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Sustainable Leaching of Cu, Ni, and Au from Waste Printed Circuit Boards Using Choline Chloride-Based Deep Eutectic Solvents

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Abstract: Electronic waste (e-waste) is becoming a serious problem that impacts the environment due to its fast-growing volume. This rise is linked to high electronic and electrical equipment production to meet the increasing demand for high-end electronic devices. Conventional e-waste recycling approaches, including hydrometallurgy and pyrometallurgy, often involve substantial water and energy consumption and the generation of by-products, such as the emission of toxic gases or hazardous effluents. Within this context, solvometallurgy has emerged as a compelling alternative, whereby green non-toxic non-aqueous solvents, namely deep eutectic solvents (DESs), are used to extract and recover the metals with minimal water and harsh acid/base chemical use. The current study presents the solvo-leaching results of critical and strategic metals, i.e., copper (Cu) and nickel (Ni), and precious metals, i.e., gold (Au), from waste printed circuit boards (PCBs). Five different DESs were tested at mild conditions, namely at a temperature of 65 °C, a stirring speed of 300 rpm, a solid/liquid ratio of 10 g/L, and in the presence of iodine (I_2) for 96 h. Among the different solvents tested, the one consisting of choline chloride (ChCl), acetic acid (AA), and I_2 emerged as the optimal solvent, leading to the selective extraction of 99% of Cu, 92% of Ni, and 90% of Au from the PCB powder.

Keywords: sustainable; solvometallurgy; leaching; printed circuit boards; deep eutectic solvents; critical and strategic metals; precious metals

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1. Introduction

The population growth combined with the thirst of our modern societies for high-tech products has led to a significant increase in electronic waste (e-waste), which is considered a rich secondary resource for metals, including critical-strategic metals (CSMs) and precious metals [1–3]. In 2022, the amount of e-waste totalled 59.4 million tons and it is projected that, by 2030, e-waste will reach 74.7 million tons [4]. These skyrocketing volumes of end-of-life electronics generated per year have given a serious worldwide alert that rises to a multitude of negative repercussions for soil quality, water, and human health [5]. Therefore, it is of paramount importance to develop new efficient mineral and metal processing technologies to recover and recycle the metals from e-waste while meeting environmental regulations around e-waste management [6–10].

Printed circuit boards (PCBs) represent a specific part of e-waste, with a volume exceeding 2 million tons in 2022 [11,12]. According to the US Environmental Protection Agency, around 85% of end-of-life PCBs are disposed of through incineration and landfill applications [4,13]. PCBs are considered a major component of high-tech products,

including electronic devices and automotive parts. They are known to contain valuable metals, such as CSMs and precious metals, making them an important secondary resource for metal recovery [14,15]. However, current conventional recycling processes, such as traditional extractive metallurgy, including pyrometallurgy and hydrometallurgy, are energy and water demanding, often generating toxic effluents and greenhouse gases [16,17]. On the one hand, pyrometallurgy, the oldest branch of extractive metallurgy, consists of recovering metals (e.g., iron (Fe), copper (Cu), lead (Pb)) in a liquid state following a high thermal treatment [18]. Pyrometallurgy often achieves high metal recovery efficiencies, making it suitable for large-scale operations. Furthermore, it involves a relatively simple infrastructure and few chemical reagents, and it can be adapted to treat a wide range of ores and concentrates, including those with complex compositions [19,20]. However, pyrometallurgy is considered an energy-intensive extractive process that often leads to emissions of gases of environmental concern and generates significant solid waste, which often causes additional environmental challenges [21]. On the other hand, hydrometallurgy is viewed as a greener alternative developed to extract metals [22]. It relies on the use of aqueous solvents to extract and recover metals. However, not all hydrometallurgical processes are selective or convenient for metal recovery from natural or secondary resources. Consequently, the dissolution of metals of interest is often accompanied by the co-extraction of impurities, which reduces the process efficiency due to increased acid/base consumption and the need for more separation/purification steps [16,23]. Additionally, hydrometallurgy also produces effluents, including chemical by-products and residual materials, which can impact the environment [16,24]. To address these issues, effluent treatment techniques are necessary in order to allow water purification and recycling in the process circuit, thus allowing near-zero liquid discharge circular hydrometallurgy processing [25–28].

