2017), found that while the DESs have poor solubility for metal ions at higher viscosities, it will have acceptable fluidity at lower viscosities.[42,43] Addition of water to DES during the time of leaching will results in low viscosity and eventually results in improvement of mass transfer.[41]

3.2.2 Density. Density plays crucial role in characterisation of DESs. While using DESs for metal recovery from PCBs, it affects mass transfer rates; higher densities lead to complexation capabilities and improve ion interactions, which raise the target metals' solubility in the DES leachate. One of the reasons for higher densities of DESs are the closer hydrogen bonding

Table 3 Viscosity of common ChCl-based DESs[a][58,76]

DES system (ChCl-Based)	HBD component	Molar ratio	Viscosity range (mPa s)	Remarks
ChCl : urea	Urea	1 : 2	750–950	High viscosity; decreases significantly with temperature
ChCl : EG	Ethylene glycol (EG)	1 : 2	35–50	Very low viscosity; excellent fluidity and mass transfer
ChCl : glycerol	Glycerol	1 : 2	200–300	Moderately viscous; more fluid than ChCl–Urea DES.
ChCl : LA	Lactic acid (LA)	1 : 2	150–200	Moderate viscosity; stable and biodegradable
ChCl : malonic acid	Malonic acid	1 : 1	2200–3000	Very viscous due to strong hydrogen bonding of dicarboxylic acid
ChCl : OA	Oxalic acid (OA)	1 : 1	3000–5000	Extremely viscous; often requires dilution for processing
ChCl : citric acid	Citric acid	1 : 1 or 1 : 2	>10 000	Extremely high viscosity; impractical without heating or co-solvents
ChCl : EG : H_2O_2	EG + hydrogen peroxide	1 : 2 : 0.5	15–60	Addition of water/peroxide drastically reduces viscosity

[a] *Temperature 25 °C

Table 4 The density values for various types of DESs[58,76]

DES composition	Molar ratio	Density[a] (g cm^{-3})	Remarks
ChCl : urea	1 : 2	1.25–1.27	Widely used DES; moderate density
ChCl : EG	1 : 2	1.11–1.13	Medium density; good fluidity
ChCl : glycerol	1 : 2	1.18–1.20	Transparent, low-density DES.
ChCl : malonic acid	1 : 1	1.32–1.36	Higher density due to strong hydrogen-bonding
ChCl : oxalic acid	1 : 1	1.30–1.35	Dense and highly viscous; good for metal dissolution
ChCl : lactic acid	1 : 2	1.18–1.21	Biodegradable DES with moderate density
ChCl : citric acid	1 : 1	1.25–1.28	High density from compact molecular packing
ChCl : acetamide	1 : 2	1.08–1.12	Low viscosity and low-density DES.
Betaine: lactic acid	1 : 2	1.18–1.22	NADES; environmentally benign alternative
ChCl : EG : H_2O_2	1 : 2 : 0.5	1.15–1.17	Partial H-bond disruption reduces density slightly
ChCl : urea : OA : I_2	1 : 2 : 1 : 0.5	1.30–1.35	Multi-component DES; density varies with water content

[a] *Temperature 25 °C

structures between HBAs and HBDs. Higher density in general correlates with stronger solvent–solute interactions which affects solubility and diffusion of metal ions or solutes, which is important in recovery of metals from PCBs.[44] DES density decreases with increasing temperature, and studying this variation provides information about thermal expansion, a parameter used in thermodynamic modelling. This is important for designing temperature-controlled leaching or electrodeposition processes.[41] However, high density usually accompanies higher viscosity, which might result in a reduction in mass transfer efficiency.[45]

In general, DESs exhibits densities in between 1.0–1.3 g cm^{-3}, which is more than water, while metal salt based DESs can reach 1.3–1.6 g cm^{-3}. Research by Basaiahgari *et al.* (2018), finds that DESs based on EG are less dense than those based on glycerol.[46] Because of this, HBDs include more hydroxyl groups, which influences density and facilitates the formation of hydrogen bonds.[47] Shafie *et al.* (2019) described how the density of DES decreases when the quantity of ChCl proportional to citric acid is increased.[48] Efficiency of DES in recovering target metals during metallurgical operations may be determined by their density.[49,50] During solid–liquid or liquid–liquid separation, higher density DESs are readily isolated from other solvents that are green or aqueous phases, assuring the highest potential metal recovery.[47] Table 4 shows the different density values in different molar proportions of various types of DESs.

3.2.3 Polarity.

Polarity is a crucial characteristic of DESs which influences the solvation, extraction, and separation capabilities of DES. The composition and proportion of DES's HBAs and HBDs significantly influence its polarity, and it can be prepared based on the target metal recovery. DES generally shows moderate to high polarity, comparable to conventional polar solvents like alcohols or ILs.[51] In a recent study by Hayyan *et al.* (2013), the polarity of DES systems was evaluated using solvathochromic probes. ChCl based DES showed high polarity, with ETN values (normalized Reichardt's dye scale) ranging in between 0.7 to 0.9, depending on the HBD. As the amount of hydroxyl groups in HBDs increases, polarity also increases (glycerol > EG > urea). Addition of excess amount of water to DES further increases polarity but may break down the hydrogen bonding network if added excessively.[51] DESs' polarity is an essential property that allows them to be applied in contrast to traditional solvents which are organic in metallurgy, chemical procedures, and natural product extraction. Though their significance is high, there are limited publications that focus on the polarity of DESs. There are other ways to express polarity, but the most common ones are spectral characteristics and dielectric constant.[52] As most DESs are polar, solvatochromic characteristics are used to identify their polarity. Based on the solvent's polarity, solvatochromic dyes can be identified by their hypochromic (blue) or bathochromic (red) shift in UV-Visible bands. Solvatochromic negative dyes include Reichardt dye, whereas positive solvatochromic dyes include Nile red.[53–55] Abbott *et al.* (2011), measured DES polarity from various ChCl : glycerol ratios where the results indicated a linear rise in polarity with ChCl concentration.[56] Using a wide range of optical spectroscopic probes, Pandey *et al.* (2014) examined regular DESs namely glycerine, ethanol, reline and maline, a mixture of ChCl HBAs and glycerol, urea, 1,2-ethanol, and malonic acid HBDs in some molar proportion, respectively. They discovered that the type of HBD significantly affected high polarity, with the ChCl : glycerol in 1 : 2 molar proportion having the maximum polarity attribute.[57] Acetonitrile, toluene, hexane, and ethyl acetate are insoluble in DESs, whereas ethanol, methanol, water, and other solvents are highly soluble. Accordingly, solvents are regarded as exhibiting the miscible quality if they can establish stable bonds of hydrogen with the chloride ion.[58] Abbott *et al.* (2003) investigated at 50 °C the characteristics of ChCl and urea DESs in 2003. DESs are thought to be effective for dissolving molecules such as inorganic salts, amino acids, and salts like AgCl that will not dissolve in water readily. Because DESs have a high anion concentration, they may dissolve a wide range of metal oxides.[58] DESs have unique solvent characteristics in contrast to the majority of molecular solvents. They are compared to ILs in which the strength of hydrogen bonding has a considerable impact on solvation characteristics. HBDs plays a central role in determining physical characteristics of DES.[52] Table 5 shows the values of polarity of different DESs.

3.2.4 Melting point.

A DES is distinguished by its melting point (T_m) depression as shown in Fig. 3. Comparing to their

Table 5 Polarity parameter of the various DESs[58]

DES type	Molar proportion	ET (30) value kcal mol^{-1}	Remarks
ChCl : urea	1 : 2	56–60	Medium polarity, often used in metal leaching
ChCl : glycerol	1 : 2	54–58	High hydrogen bonding capacity
ChCl : EG	1 : 2	53–57	Lower viscosity than glycerol system
ChCl : OA	1 : 1	57–61	More acidic, slightly higher polarity
ChCl : malonic acid	1 : 1	∼60	High polarity due to more –COOH groups
ChCl : LA	1 : 2	55–59	Biodegradable, used in biomass dissolution
ChCl : citric acid	1 : 1	∼62	Strong hydrogen bonding and acidic medium
Non-choline-based DESs (alternative HBAs)			
Betaine : glycerol	1 : 2	∼59	Non-toxic, high viscosity
TBAB (tetrabutylammonium Br) : urea	1 : 2	∼52	Lower polarity due to bulky HBA
Lidocaine : menthol	1 : 1	∼46	Hydrophobic DES
Thymol : urea	2 : 1	∼40–44	Less polarity, hydrophobic DES

pure components, DESs have lower melting points. Information on the binary phase diagrams and the chemical structures of DESs is still limited. This emphasizes how vital it is to have phase diagrams for each DES under research, as it provides researchers insight into the range of temperatures and compositions that can be expected from a liquid, assisting them in designing DES systems for their exact uses.[59] According to Chaudhary *et al.* (2021), the strong interaction between HBAs and HBDs is one of the reasons behind the lowering of the eutectic point of melting.[60] DESs with melting temperatures under 49.85 °C are some of the most researched and well deserved since they are reasonably priced and have the ability to be employed as solvent substitutes in a various industrial application.[61] As seen in Table 6, the molecular mass ratio of organic salts, HBDs, and the alkyl chain length, is having a critical impact on the melting point of DES. Anions also affect melting points of DESs. As previously mentioned, the DESs melting points are greatly impacted by grid energy, entropy shift caused by the liquid phase growth and the synergy between the salt anion and donors.[62–64]

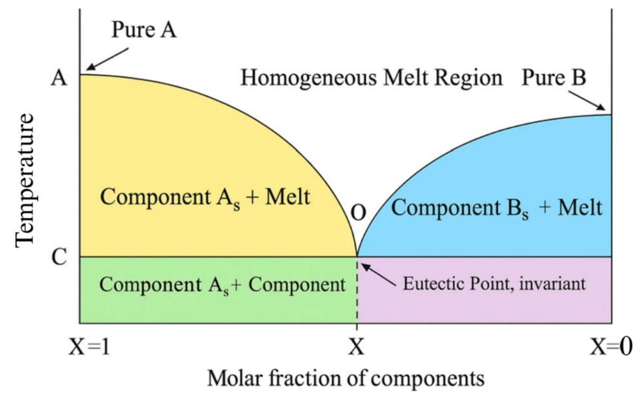

Fig. 3 Schematic binary phase diagram illustrating DES formation between a HBA and HBD. The melting temperatures of the pure HBA and HBD are shown at the left and right ends of the composition axis, respectively. The solid–liquid equilibrium curves indicate the melting behaviour of each component upon mixing. The eutectic point represents the specific molar composition at which the mixture exhibits the minimum melting temperature, significantly lower than either pure component, resulting in a stable liquid DES at or near room temperature. The liquid region corresponds to compositions where strong hydrogen-bonding interactions disrupt the individual crystal lattices of the components, enabling DES formation[60]

3.2.5 The effect of temperature on the property of DESs.

Temperature significantly affects DES's physicochemical properties and effects their efficiency in recovering metals, leaching, and other hydrometallurgical processes. DES properties including density, conductivity, solubility, and viscosity are all impacted by temperature.[26] As the DESs are closely linked to the transfer characteristics of both mass and electric charges, solvents viscosity and conductivity are considered very important. The relatively high viscosity and low ionic conductivity of DESs at ambient temperature are intrinsic consequences of their extensive hydrogen-bonded supramolecular networks. These characteristics strongly influence DES performance in hydrometallurgical applications by limiting mass and charge transfer.[65] Disruption of this hydrogen-bonding network, either through the controlled addition of water or by increasing temperature, significantly alters the physicochemical properties of DESs. Abbott *et al.* (2007) demonstrated that when the water content reaches approximately 50 wt%, the labile supramolecular interactions characteristic of eutectic mixtures are largely disrupted.[66] Similarly, increasing temperature weakens hydrogen bonding interactions, leading to a marked decrease in viscosity and a corresponding increase in ionic conductivity, thereby enhancing metal leaching kinetics.[67,68] The hole hypothesis may provide a detailed explanation of how temperature affecting the conductivity and viscosity. These liquids are believed to have portable voids of random size and position, when the size of the hole remains the same or is greater than that of the ion next to it, the ion may migrate. As the supramolecular hydrogen bonding network becomes weaker when heated, the vibrations of HBAs as well as HBDs in DES cause changes in molecules and a rise in vacancy size. Therefore, DES becomes more conductive and less viscous as a result of this.[69,70]

With a rise in temperature, the conductivity of DESs increases. At ambient temperature, three systems conductivities vary little from one another and fall with an increase in

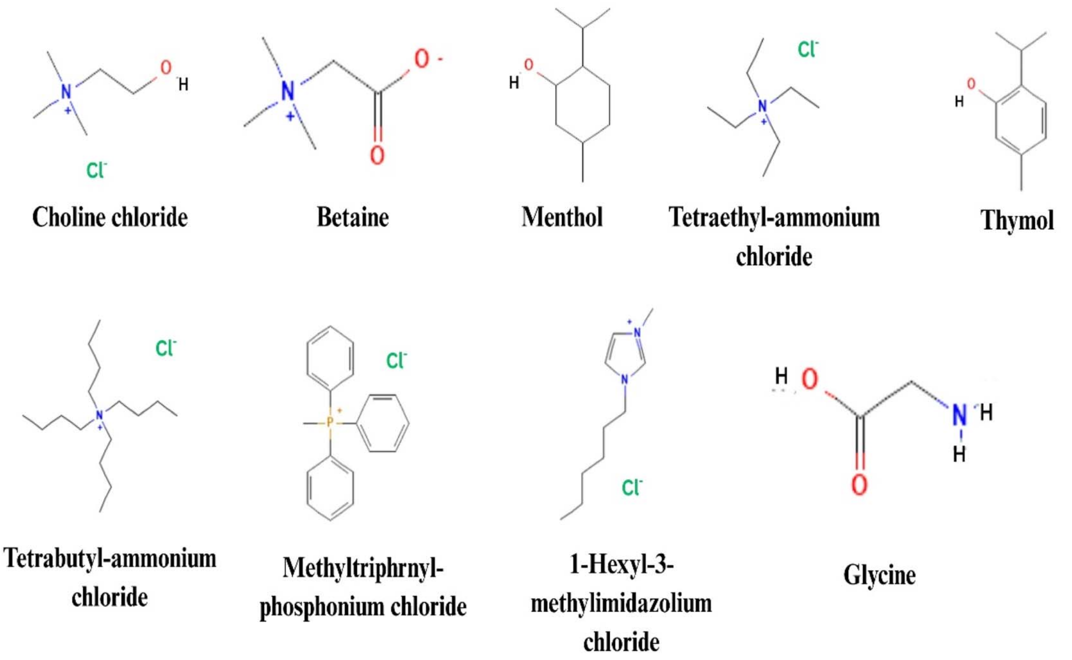

Fig. 4 Various chemical compositions of HBAs for preparing DESs[34]

oxyethylene units. Specifically, ChCl/diethylene glycol conductivity (2.9 mS cm^{-1}) is twice to ChCl/triethylene glycol (1.49 mS cm^{-1}) and thrice to ChCl/polyethylene glycol 200's (0.92 mS cm^{-1}); this difference may be the result of the three DESs under investigation having varying ChCl concentrations. There is a noticeable increase in conductivity with temperature, reaching 373 K, which is around ten times greater than the value at 298 K.[65] Since conductivity and viscosity are strongly correlated, DESs have comparatively less electrical and ionic conductivity because they have high viscosities at room temperature. At ambient temperature, most DESs typically exhibits low ionic potentials.[71,72] Since the conductivity is completely temperature dependent, an Arrhenius behaviour type may be assumed.[73] Abbott *et al.* (2003), conducted the

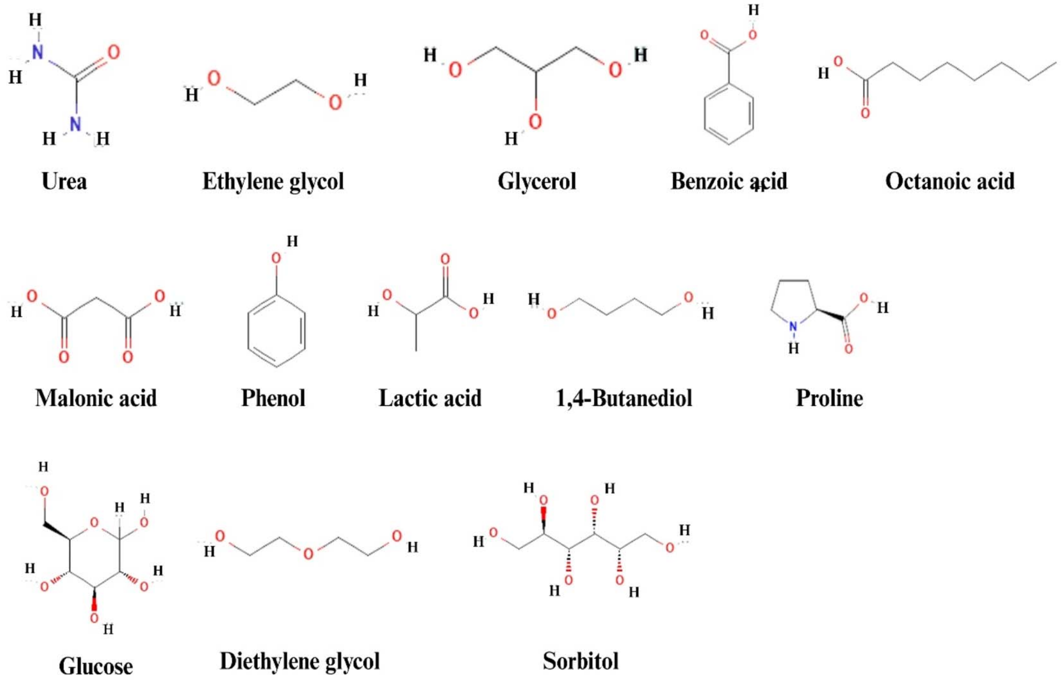

Fig. 5 Various chemical compositions of HBDs for preparing DESs[34]

Table 6 Melting point values of different DESs[58,76]

HBA : HBD	Molar proportion	Melting point (°C)	Remarks
ChCl : urea	1 : 2	∼12	First reported DES with low melting point
ChCl : glycerol	1 : 2	∼40	Low melting point compared to EG
ChCl : EG	1 : 2	∼66	Strong hydrogen bonding and high molecular flexibility lower the lattice energy
ChCl : OA	1 : 1	∼30	Slightly higher due to stronger hydrogen bonding
ChCl : malonic acid	1 : 1	∼18	Forms stable DES with low melting point
ChCl : citric acid	1 : 1	∼55	High viscosity results in high melting point
ChCl : LA	1 : 2	∼35	Biodegradable, low melting
ChCl : acetamide	1 : 2	∼12	Moisture-sensitive

initial ChCl–urea conductivity studies in 2003 and found that, the conductivity significantly increased with temperature. With a decrease in viscosity, the conductivity rises with temperature by breaking the hydrogen bonding network and enhancing their ionic mobility.[26]

3.2.6 Acidity and alkalinity (pH). Acidity and alkalinity are considered one of the important characteristics that will allow DESs to be used in a variety of industrial sectors. Also, this characteristic influences the selection of reaction tanks, pipe materials, and other manufacturing process components in any factories or industries. Therefore, it is considered as an important consideration while selecting DES in hydrometallurgical methods, namely leaching and metal recovery.[74] In hydrometallurgy method, hydrogen ions (H^+) and pH play a crucial role. Aqueous solution's H^+ ion concentration is referred to as pH. The negative logarithm of H^+ ion concentration is used to define pH. The word "aqueous solution" describes either purest water, or solvent with almost no molten substance involved. Based on the proton transfer between solvents, pH levels in various mediums are connected according to Gibbs free energy. However, it has proven hard to compare pH values across various mediums, even at the theoretical level. The pH scale indicates the acidic or basic of a given solvent. But pH is not the same as alkalinity or acidity.[75] An ability of a solution to withstand a pH shift is known as its alkalinity or acidity. The amount of an acidic or basic solution, as appropriate, with a specified concentration needed to totally neutralize the aqueous solution's alkalinity or acidity is how pH is measured.[75] Combining bases with Lewis or Brønsted acids results in forming DESs. This results, acceptors and donors' acidity and basicity control the DESs system's pH. The molar ratio and type of the pure ingredients determine this acidity and basicity. Nonaqueous solvents' Brønsted acidity or basicity is determined using the Hammett acidic equation or a pH test.[76] The probability that a basic solution will trap nucleons is determined by the Hammett function.[77] The definition of the Hammett function is

$$\mathrm{H} = \mathrm{p}K(\mathrm{HI}) + \log([\mathrm{I}^-]/[\mathrm{HI}])$$

where pK(HI) represents the indicator's thermodynamic ionization constant in water, and $[\mathrm{I}^-]$ and [HI] indicates the ratios of the indicator's neutral and ionic forms, respectively.

Molecular composition of HBDs affects the acidic and alkaline strength of DESs. Numerous research studies assessed the impact of HBDs on DES pH which showed that rising fructose molar ratios raised DES pH. Adding ions of chloride to the ChCl, as Farooq *et al.* (2020) confirms DESs become less acidic when a glycerol is added, and the and the pH of the resulting mixture becomes slightly basic.[78] The pH values of several DESs are tabulated in Table 7.