Another approach to addressing these challenges consists of developing novel sustainable extractive metallurgy processes able to selectively extract the metals of interest while further reducing water consumption and the environmental burden. In this context, solvometallurgy, the newest branch of extractive metallurgy, has been proposed as an alternative. Solvometallurgy started to show up in the mid-20th century, when researchers started to develop an extractive process to recover uranium from uranium ores via leaching with organic solvents, namely with acetone-HCl and alkyl phosphoric acids in kerosene [29]. In 1985, Marcus Yizhak [30] used the term "solvometallurgy" in his book to explain the capacity of hydrometallurgy to use solvents other than water, including molecular organic solvents, ionic liquids (ILs), and deep eutectic solvents (DESs) [16,31–33]. Solvometallurgy can extract metals from primary and secondary resources using less energy, water, and harsh chemicals. However, despite these advantages, solvometallurgy still faces challenges regarding its industrial applicability. Binnemans et al. [34] identified a mismatch between academic research and industrial applications mainly due to limited pilot studies conducted on solvometallurgical processes and the physicochemical properties of the solvents (i.e., viscosity and chemical stability) under typical metallurgical processing conditions.

To date, DESs have emerged as leading candidates among the various non-aqueous solvents that can be used in solvometallurgy [35,36]. These solvents have been discovered since the apparition of ILs [30,37]; the difference between ILs and DESs lies in their composition and formation mechanism. DESs are mixtures of two or more compounds, hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), that form a eutectic liquid mixture at room temperature [38]. These mixtures exhibit a lower melting point compared with their individual components due to interactions caused by hydrogen bond (H-bond) formations [38,39]. The ability to adjust DESs' physiochemical and thermal properties, such as density, viscosity, and polarity, by controlling their composition, makes DESs suitable for a wide range of applications [35,38,40].

The objective of this study was to identify a DES capable of selectively extracting CSMs and precious metals, i.e., copper (Cu), nickel (Ni), and gold (Au), from PCB powder. The DES systems studied were based on choline chloride (ChCl) as the HBA; ChCl is one of the most commonly used ingredients in DESs, as it is inexpensive, biodegradable, and non-toxic [38]. The HBA was combined with various HBDs, including ethylene glycol (EG), acetic acid (AA), malonic acid (MA), citric acid (CA), and levulinic acid (LA). A small amount (0.1 mol/L) of iodine (I_2) was added to the DESs studied as an oxidizing agent to promote the oxidation of target metals, thereby facilitating their dissolution and improving the overall leaching efficiency. A series of leaching tests were conducted to evaluate the selectivity of the DESs and identify the most promising DES for the extraction of Cu, Ni, and Au from the PCB powder.

2. Materials and Methods

2.1. DES Preparation

For the preparation of the DESs, choline chloride (ChCl, $HOC_2H_4N(CH_3)_3{}^+Cl^-$, 99%, Sigma Aldrich) was dried at 50 °C under vacuum for 24 h before its use. Ethylene glycol (EG, $C_2H_6O_2$, >99%, Sigma Aldrich, St. Louis, MO, USA), malonic acid (MA, $CH_2(COOH)_2$, 99%, Sigma Aldrich), levulinic acid (LA, $CH_3COCH_2CH_2COOH$, 99%, Sigma Aldrich), acetic acid (AA, CH_3CO_2H, >99%, Sigma Aldrich), citric acid (CA, $HOC(COOH)(CH_2COOH)_2$, 99.5%, VWR), and iodine (I_2, >99.8%, Sigma Aldrich) were used as received. Figure 1A illustrates the preparation flowchart of DESs with I_2.