Other parameters affecting the DES's pH include temperature, which causes a linear drop in pH when temperature increases.[78] Such drop is dependent on HBDs, such as alcohol-based DESs, whose pH gradually reduces as temperature rises. However, the pH of DESs made from carboxylic acids drops sharply as temperature increases. pH 7 was noted among 298 and 318 K by Hayyan *et al.* (2013), who also noted a minor linear

Table 7 pH values of various DESs[58,76]

HBA : HBD	Molar proportion	pH value	Nature
ChCl : urea	1 : 2	9.0–10.5	Mildly basic
ChCl : EG	1 : 2	7.0–8.0	Neutral/slight basic
ChCl : glycerol	1 : 2	5.5–7.5	Near neutral
ChCl : malonic acid	1 : 1	2.5–4.5	Acidic
ChCl : citric acid	1 : 1	1.5–3.5	Strongly acidic
ChCl : OA	1 : 1	1.5–2.5	Strongly acidic
ChCl : LA	1 : 2	2.5–4.0	Moderately acidic
ChCl : acetamide	1 : 2	∼7.0	Neutral
ChCl : phenol	1 : 2	∼4.0	Slightly acidic
ChCl : urea : OA	1 : 2 : 1	∼3.5–5.0	Moderately acidic
ChCl : H_2O_2 : EG	1 : 0.5 : 2	6.0–7.5	pH may shift due to H_2O_2 decomposition
ChCl : LA : EG	1 : 1 : 1	∼3.0–4.5	Suitable for leaching metals

relationship with the temperature rise at 358 K. With the use of D glucose DESs, the pH was measured for ChCl at different molar proportions. An identical pattern had been noted in a study of this behaviour by Farooq *et al.* (2020), a rise in temperature that causes the pH to decrease.

4 Methodology

4.1 Techniques for preparation of DESs

To develop a product or products, every chemical synthesis usually involves one or more chemical reactions comprising multiple reactants. However, DESs are prepared by simply combining an HBD and an HBA.[26,52] Since there is technically no chemical reaction involved, DESs are prepared rather than created. It is improper to use the term "synthesis of DESs" in published papers, "preparation of DESs" is a better term to use.[79] Before using DESs in any application, a number of aspects should be considered, such as its storage and drying of synthesized DESs, as well as the volume of water and purity of each component. Variations in these variables may result in differences in the physio-chemical characteristics of DESs, which impacts negatively on the preparation's repeatability, and ultimately hinder the intended uses.[61,80] High hygroscopicity makes it simple for HBDs like diols and carboxylic acids, as well as HBAs like ChCl and tetrabutylammonium chloride ($[N_{4444}{}^{+}][Cl^{-}]$), to absorb humidity from the atmosphere.[81] High humid conditions result in an inaccurate stoichiometric calculation. These substances and reagents must be stored away from moisture, which can be done by storing them in a desiccator. To prepare DESs, multiple methods have been adopted in order to assure their consistency and repeatability. Roto-evaporation can be used to dry starting materials at reduced pressure, or they can be kept in an oven under vacuum for a few hours before use.[80] Furthermore, water has been extracted from starting materials using activated molecular sieves, especially those with high vapor pressure that may evaporate under vacuum like alcohols and carboxylic acids.[82] Alternative methods include drying the final DES in a vacuum desiccator with a drying agent like silica gel or Schlenk line to remove water from it. Through recrystallization, chemical contaminants in reagents can be eliminated.[32,52,80] There have been several DES preparation techniques used and documented in the literature.[32,52,80,83–86] In general, every approach has its own benefits, drawbacks, and restrictions. DESs must be highly pure and stable for longer period in order to use it for spectroscopic analysis and separation. A range of analytical applications can also benefit from diverse preparation techniques, some of which make it simple to scale up the process and others of which enable the addition of biological molecules.[83,84]

4.1.1 Heating and stirring method.

Initially Abbott *et al.* (2003) prepared DESs by studying the properties of urea and ChCl combinations. But, detailed process of preparation of DES is not mentioned clearly. In further studies, HBAs are combined in stoichiometric ratios with multiple HBDs. To create a uniform mixture, two elements with 100 °C temperature are heated and continuously stirred.[52] Several investigations have used temperatures ranging from 20 °C to 130 °C for short duration, relying on the compounds boiling and melting points as well as their endurance.[87–90] Ruggeri *et al.* (2019) used somewhat a different technique in which instead of heating a beaker having the HBA and HBD components directly on a hot plate, incorporated a water bath set at 65 °C for heating uniformly for three hours.[91] Following heating to a homogeneous, colourless eutectic solvent, the DESs were either desiccator-dried, vacuum-oven-dried, or roto-evaporated. DESs can be prepared easily with heating and stirring method. However, there are some limitations that need to be considered before preparing DESs. An interesting discovery of crystal formation over time was reported by Gurkan *et al.* (2019), when two equivalents of EG were combined with $[Ch^{+}][Cl^{-}]$ HBA.[79] An excessively low temperature during the preparation process, as well as short heating and stirring durations, are frequently linked to crystal formation. Fig. 6 shows the formation of crystals due to inappropriate heating and stirring. For the effective DES preparation, appropriate temperature and stirring duration must be determined in order to properly homogenize all the components.[79] It has been demonstrated that using high temperatures for extended periods of time causes breakdown and the creation of byproducts.[84,92,93] Skulcova *et al.* (2017) have concentrated on the carboxylic acid-based DESs' thermal stability.[94,95] Additionally, Rodriguez *et al.* (2019) conducted a thorough investigation on the esterification rate that contains carboxylic acid as HBD and ChCl as HBA at various temperatures.[92] For example, using 100, 80 and 60 °C respectively, enhanced the shaping of ester by heating and stirring ChCl, OA from 10, 29, and 34 molecular percent. As a by-product of esterification, water is also produced, and Karl Fischer titration revealed that the mixture's water content had doubled. Also, even at room temperature, some amounts of esterified products have been found, and these levels rose when the same combination was examined after a few months.[92] This observation provides important information on the potential for long-term chemical reactions or the use of high temperatures in specific HBAs and HBDs. For the resultant DES to retain long-term stability, it is crucial to characterize suitable HBA and HBD combinations. To describe and characterise DESs' molecular dynamics, some analysis using spectroscopy such as Raman, infrared, UV-Visible, and fluorescence correlation have been utilized extensively.[96–98] Although it's often accepted that DESs should be colourless like

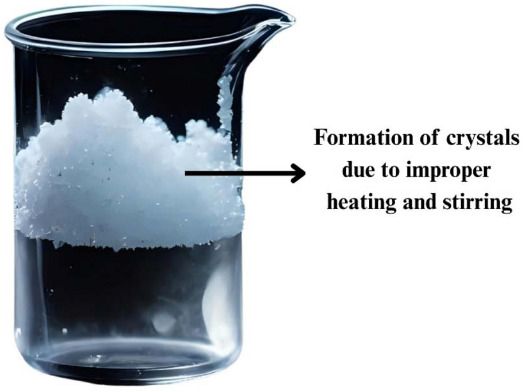

Fig. 6 Crystal formation in DESs due to improper heating and stirring.

their IL counterparts, this is not always true in all cases. DESs sometimes can be seen to have a yellowish colour, and in severe situations, when high temperatures are used for long hours, a brownish colour appears.[99–101] However, the decolorization of DESs has not yet been thoroughly investigated in any research. Hence, it is crucial to use the appropriate temperatures to prevent discoloration and produce homogeneous and consistent eutectic mixtures.[80]

4.1.2 Freezing-drying method. To create an aqueous solution of around 5%, stoichiometric quantities of HBAs and HBDs are added and then diluted with distilled water using the freezing-drying process. Following the freezing of the aqueous solution at low levels between −196.15 °C and −20.15 °C, it is freeze-dried through lyophilization resulting in a transparent, viscous liquid.[83,102–104] In DESs, this method employs the use of organic self-assemblies, including protein-based polymers, microorganisms, and huge unilamellar liposome vesicles.[83,102,104] The production of liposomes requires the presence of water. A direct water solution of both DES ingredients may be produced, nonetheless, by directly combining liposomes with plain DESs in aqueous solution.[105] DESs are applicable to a variety of biological and pharmacological areas by including micelles and vesicles, which are capable of serving as capsules and nanoreactors.[83]

4.1.3 Vacuum evaporation method. DESs prepared by this method, involves dissolving the HBAs and HBDs in aqueous solutions and then using rotational evaporation to evaporate the water at 50 °C.[32,61,106,107] Dai *et al.* (2013) developed NADES using vacuum evaporation process. NADES are processed using natural substances, particularly the primary substances like glucose, organic acids and OA.[108] Using silica gel, the liquid that is left behind after water evaporates is dried in a vacuum chamber or vacuum desiccator till its mass remains unchanged.[32] subsequently the majority of organic compounds employed in its preparation have high points of melting, this procedure is relevant for the preparation of NADES and requires comparatively fewer degrees compared to the first method.[32] All ingredients are required to dissolve in water to incorporate this method. Removing the water from the formed solution at 50 °C might be challenging and time taking.

4.1.4 Twin screw extrusion method. Crawford *et al.* (2016) employed a twin-screw extruder (TSE) to solve some potential challenges regarding the heating and mixing procedure. This method is a mechanochemical process to synthesize DESs on a large scale.[84] Similar techniques have been used for the preparation of a wide variety of organic compounds without the need of solvents.[109,110] TSE technique is being utilized to produce synthetic films using eutectic mixtures.[111] TSE contains stainless-steel barrel with two counter-rotating screws, made of conveying and rotating components. While the rotating parts give the material a considerable compression and shear force as it passes through, the sections that convey the materials forward. When batch sizes are massive, the acceptor and donor components are combined with the utilization of a planetary