The HBA:HBD mixtures were stirred at 80 °C until each DES was formed; the HBA:HBD molar ratios used to form the DESs tested in this work are presented in Table 1. A 0.1 mol/L concentration of I_2 was added to all the DESs. This amount was selected based on a study conducted by Jenkin et al. [41], who followed the procedure of Abbott et al. [42]. Their findings demonstrated that the addition of I_2 increases solubility, accelerates electron transfer, and enhances the oxidation capability for most elements, including Cu, Ni, and Au. Additionally, 15 wt.% ultrapure water from a Purelab Flex system was incorporated to adjust the viscosity of highly viscous DESs, such as ChCl:MA and ChCl:CA [35,43,44].

Table 1. Molar ratios of DESs used in the leaching experiments adapted from Ref. [37].

DES	Molar Ratio
ChCl:EG	1:2
ChCl:CA	1:1
ChCl:MA	1:1
ChCl:AA	1:2
ChCl:LA	1:2

2.2. PCB Pre-Treatment and Digestion

Figure 1B presents the pre-treatment method and digestion of PCB powder. The PCBs were obtained from Centre Carrefour Environment Saguenay through CTTÉI (Centre de Transfert Technologique en Écologie Industriel, Sorel-Tracy, QC, Canada), where the electronic components had already been dismantled. The collected PCBs were entirely cut and ground by a Universal Cutting Mill Pulverisette 19, from FRITSCH Milling (Pittsboro, NC, USA), to produce the PCB powder. The latter was sieved and separated to obtain a portion of powder smaller than 1 mm. This PCB powder was subsequently homogenized with riffle splitters and digested following the procedure for digesting PCB described in a previous study [45]: 15 mL of hydrochloric acid (HCl, hydrochloric acid, 36%, technical, Thermo Fisher Scientific, Waltham, MA, USA), 5 mL of nitric acid (HNO_3, 65–70%, 99.999% (metals basis), Thermo Fisher Scientific), and 5 mL of hydrogen peroxide (H_2O_2, 25–35%,

≥30%, Sigma-Aldrich) were used to digest 0.5 g of PCB powder. The digestion was carried out in a Microwave MultiVIEW from SCP SCIENCE (Quebec, QC, Canada) at 220 °C, 45 bar, and 1000 W for 40 min. The digested samples were filtered using Whatman quantitative ashless filter paper with a pore size of 20 µm and analyzed by microwave plasma atomic emission spectroscopy (MP-AES, Agilent Technologies (Santa Clara, CA, USA) 4100 upgraded to a 4200 torch system) to determine the initial metal content of the PCBs.