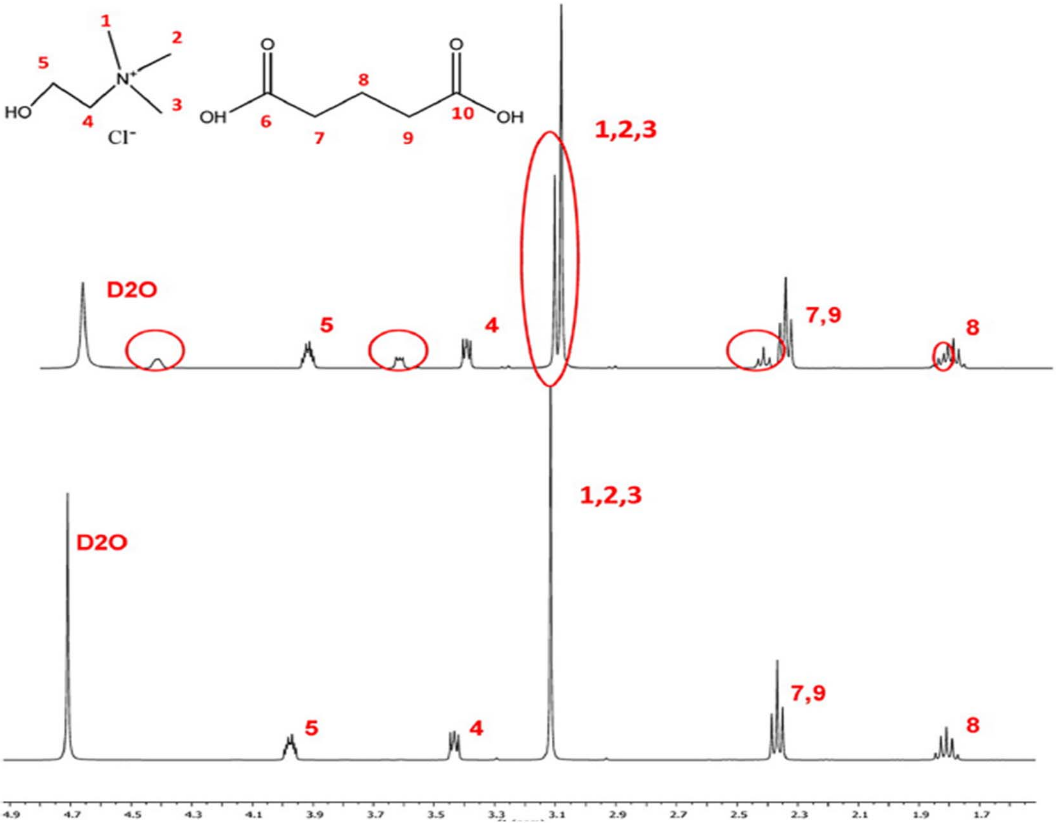

Fig. 7 Comparison of the ^{1}H NMR spectra of ChCl : glutaric acid (1 : 1) prepared by grinding (bottom) and heating-stirring (top). This figure has been adapted from Florindo *et al.*[80] with the permission from ACS Sustainable Chemistry & Engineering, copyright 2014.

ball mill. Prior to introduction through the feed port, the HBA and HBD components are preheated and then fed into the extruder at stoichiometric proportions. The produced colourless DES is collected and stored in a container under room conditions.[84]

4.1.5 Grinding method. Florindo *et al.* (2014) have used the grinding method for preparing DESs without use of external heat.[80] The acceptor and donor elements are blended and grounded in a pestle and mortar at ambient conditions till a clear viscous liquid is formed.[44,80,112,113] In view of its hygroscopic properties, ChCl is vacuum evaporated in a furnace for a couple of days maintaining a temperature of 40 °C before being placed for four days in a Schlenk with an elevated vacuum in order to eliminate moisture. The DES's quality was compared with the above methods.[80] Fig. 7 shows the proton nuclei magnetic resonance (^{1}H NMR) spectra of ChCl : glutaric acid DES preparation using heating-stirring process and grinding method. The red coloured circles show the apexes of chemical shifts at 4.5, 3.6, 3.3, 2.4 and 1.9 ppm respectively, which shows the production of ester between the HBA and HBD. First method resulted in 5–30% weight esterification, but the grinding method yielded no esterification.[80]

4.1.6 Microwave irradiation method. According to Gomez *et al.* (2018), microwaves are used in preparing DES.[85] This method is environmentally benign as it lessens energy and time associated with DES preparation.[114,115] The easiest way is placing HBA and HBD chemicals in a flask subjecting it to a radiation for some time. Compared to the first method discussed, this method consumes 650 times less energy and decreases the duration for formation of DES.[85] Compared to traditional procedures, the microwave irradiation approach is often quicker, less expensive, simpler, and more effective for DES preparation.[85,114]

4.1.7 Ultrasonic assisted preparation. Preparation of DESs using ultrasonic waves or energy is one of the novel approaches.[86,114,116,117] Using this procedure, a glass vial is filled with stoichiometric quantities of HBAs and HBDs. Afterward, the vial is sealed and, depending on the components of the DES, heated from ambient temperature to 60 °C for 1 to 5 hours in an ultrasonic bath. After preparation, the DESs are collected and stored in the same flask at ambient conditions for 24 hours till a homogeneous mixture form. DESs prepared using this technique do not crystallize even after a few days and remain stable over time.[86]

4.2 DESs applications in hydrometallurgy

The demand for metals keeps increasing due to technological advancements and energy transitions, which demands a search for better ways in recovering metals from inferior ores, hazardous waste, and other byproducts.[35] With an emphasis on sustainable practices, DESs have emerged as more ecologically friendly substitute for conventional solvents. Hydrometallurgy is still the most common technique for recovering metals. However, when recycled, it generates a lot of corrosive and acidic waste chemicals and is adversely affected by various pollutants. DES reduces the consequences of complicated reaction conditions in waste due to its diverse chemical and physical characteristics, ensuring efficient recovery while lowering the amount of waste liquid generated.[118] This suggests that DES can be beneficial in the recovering important metals. The selection and design of HBA and HBD ensures that it shows a high degree of complexity with the target metal when it is employed to recover a single metal. This guarantees that only the target metal is successfully recovered and reduces the leaching of contaminant metals. As an alternative, DES can be developed to take advantage of certain target metal chemical characteristics in the specified environment in order to allow specific extraction.[119]

4.2.1 Comparison of DESs over other green solvent systems. DESs have transformed the landscape of hydrometallurgy by addressing several challenges associated with earlier green solvent systems such as ILs, bio-solvents, and aqueous biphasic systems (ABS). Although ILs were the first generation of green solvents applied in metal recovery, their large-scale implementation has been hindered by high preparation cost, limited biodegradability, and residual toxicity.[120] In contrast, DESs provide comparable physicochemical benefits such as a wide electrochemical window, strong solvation ability, and thermal stability while offering low cost, simple preparation, and biodegradable components. DESs formed from combining HBAs and HBDs can selectively dissolve metal oxides and chlorides under milder conditions, reducing both energy demand and secondary waste generation compared with conventional ILs.[34]

When compared to bio-solvents, which include naturally derived compounds such as amino acids, sugars, and organic acids, DESs exhibit superior chemical stability and metal selectivity. While bio-solvents are biodegradable and non-toxic, they generally possess lower metal solubility and are less recyclable.[121] The formation of a strong hydrogen-bond network in DESs enhances complexation and redox control, enabling selective extraction of transition and PMs. For example, ChCl : EG and ChCl : OA systems effectively leach Cu, Ni, and Au, respectively, while maintaining recyclability and minimal vapor emissions.[122]

Compared with ABS, which depend on polymer-salt or IL salt phase separations for metal partitioning, DESs offer the advantage of a single-phase system with high coordination efficiency. ABS typically require large solvent volumes and generate saline or polymeric residues that need further treatment.[123] DESs eliminate this by combining extraction and complexation capabilities in one medium, thus reducing solvent loss, effluent generation, and downstream purification steps. Additionally, DES-based leaching systems can be readily integrated with electrochemical or photochemical recovery processes, allowing direct electrodeposition of metals such as Cu, Ag, and Co from the leachate without phase transfer.[124]

4.2.2 Recovery of lithium. The growing number of electrically driven vehicles (EVs) necessitates recycling LIBs. Lithium (Li) recovery from LIBs is still challenging.[125] Conventional methods, such as hydrometallurgical and pyrometallurgical techniques, always have problems.[126] LIBs recycling may thus be done effectively to reduce the impact of these wastes and prevent secondary contamination. Li recovery is usually carried out prior to Ni, Co, and Mn separation since the majority of Li

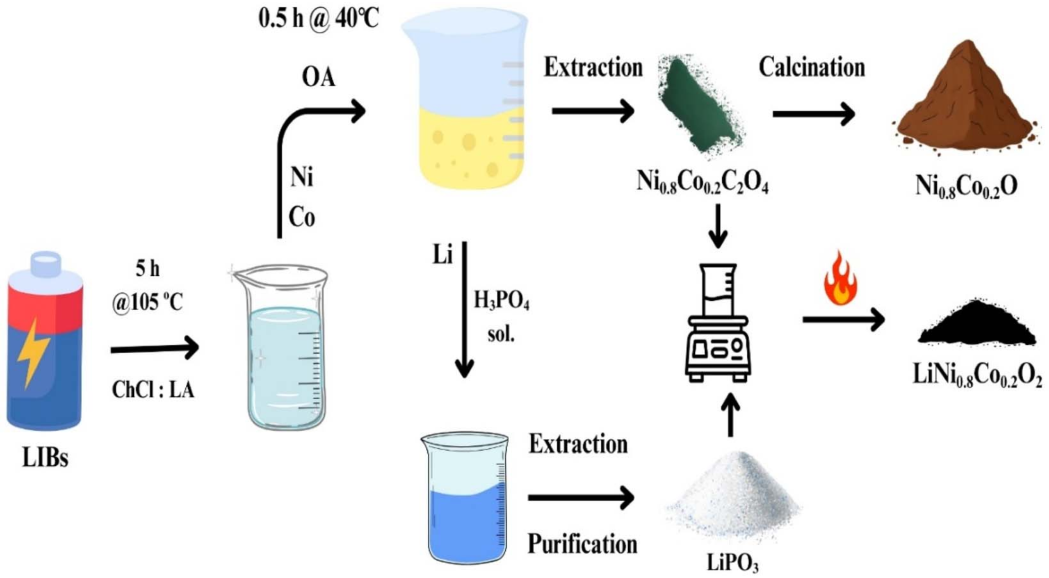

Fig. 8 The image shows a flowchart for recycling spent LIBs into a new $LiNi_{0.8}Co_{0.2}O_2$ cathode material. Spent LIBs are leached in a choline chloride–lactic acid solvent, then Ni and Co are extracted with oleic acid and calcined to $Ni_{0.8}Co_{0.2}O$. Lithium in the leachate is precipitated as $LiPO_3$ using phosphoric acid. Finally, $Ni_{0.8}Co_{0.2}O$ and $LiPO_3$ are heat-treated together to regenerate $LiNi_{0.8}Co_{0.2}O_2$.[128]

ions in LIBs are easily dissolved in water, whereas other metal components such as Co, Mn and Ni are often more balanced and challenging to extract. Li ions are often transferred from the DES solution to a different aqueous solution in order to recover Li from LIBs using DES.[127] Then Li is separated using traditional techniques such as metal extraction and chemical precipitation. However relatively easy to use and prevalent, the recovery process's usage of ionized hydrogen and complexing molecules in DES may alter the material's composition and performance, reducing its reusability.[47] Morina *et al.* (2022), synthesized $LiPO_3$ by using a solution containing H_3PO_4 as a precipitate for ChCl-LA DES. Li was first leached using ChCl and LA, and then Li ions were precipitated by adding OA straight to the DES leachate. The following metals were either utilized immediately with the $LiPO_3$ created in the previous phases or were not separated. By lowering complex ion consumption, it preserves the structure of DES and makes reclamation easier.[128]

The "easily recoverable metal-other target metals" approach is used in the majority of research. For example, the majority of researchers give priority to the selective separation of Li in LIBs because of the structural differences between Li and other PMs. This recovery procedure is a realistic solution as it accomplishes both the selective separation and effective recovery of Li at the same time. However, DES may experience proton consumption and complex ion loss during the Li recovery process, which would impair the DES's functionality.[47] Fig. 8 shows the process of separation of Li from discarded LIBs.