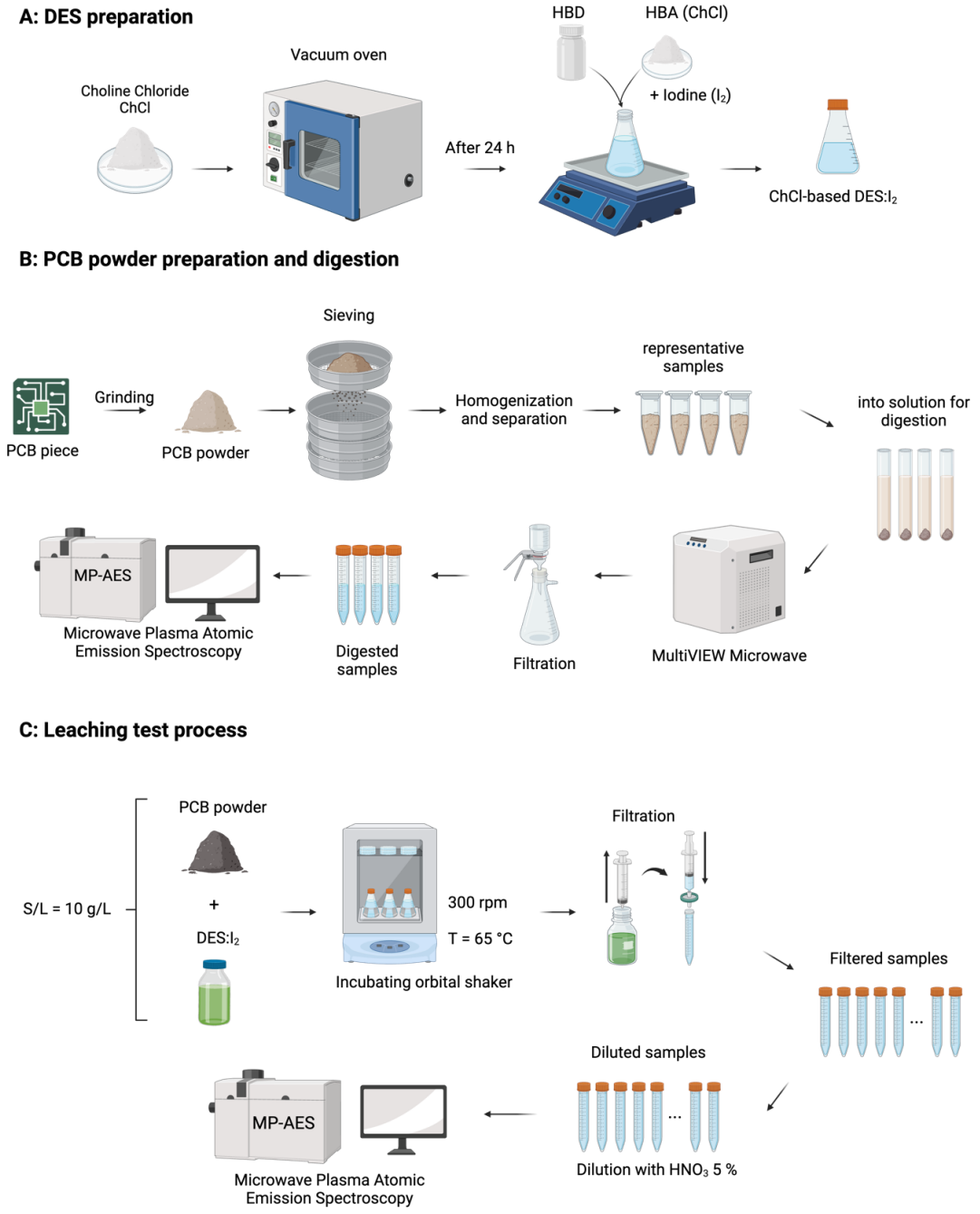

Figure 1. Flowchart of the methodology: (**A**) DES:I2 preparation, (**B**) PCB powder preparation and digestion, and (**C**) leaching test process.

2.3. Leaching Experiments

Figure 1C presents the series of preliminary leaching tests carried out in 100 mL bottle jars in a VWR incubating 3500 orbital shaker by fixing all the process parameters: solid/liquid ratio S/L = 10 g/L, temperature T = 65 °C, leaching time t = 96 h, and stirring

speed = 300 rpm. Samples were collected during predetermined time intervals (t = 0, 5, 15, 30, 45 min, and 1, 2, 4, 6, 24, 48, 72, 96 h) using Henke-Ject sterile syringes (Thermo Fisher Scientific) and were filtered through Nalgene sterile syringe filters with a pore size of 0.45 µm (Thermo Fisher Scientific). The samples obtained were then diluted with 5 wt.% HNO_3 and analyzed using an MP-AES method described in the literature for determining the concentration of metals dissolved in DES [46].

The extraction of each element i (i = Cu, Ni, Au, Al, or Fe) at each sampling time interval mentioned above was determined by Equations (1)–(4):

$$E_i = \frac{m_i}{m_{PLS} + m_{i-R}} \cdot 100 \quad (1)$$

where E_i is the extraction (%), m_i is the element weight (mg) in the leach solution, m_{PLS} is the element weight (mg) after 96 h in the pregnant leach solution (PLS), m_{i-R} is the element weight (mg) in the solid residue remaining after leaching.

$$m_i = C_i \cdot V_t \quad (2)$$

$$m_{PLS} = C_f \cdot V_f \quad (3)$$

$$m_{i-R} = C_{m_R} \cdot m_R \quad (4)$$

where C_i is the element concentration (mg/L) in the leach solution, C_f is the element concentration (mg/L) in the PLS, V_t is the volume (L) of the leach solution at a specific time during leaching (t = 0 to 96 h), V_f is the volume (L) of the leach solution at the final time (t = 96 h), C_{m_R} is the element weight concentration (mg/g) in the solid residue after leaching, m_R is the weight (g) of the solid residue after leaching.