4.2.3 Recovery of cobalt.

It is still difficult to selectively extract additional PMs, especially Ni and Co, from discarded LIBs. The proposal of utilizing DESs in recovering Co from discarded LIB was initially made by Tran *et al.* (2019) without using either acidic or alkaline solutions, they were able to efficiently recover Co from used LIBs using a simple technique by combining DES made of ChCl and EG. Additionally, this made it possible to collect and reuse the DES, creating a new recycling pathway for LIBs.[129] Li *et al.* (2022) recovered components from discarded LIBs using an OA and ChCl DES. The process for leaching of Co was accomplished in just 10 seconds with a temperature of 180 °C. By varying the amount of pure water injected, they were able to alter the solubility of Co ions and facilitate their separation. Closed-loop cobalt recovery from LIBs is made possible by the evaporation of the deionized water, which also makes it easier to reuse the DES.[130] Schiavi *et al.* (2021)[131] used formic acid to selectively leach Li, leaving Co in the carbon black, polyvinylidene fluoride (PVDF), and leaching residue.[131] Subsequently, Co was leached and recovered using the ChCl-FA DES. Li leaches and trivalent ions containing Co were reduced using formic acid (FA) in the first phase of the leaching process. Addition of Na_2CO_3 to the leachate results in precipitation of Li and finally extracted. In the end, residual ions in the leachate were recovered using the ChCl-formic acid DES. The reduced metal losses compensate for the two-step process increased complexity, results in the effective and separate recovery of both metals.[18]

4.2.4 Recovery of nickel.

The metal targeted design of DES structures may also be used to recover Ni selectively from discarded LIBs and other wastes.[28] Li, Co, and Mn were dissolved and separated from used LIBs using ChCl/EG DES under varying conditions, taking advantage of the different conditions needed for the generation of $[Ni(EG)_3]^{2+}$ and $[CoCl_4]^{2-}$. As $[Ni(EG)_3]^{2+}$ preparation require more adverse circumstances, the leaching residue still contains Ni. Fig. 9 depicts the technical path.[131] In this study, complex metal compounds were successfully separated using DES along with other non-aqueous solvents, with a focus on selective metal recovery depending on the properties of certain metals. The separation as well as

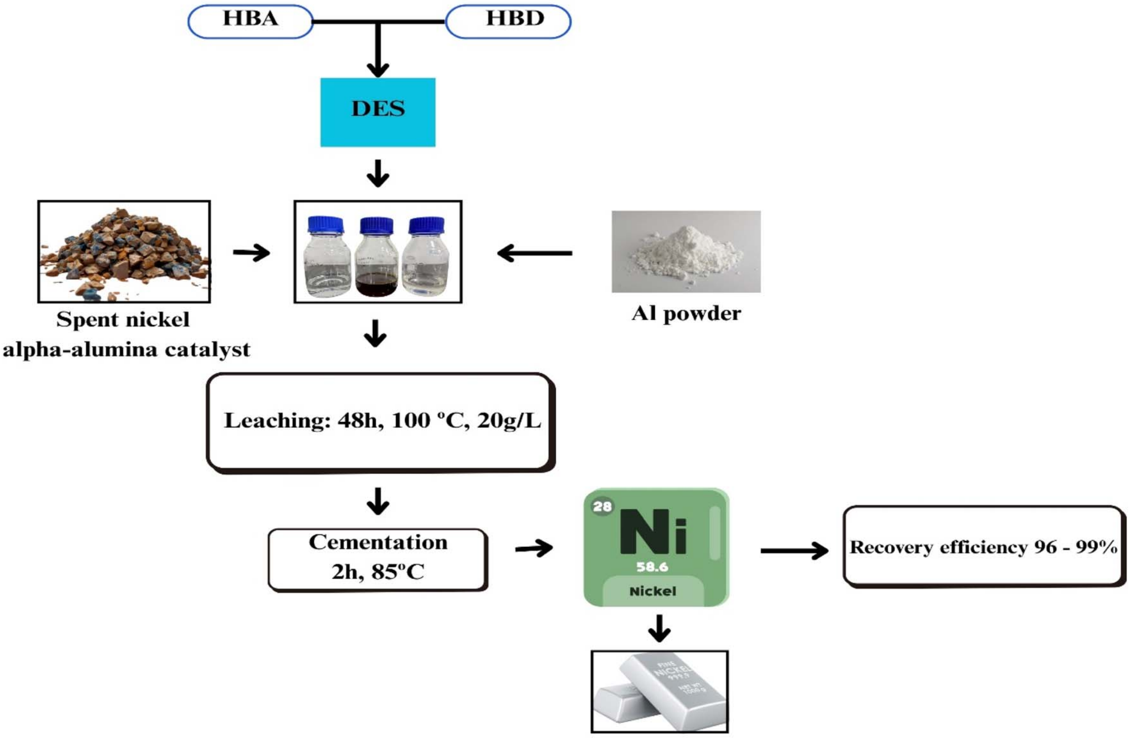

Fig. 9 The image illustrates a process for recovering nickel from a spent nickel alpha-alumina catalyst using a deep eutectic solvent (DES) made from a hydrogen bond acceptor (HBA) and donor (HBD). Spent catalyst is leached in the DES for 48 hours at 100 °C (20 g L^{-1}), then nickel is recovered *via* cementation at 85 °C for 2 hours using aluminium powder, yielding metallic nickel with a reported recovery efficiency of 96–99%.[28,180]

recovery were accomplished satisfactorily using the multistage recovery technique. Gonzalez *et al.* (2022)[21] investigated the metal dissolution such as PbO, MnO, NiO, CoO MnO_2, and Co_3O_4 in DES made with LA, AA, PA, and OA dihydrate. According to the results generated, CoO was about 400 times more soluble than NiO in ChCl/OA dihydrate DES. Based on how NCM cathode components leach in DES based on ChCl-OA dihydrate, another research by Chang *et al.* (2022) shows that, Co absorbed in the leachate as $[CoCl_4]^{2-}$, whereas Ni left in the leach liquor as $NiC_2O_4 \cdot 2H_2O$ resulting from the variations in solubility.[172] Therefore, selective separation is irreplaceably impacted by the pairing ability among DES constituents and PM ions in LIBs cathode materials, enabling the formation of DES components distinct for particular ions. Eight different DES have been studied by Ebrahimi *et al.* (2023) due to their effectiveness in recovering Ni from different types of spent hydro treating catalysis.[132] Compared to layered transition metal structure in discarded LIBs, Ni is mostly found in the form of oxides in spent catalysts. Selective leaching of Ni from waste catalysts is more challenging than with discarded LIBs because the underlying environment is complicated, and Ni is mostly surrounded by other matrix components. With >90% recovery efficiency, ChCl-PTSA (PEG-400/*p*-toluene sulfonic acid (PTSA))-EG are determined to be the best leaching agents following the experimental screening. Fig. 9 shows the experimental procedure and outcomes. Since no redox reactions during leaching was encountered, the PTSA components cab be extracted into DESs to the complexes that Ni(II) ions formed with them.[132]

4.2.5 Recovery of PMs and Pt group metals. One of the initial investigations on the application of DES in PMs extraction had been published in 2019 with a focus on the recovery of Au. Following this, Geng *et al.* (2019) examined DESs based on salts of quaternary ammonium.[133] DESs with hydrophobic nature like $[N_{8881}]Br$ $[N_{3333}]Br$, and $[N_{4444}]Br$ as acceptors and *N*-hexanoic acid as donors in a molar proportion of 1 : 1 was filtered out in recovering Au from different solutions of hydrochloric acid with varying pH. Combining UV-Visible and FTIR spectroscopic data resulted in the hypothesis of an anion exchange process. $AuCl_4^-$ replaces the anions with $[C_5H_{13}–COOH\cdots Br]^-$ all over the recovery procedure. $N_{8881}Br$ has the greatest ability to extract Au and is the most resilient to increasing salinity, based on the data obtained under different conditions.[133] As a stripping agent, 0.1 mg L^{-1} of $NaBH_4$ solution was used. Over the course of five extraction cycles, DESs capacity to extract Au was maintained. A 1 : 2 molar proportion of ChCl to phenol was incorporated for the process of extracting Au.[134] To determine the presence of Au residues in plating bath solutions, a sensitive technique needed to be developed. To perform this, a combination of methods was employed such as using slotted quartz tube atomic absorption spectroscopy in flame and DES based liquid phase microextraction with a complexing agent present in it. Based on the mixing procedure, the conventional extraction efficiency characteristics are also examined. Among vortexing, ultrasonic bathing, mechanical shaking, and manual mixing, the most efficient technique was identified. Emulsification of DES was done using tetrahydrofuran to improve phase separation.[134] Panhwar *et al.* (2019) employed a similar methodology and a DES of the same kind for the extraction of palladium in conjunction with the detection of FAAS in environmental samples.[135] Using a syringe, eight cycles of fast uptake and discharge were carried out in the sample solution to disperse the ChCl : phenol combination in a molar proportion of 1 : 4, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone as a chelating agent, and tetrahydrofuran as an emulsifying agent. The existence of Cr(II), Mn(II), Pb(II), Ni(II), Cu(II), Zn(II), Cd(II), and Co(III) ions was used to examine the selectivity of Pd(II) extraction. ALOthman *et al.* (2020) used a four-component $FeCl_3$ based DES for palladium dispersive microextraction and FAAS measurement.[136] DES disodium 4,5-dihydroxy-1,3-benzenedisulfonate was created by mixing phenol, chlorides of iron(III), and hydroxylammonium chloride in 1 : 2 : 1 : 1 molar proportion. Adding $FeCl_3$ produces coordination interactions along with donor ligand oxygen atoms besides the usual polar bonding networks, which guarantee the production of a liquid. This developed method removes the complexing agent and recovers Pd quantitatively and resistant to the presence of common matrix ions.[136] Abdi *et al.* (2020) suggested a different type of DES for palladium extraction. The developed DES was disseminated together in the sample solution with the 1-(2-pyridylazo)-2-naphtol complexing agent after DL-menthol and phenyl salicylate in the molar ratio 1 : 1 was combined. When the homogenous solution was prepared, the recovery process was conducted at high temperature of 65 °C. The ETAAS determination method might be used to reach the low limit of detection.[137] In order to extract palladium from acidic solutions, Tang *et al.* (2021) looked into the previously mentioned long chain quaternary ammonium salt.[138] $N_{8881}Cl$ was combined with either fatty alcohols or saturated fatty acids in 1 : 1 or 1 : 2 molar ratio for preparing DES. The recovery efficiency was verified by ^1H NMR, UV-Vis, and FTIR analysis using an anion exchange mechanism. The authors suggested removing Pd from DES using the hydrated hydrazine reduction process. Five cycles of Pd(II) recovery were performed using the regenerated DES.[138] Recovering all the Pt group metals from acidic solutions containing concentrations of ions and matrix components of chloride was investigated using DES which rely on carboxylic acids and $[N_{8888}]Br$ respectively.[139] In order to acquire separate portions of required metals with a purity having more than 99.9%, a plan for recovering Pt(IV) and Pd(II) along with some scarce metals of Pt group are developed for refining technical solvents.[139] Several HBD reagents have been used, with trioctylphosphine oxide (TOPO) acting as the HBA, in creating the recovery methods for Pt(IV).[140] It was advised to use TOPO-L-menthol, TOPO-1-hexanol and TOPO-1-butanol, for recovering Pt(IV) in more salinized and acidic environments. Two protonated groups of P=O in the molecule joined along with platinum hexachloride under the recovery mechanism, showing an ion-association mechanism of recovery. When utilizing NaOH as a stripping agent, butanol TOPO-1 had the greatest recovery efficiency of Pt(IV).[140] Table 8 gives the various applications of DESs for PMs recovery.

Vargas *et al.* (2021) and Schaeffer *et al.* (2020) conducted one of the most demanding and thorough studies. Comparing the TOPO-based DES to a comparable extractant system in an organic diluent, the studies revealed the characteristics of Pd(II) and Pt(IV) recovery. This work results are highly significant.[141,142] At the molecular level, diluent organic systems and TOPO require minute extractant molecules in forming metal complexes with decanoic acid and TOPO DES. Before the metal extraction, the DES components encounter strong interactions with hydrogen bonds between macromolecules and generating

Table 8 Applications of DESs for precious metal recovery[133–140]

Target metals	DES composition (HBA : HBD)	Operating conditions (simplified)	Key outcome
Pd(II)	$FeCl_3$-based DES (phenol : $FeCl_3$: hydroxylammonium chloride, 1 : 2 : 1 : 1)	Mild conditions; used with PAN as complexing agent	Strong coordination between Fe^{3+} and donor ligands enables quantitative Pd recovery, even in presence of other matrix ions; suitable for FAAS.
Pd(II)	DL-menthol : phenyl salicylate (1 : 1)	∼65 °C; with PAN	DES disperses efficiently in solution, enabling high Pd recovery and very low detection limit (ETAAS)
Pd(II), Pt(IV)	N8881Cl : fatty alcohols/fatty acids (1 : 1 or 1 : 2)	Acidic medium (0.1–0.3 M HCl); hydrazine solution for metal stripping	Metal extraction follows anion-exchange mechanism; DES regenerated and reused for 5 cycles with good efficiency
Pt(IV), Pd(II) + PGMs	Octanoic acid : N8888Br	2 M HCl for extraction; NH_4OH/HNO_3 for selective stripping	Achieves high-purity (>99.9%) separation of Pt-group metals through selective phase interactions
Pt(IV)	Trioctylphosphine oxide (TOPO) with menthol/1-hexanol/1-butanol	HCl (1–4 M); NaOH stripping	Pt recovery occurs *via* ion-association with PO functional groups; TOPO–butanol system shows highest efficiency
Pd(II), Pt(IV)	Various TOPO-based DESs	Multiple extraction–stripping cycles	DES systems outperform organic diluent-based extractants, achieving improved selectivity and sustainability

H^+ …. TOPO adduct. Concentration of HCl at which metal extraction takes place increases with the HBD content in the DES. The method of extracting DESs will not generate 3rd phase, even at 8 M HCl, like extractants in diluents with highly developed hydrogen bonded network. The separation factors of Pt(IV) or Pd(II) may be adjusted by donor selection. For instance, in thymol-TOPO system, Pt(II) recovery is hindered at lower HCl concentrations, whereas Pt(IV) extraction remains unaffected.[142]

Furthermore, DESs may form stable complexes with metal ions, they have a strong solubilizing capability for noble metals, especially those based on ChCl with HBDs like urea or EG. According to a study by Abbott *et al.* (2004), under moderate conditions, a ChCl–urea–iodine combination may efficiently dissolve Au and Ag without producing harmful byproducts that are usually connected to cyanide leaching or aqua regia.[143] Recent research by Zante and Boltoeva, (2020) showed the efficiency of DESs in urban mining applications using ChCl and EG in 1 : 2 molar proportion with iodine allows selective leaching of Au with 90% efficiency.[118] The adjustable and selective characteristic of DES-based systems has also been demonstrated by the effective leaching of Ag utilizing DESs in conjunction with oxidizing agents like H_2O_2 or iodine.[118,144]

4.3 Mechanistic insights, limitations, and research controversies in DES-based hydrometallurgy

Although numerous studies have demonstrated the excellent performance of DESs in leaching and recovering metals from complex matrices, the mechanistic basis of their selectivity and long-term sustainability remains under active discussion. The selectivity of DESs for specific metals primarily arises from HBD and HBA interactions and the resulting supramolecular organization within the liquid. The donor components such as urea, EG, oxalic or LA generates a hydrogen-bonding network that stabilizes intermediate metal–ligand complexes, while the acceptor typically ChCl or betaine provides chloride or amine sites capable of coordinating and solvating metal cations.[145,146] Molecular-dynamics and spectroscopic studies have revealed that this micro-structural heterogeneity determines the local polarity, viscosity, and proton activity of DESs, which directly control metal speciation during leaching.[147] The competitive complexation of metal ions with chloride, hydroxyl, and carboxylate groups within DESs explains the enhanced dissolution of Cu, Ni, and Au compared with aqueous media.

Despite these promising features, several limitations and controversies remain. First, the lack of unified mechanistic models hinders quantitative prediction of metal extraction efficiencies. Most reports provide empirical results rather than theoretical frameworks correlating donor acidity, anion basicity, and metal ligand stability constants. Second, viscosity and mass-transfer constraints still limit industrial-scale operation, especially for highly viscous carboxylic-acid-based DESs. Adding water or co-solvents can reduce viscosity but may disrupt the hydrogen-bond network and alter leaching selectivity.[148,149]

Another challenge lies in DES degradation and recyclability. Although often described as stable and "green," several studies indicate that DESs may undergo hydrolysis, oxidation, or esterification under prolonged heating or in the presence of oxidizing agents like H_2O_2 or I_2, producing by-products such as aldehydes, amides, or ammonium salts[35] Such degradation changes solvent polarity and metal complexation ability over successive reuse cycles. Moreover, the accumulation of residual metal ions and chloride species during recycling can affect viscosity and conductivity, ultimately reducing extraction efficiency.[28] A growing controversy concerns the true biodegradability and toxicity of DES components when used repeatedly. While ChCl-based DESs are generally considered low-toxic, the presence of phenolic, halogenated, or aromatic donors in task-specific DESs may introduce ecotoxicological risks.[150] Furthermore, data on long-term environmental fate and life-cycle impacts remain scarce, emphasizing the need for standardized biodegradation and recovery protocols.

4.4 Environmental considerations and ultimate disposal of DESs

DESs have low vapor pressure, non-flammability, and are biodegradable in nature. Hence, they are considered eco-friendly. However, after being used in metal recovery process, their characteristics change. Organic degradation products, residual leachates, and dissolved heavy metals are common components of used DESs that can cause toxicity and make disposal difficult. To avoid contaminating the ecosystem, these changed physicochemical characteristics require careful treatment as well as safe disposal.[30] To reduce toxicity and allow for future solvent reuse and leaching, it is crucial to recover dissolved metals from DESs before its disposal.[30] Chemical precipitation, solvent extraction, and electrodeposition are some of the common techniques. For instance, Au, palladium, and Cu have been successfully removed from DESs using reducing agents such as sodium borohydride, thiourea, and hydrazine hydrate.[58] This procedure reduces the harmful load of discarded solvents while simultaneously facilitating resource recovery.[58] The appropriate disposal method depends on the DESs formulation and the extent of contamination. Biodegradable DESs such as those formed from ChCl and urea can be diluted, neutralized, and subjected to biological treatment after metal removal. In contrast, DESs that include phenolic, halogenated, or aromatic components are typically unsuitable for such treatment and require incineration or hazardous waste handling.[151] Neutralization of acidic or basic residues and stabilization of remaining contaminants are also essential steps prior to final disposal.[151] DESs are not always safe in some situations after their intended use, even if they are categorized as "green solvents." Frequent recycling cycles can impair performance and raise disposal risk by causing impurity accumulation and solvent component deterioration. Environmental impact studies and thorough lifecycle evaluations for DESs are also lacking in recent studies. Future research should concentrate on creating DESs that can degrade in an ecologically friendly manner in addition to being efficient and recyclable. To fully achieve the sustainability potential of DESs in metal hydrometallurgy, disposal and regeneration paths must be incorporated into the design phase.[152] Table 9 gives the information on DES disposal methods based on composition and contaminants.

Table 9 DES disposal methods based on composition and contaminants[151,152]

DES type	Post-use contaminants	Recommended disposal method	Result
ChCl : urea	Metal ions (*e.g.*, Au^{3+}, Cu^{2+}), minor degradation products	Dilution, metal stripping, biological treatment	Biodegradable and low toxicity
ChCl : phenol	Heavy metals, aromatic compounds	Incineration or hazardous waste disposal	Not suitable for biological degradation
Menthol : thymol	Degradation products, organics	Thermal treatment or solvent recovery	Low water solubility; possible reuse if regenerated
DESs with halogenated acids or deep aromatics	Metal salts, halogenated organics	Certified hazardous waste incineration	Requires neutralization and solid waste stabilization before disposal

4.5 Environmental trade-offs and life-cycle considerations of DESs

While DESs are widely considered as "green" alternatives to conventional acids and ILs, their overall environmental sustainability must be assessed through a life-cycle and toxicity-based perspective. Recent comparative LCAs reveal that the environmental impact of DESs strongly depends on the origin of their components, energy consumption during preparation, and recycling efficiency after multiple leaching cycles.[122,153] For example, ChCl–urea and ChCl–LA systems generally exhibit 60–75% lower global warming potential and eutrophication impact compared with ILs such as [Bmim]Cl or [Emim][BF_4], largely due to bio-derived feedstocks and low-temperature formation (<100 °C). However, when DESs are synthesized from petrochemical-based EG or synthetic organic acids, their embodied carbon footprint may approach that of traditional solvents.[154] From a toxicity point of view, DESs are not uniformly benign. ChCl based systems formed with natural HBDs demonstrate low cytotoxicity toward aquatic organisms ($EC_{50} > 500$ mg L^{-1} for *Daphnia magna*), whereas systems containing aromatic, phenolic, or halogenated donors display significantly higher toxicity ($EC_{50} < 50$ mg L^{-1}).[155,156] Although most biodegradable DESs decompose into CO_2, NH_4^+, and organic acids within 28 days, some task-specific DESs persist longer in aquatic and soil environments due to strong hydrogen-bonding networks and low volatility.[157] Moreover, during repeated metal recovery cycles, accumulated metal ions, oxidized species, and organic degradation products may alter toxicity and hinder biodegradation, underscoring the need for post-use regeneration or neutralization steps prior to discharge.[158] Table 10 gives the information on comparative and analytical data on metal recovery methods.

End-of-life management remains one of the least developed areas in DES research. Current studies emphasize laboratory-scale solvent regeneration by metal stripping, adsorption, or electrowinning, but industrial-scale recovery efficiency and cost data are limited.[7,159] Incomplete regeneration can lead to DES dilution, property drift, and increased waste generation. Furthermore, solvent incineration, though effective for hazardous DESs, produces CO_2 and potentially halogenated by-products, contradicting sustainability objectives.[160] Life-cycle modelling studies recommend integrating closed-loop recycling systems and biobased feedstock selection to reduce cumulative energy demand and global warming potential by up to 80%.[161]

4.6 Techno-economic evaluation of DES based hydrometallurgy

The techno-economic viability of DES based hydrometallurgy depends on solvent cost, recyclability, energy consumption, and scalability of the leaching recovery process. Comparative studies between DES based and conventional acid-based systems reveal that DESs offer 20–40% lower operating costs and 30–35% lower energy requirements per ton of processed E-waste.[144,162] In a cost–benefit analysis by Saffaj *et al.* (2025), the total treatment cost for one ton of PCBs using ChCl : EG DES was USD 450–520, compared with USD 750–880 for aqua regia-based leaching, due to the

Table 10 Comparative and analytical interpretation of metal recovery technologies highlighting process efficiency, economic viability, and environmental performance[155–160]

Parameter	Pyrometallurgy	Acid/Alkaline hydrometallurgy	DES hydrometallurgy	Key insight
Temperature	1200–1500 °C	50–300 °C	40–100 °C	DES enables low-temperature leaching
Energy use	10–13 GJ t^{-1}	7–8 GJ t^{-1}	5–6 GJ t^{-1}	∼30% lower energy demand
Reagents	Coke, flux, lime	H_2SO_4, HCl, NaOH	ChCl-based DESs	DESs replace corrosive reagents
Recovery efficiency	85–95%	90–98%	92–99%	High efficiency with selectivity
Selectivity	Low	Moderate	High	Tunable donor–acceptor chemistry
Recyclability	None	<30%	>85%	DESs reusable for multiple cycles
Toxicity/Safety	High	Moderate–high	Low	Non-volatile, non-flammable
Equipment needs	High-cost refractory	Acid-resistant reactors	Standard SS/polymer	Lower capital cost
Effluent generation	5–15 kg kg^{-1}	2–5 kg kg^{-1}	0.2–1 kg kg^{-1}	Minimal effluent
Carbon footprint	2.4–3.0 kg CO_2/kg	1.0–1.2	0.2–0.3	∼80% reduction
E-factor	15–25	8–12	1–3	Least secondary waste
Atom economy	50–70%	75–85%	95–100%	Near-complete utilization
Circularity index	0.4–0.5	0.6–0.7	0.8–0.85	Closed-loop potential

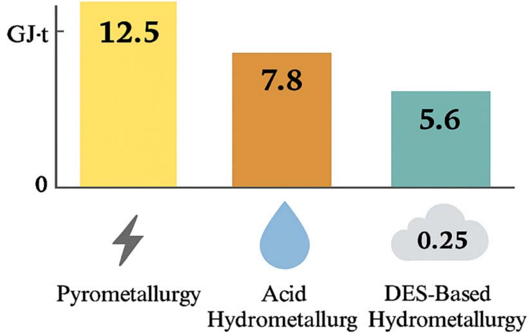

Fig. 10 Comparative analysis of energy demand and carbon emissions between conventional and DES based hydrometallurgy.

elimination of acid neutralization, gas scrubbing, and waste handling.[163] Moreover, DESs demonstrated >85% solvent recyclability with negligible efficiency loss over five cycles, reducing reagent consumption by 60%. Energy modelling using Aspen Plus simulations indicated that the specific energy demand for DES leaching (5.6 GJ t^{-1}) was substantially lower than that of acidic hydrometallurgy (7.8 GJ t^{-1}) and pyrometallurgy (12.5 GJ t^{-1}) as shown in Fig. 10 for comparable metal yields.[164]

CAPEX for small-scale DES hydrometallurgical units (1000 t per year throughput) is estimated at USD 0.9–1.3 million, mainly attributed to reactor and solvent recovery systems, whereas OPEX remains dominated by electricity (32%) and DES precursor cost (27%).[165,166] LCC analyses further demonstrate that the overall ROI is achievable within 3–4 years for DES processes under continuous operation, assuming >80% metal recovery efficiency.[167] DESs also provide flexibility for modular, decentralized recycling plants. Their non-corrosive and low-volatility nature allows replacement of costly acid-resistant infrastructure, thereby lowering maintenance costs and improving occupational safety. Economically, the cost-to-revenue ratio for DES leaching is 0.62–0.74, compared with 0.89–1.02 for traditional methods, indicating economic sustainability in medium-scale (10–50 tonnes per month) operations.[168]

4.7 Role of circular economy

Modern technological advances resulted in piling up of discarded electronic devices, where it pollutes the environment and causes potential health risks. Consumer behaviour has to be carefully observed with a purpose to combat the alarming rise in electronic trash. Consumers are liable for initial disposal into the circular economy, where it begins its trip through a number of paths such as repair, reuse and recycling. Without a shift in consumer attitudes toward green technologies, the circular economy cannot be achieved. Potential solutions exist to transform the unorganized E-waste management industry into a secure and lucrative part of the global circular economy, which aims to support the long-term development of transitional countries. Green technology plays a significant role in promoting circular economy and to achieve

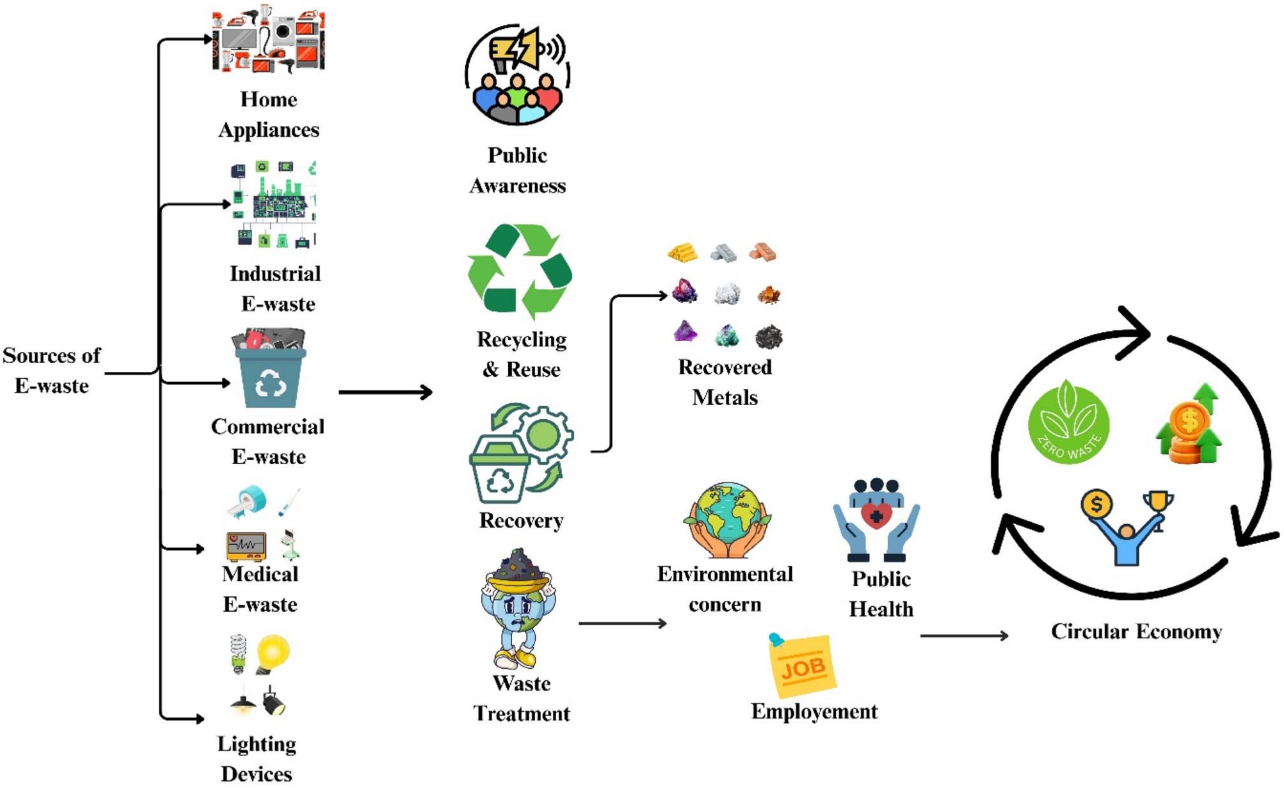

Fig. 11 The image is a conceptual diagram showing how different sources of electronic waste (home appliances, industrial, commercial, medical E-waste, and lighting devices) feed into recycling and recovery processes. E-waste is recycled, reused, and treated to recover metals, which helps address environmental concerns and improves public health while creating employment opportunities. Public awareness and proper waste treatment ultimately support a circular economy with reduced waste and economic benefits.

Table 11 Green metrics and sustainability evaluation[153,163]

Metric	Conventional hydrometallurgy	DES-based hydrometallurgy	Improvement
Atom economy (%)	60–70	95–100	No by-products
E-Factor (kg waste/kg product)	10–30	1–3	80–90% waste reduction
Energy intensity (MJ ton^{-1})	7500–8000	5000–6000	~30% reduction
Toxicity index	High	Low–moderate	Safer operations
Recyclability (%)	<30	>85	High reuse potential

sustainable waste management. These methods concentrate on extending the life of goods through reusing, recycling or refurbishment. These activities decrease waste, save resources, and produce income by repurposing used products. A comparative CI assessment by Shafique *et al.* (2025) reported that DES-based hydrometallurgy achieved a MCI of 0.82, compared with 0.58 for pyrometallurgy and 0.69 for conventional hydrometallurgy.[169] This improvement stems from solvent recyclability, reduced effluent generation, and low process emissions (<0.25 kg CO_2-eq/kg metal recovered).[170] Source reduction and minimal material utilization at every stage of production is the key moto of circular economy.[171] Based on circular economy's closed-loop system in outlining waste by optimizing product and material cycles.[172] Fig. 11 illustrates applying the concept of circular economy in E-waste management. Fe, Cu, Al, Mg, Zn, and Cr are among the many metals utilized in the production of EEE. These resources are being mined at a faster rate than they are being created naturally. Hence, there is an urgent need in proper E-waste management to address the future need.[173] Moreover, integrating DES leaching with electrowinning or selective precipitation enables nearly zero-waste process integration, achieving >95% metal recovery efficiency while recovering DES precursors through distillation or membrane separation.[3] Advanced techno-environmental analyses show that the NEB of DES-based systems is +0.45 kg CO_2-eq avoided per kg Cu recovered, whereas mineral-acid systems show a negative NEB (−0.18 kg CO_2-eq).[174] The integration of DES technology in urban mining supports multiple UN SDGs specifically SDG 9 (Industry, Innovation, and Infrastructure), SDG 12 (Responsible Consumption and Production), and SDG 13 (Climate Action). Future CE-aligned strategies should emphasize multi-metal recovery, on-site DES regeneration, and data-driven solvent design using AI-based circularity optimization models.[175]

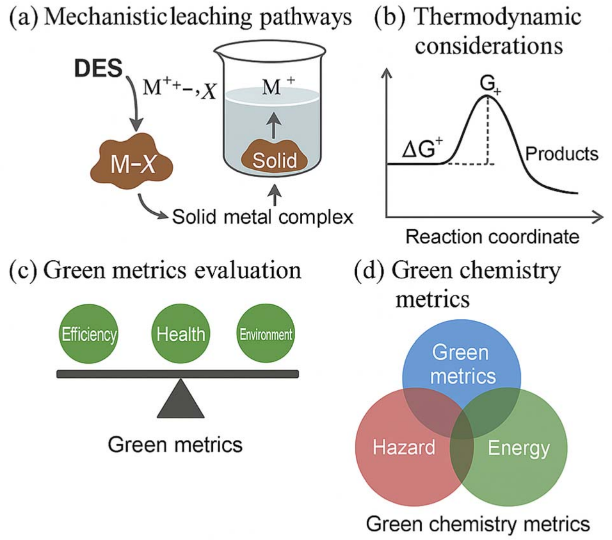

Fig. 12 Mechanistic leaching, thermodynamic and Green metric considerations of DES.

4.8 Mechanistic and conceptual framework of DES-based metal leaching

To better illustrate the underlying chemistry and sustainability aspects of DES-assisted hydrometallurgy, schematic representations have been developed to explain (i) mechanistic leaching pathways, (ii) thermodynamic interactions, and (iii) green metrics evaluation. These visual frameworks transform the descriptive data into a clear, tutorial-level understanding of DES behaviour during metal recovery.

4.8.1 Mechanistic leaching pathway in DES-based systems. Fig. 12a depicts the stepwise interaction between the metal surface (M^0 or MO_x) and DES components.

1. Hydrogen-bond network activation: the HBD such as urea, EG, or carboxylic acid donates protons to the oxide layer or metallic bonds, forming a protonated surface complex ($Me{-}OH_2^+$).

2. Ligand substitution and complexation: the chloride or carboxylate anion from the HBA (typically ChCl) coordinates to the metal cation, forming soluble complexes such as $[MeCl_4]^{2-}$ or $[Me(COO)_2]^{2-}$.

3. Oxidant-assisted dissolution: when oxidants such as H_2O_2 or I_2 are present, they oxidize metallic species to higher valence states (*e.g.*, $Cu^0 \rightarrow Cu^{2+}$), accelerating dissolution kinetics.

4. Stabilization in bulk DES: the resulting metal complexes remain stabilized by the extended hydrogen-bond network, preventing precipitation and allowing selective recovery.

This mechanistic framework highlights the dual role of DESs as both leaching agents and complexing media, integrating acid–base chemistry with hydrogen-bond-driven solvation.[25,176]

4.8.2 Thermodynamic considerations in DES–metal systems. Fig. 12b shows Gibbs free energy profile comparing traditional mineral acid leaching with DES assisted leaching. The curve shows.

1. Lower activation energy ($\Delta G‡$) in DESs due to stabilization of transition states by hydrogen-bond donors.

2. Negative overall Gibbs free energy ($\Delta G°$), confirming spontaneous dissolution of metal oxides under mild temperatures (40–90 °C).

3. Influence of temperature and viscosity on reaction enthalpy (ΔH) and entropy (ΔS) balance.

For example, leaching of CuO in ChCl : EG : OA mixtures exhibit $\Delta G° \approx -25$ to -40 kJ mol^{-1}, confirming thermodynamic

Table 12 DES alignment with Green Chemistry principles[156,157,179]

Principle	Relevance in DES hydrometallurgy	Example
Waste prevention	Low effluent; recyclable	No acid waste in ChCl : EG/AO systems
Atom economy	High metal utilization	Au leaching in ChCl : urea–I_2
Safer preparation	Non-flammable; low vapor pressure	ChCl-based DESs (EC_{50} > 500 mg L^{-1})
Safer chemicals	Biodegradable components	Lactic acid-based DESs
Safer solvents	DES acts as solvent + catalyst	One-pot oxidation/leaching in ChCl : EG : I_2
Energy efficiency	Operates <100 °C	Cu leaching at 60 °C
Renewable feedstocks	Bio-derived HBDs	LA, citric acid
Reduce derivatives	No derivatization	Simple mixing; 100% atom economy
Catalysis	Acid/base catalysis	Oxalate complexation in ChCl : OA
Design for degradation	Biodegradable after metal stripping	ChCl–urea DES degraded 80% in 28 days

feasibility under ambient conditions.[177,178] This figure reinforces the energy-efficient nature of DES-based hydrometallurgy.

4.8.3 Green metrics and sustainability evaluation. Table 11 and Fig. 12c and 12d summarizes the green chemistry performance indicators for DES systems relative to traditional solvents.

4.9 Alignment of DES based hydrometallurgy with green chemistry principles

The integration of DESs into hydrometallurgical metal recovery directly supports several of the 12 principles of Green Chemistry proposed by Anastas and Warner (1998), emphasizing waste prevention, energy efficiency, and safer materials design. Table 12 summarizes how DESs contribute to each relevant principle, while also highlighting areas needing further optimization.

5 Conclusions

This review establishes DESs as a transformative class of green hydrometallurgical media capable of enhancing metal recovery from PCBs, LIBs, and other secondary resources. DESs, particularly choline chloride-based systems with urea, ethylene glycol, lactic acid, or oxalic acid, consistently demonstrate high dissolution capacity for Cu, Ni, Au, Ag, Co, Li, and Pt-group metals under mild operating conditions, often outperforming many mineral acid systems. Their tuneable chemical structure, low toxicity, strong complexation ability, and compatibility with electrochemical recovery present a viable alternative to conventional leaching systems and enable single-phase extraction without large solvent volumes or saline residues.

At the mechanistic level, the review highlights that hydrogen-bond-driven structuring in DESs governs viscosity, polarity, proton activity, and metal–ligand stabilization, directly influencing leaching selectivity and kinetics.

Metal dissolution in DESs proceeds predominantly through protonation of surface hydroxyl groups and formation of stable metal–ligand complexes enabled by chloride, hydroxyl, or carboxylate functionalities, while DES micro-heterogeneity and donor–acceptor interactions regulate localized polarity and mass-transfer behaviour. Integration of oxidants such as H_2O_2 or I_2 further enhances metal dissolution rates without generating the hazardous by-products associated with traditional oxidizing leachates, and enables rapid, selective recovery of Li, Co, Ni, Cu, Ag, and Co *via* direct electrodeposition from DES leachates, thereby reducing downstream processing steps.

Despite these advantages, the review identifies several critical research gaps that must be addressed before widespread industrial adoption of DES-based hydrometallurgical processes. High viscosity in many DES formulations restricts mass transfer and scalability, and while dilution improves fluidity, it can disrupt hydrogen-bond networks and diminish metal selectivity. Moreover, long-term solvent degradation, esterification, and oxidation—especially under elevated temperature or oxidizing conditions—remain insufficiently quantified, complicating assessments of recyclability, environmental impact, and true "green" credentials when post-use mixtures accumulate heavy metals and degradation products.

Another major gap lies in the limited mechanistic and predictive understanding of DES behaviour in metal extraction. Existing studies are largely empirical and often lack robust models linking DES molecular structure, micro-heterogeneity, and hydrogen-bond networks to extraction performance, speciation, and selectivity. Furthermore, while initial lifecycle and techno-economic analyses indicate promising reductions in emissions and secondary waste compared with traditional systems and ionic liquids, large-scale industrial assessments of process efficiency, solvent regeneration, and long-term environmental impact remain scarce and fragmented.

Looking forward, the review emphasizes that designing task-specific DESs will be crucial, particularly formulations with lower viscosity, improved thermal and oxidative stability, and metal-specific coordination motifs tailored for selective dissolution and separation. Future research should focus on integrating mechanistic modelling with experimental studies to develop predictive frameworks that connect DES structure to leaching kinetics, speciation control, and separation efficiency across complex waste streams. A combined approach that couples solvent recyclability optimization, robust solvent management strategies for contaminated and degraded DESs, and circular-economy metrics with comprehensive lifecycle and techno-economic analyses will be essential to translate laboratory-scale advances into sustainable, industrial-scale DES-based metallurgical processes.

Author contributions

Lakshmi Kanth Moganti: conceptualization, methodology, writing – original draft. Dr Deblina Dutta: supervision, writing – review & editing.

Conflicts of interest

Authors declare that they have no known competing financial interests or personal relationships that could have influenced the work presented in this manuscript.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Abbreviations

DESs	Deep eutectic solvents
PCBs	Printed circuit boards
E-waste	Electronic waste
EEE	Electronic and electrical equipment
PMs	Precious metals
BMs	Base metals
REEs	Rare earth elements
ChCl	Choline chloride
HBAs	Hydrogen bond acceptors
HBDs	Hydrogen bond donors
EG	Ethylene glycol
LA	Lactic acid
OA	Oxalic acid
ILs	Ionic liquids
NADES	Natural deep eutectic solvents
TSE	Twin-screw extruder
EVs	Electric vehicles
LIBs	Lithium-ion batteries
FAAS	Flame atomic absorption spectrophotometer
LCA	Life cycle analysis
CAPEX	Capital expenditure
OPEX	Operational expenditure
LCC	Life cycle cost
ROI	Return on investment
CI	Circularity index
MCI	Material circularity index
NEB	Net environmental benefit
SDGs	Sustainable development goals

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