To maintain the recycling aspect of the process, the PLS obtained after leaching ought to undergo further treatment to separate and recover the metals and to investigate the feasibility of reusing the DES in a closed-loop process.

3. Results and Discussion

3.1. PCB Powder Characterization

The cumulative retained particle size distribution of the PCB powder used in this work was obtained by sieve analysis and is presented in Figure 2. The smaller the particles, the more efficient the leaching process, thus improving mass transfer by increasing the available particle surface area to react with the solvents [47,48]. The d values of the PCB powder used in this work were d_{10} = 0.51 mm, d_{50} = 0.25 mm, and d_{90} = 0.08 mm.

The initial metal content in the PCB powder is presented in Table 2. During the PCB powder digestion, several elements were analyzed; among them, special focus was dedicated to Cu, Ni, Al, and Fe, as they exhibited higher concentrations, >10 mg/g, compared with others. Additionally, Au was included in the analysis as, given its value, its content was significant. As such Cu, Ni, and Au were identified as the metals of interest to extract during the leaching process, while Fe and Al were considered the major impurities that ought to be monitored.

Table 2. The initial metal content in the PCB powder.

Elements	Zn	Cu	Ti	Co	Ni	Fe	Al	Au	Pb
Metal content (mg/g)	2.12 ± 0.06	322.23 ± 20.76	3.35 ± 0.37	0.03 ± 0.01	12.06 ± 0.81	10.29 ± 0.68	26.37 ± 2.02	0.22 ± 0.02	0.56 ± 0.27

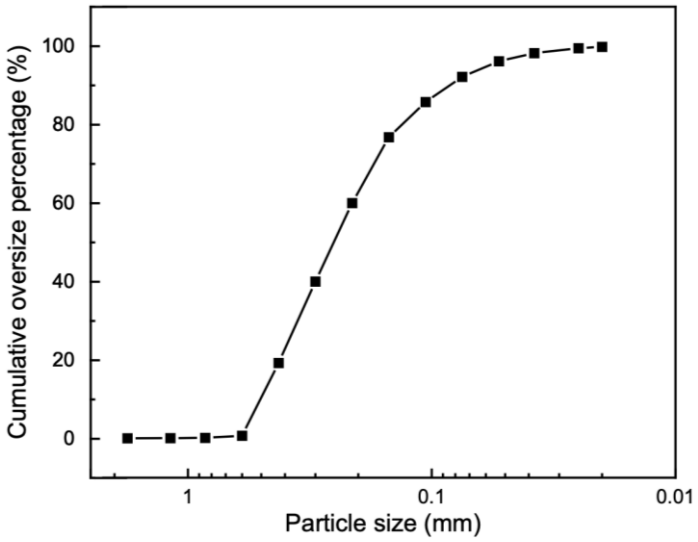

Figure 2. Cumulative oversize particle size distribution of PCB powder.

3.2. DES Characterization

The DESs' viscosity, density, and complexing capacity are properties that could influence the leaching performance and selectivity for the metals of interest [38]. In Table 3, the DESs' viscosities and their densities are reported. The density of the solvents was measured manually using a pycnometer. The viscosities were taken from the literature. Among the DESs tested, ChCl:MA and ChCl:CA with I_2 and water addition exhibited the highest densities of approximately 1.2 g/mL and 1.3 g/mL, respectively. Furthermore, they showed a high viscosity of about 721 cP for ChCl:MA, and 2852 cP for ChCl:CA [40], thus indicating that their use could be challenging. In contrast, ChCl:EG and ChCl:AA demonstrated low to moderate viscosity of around 36 cP [40] and 49 cP [49], respectively, thus allowing for practical use in leaching processes.

Table 3. Viscosity and density of DESs.

HBA:HBD	Viscosity at 25 °C from the Literature		DESs	Measured Density (g/mL)	
	(cP)	References		DES	DES:I_2
ChCl:EG	36	[40]	ChCl:EG	1.114	1.134
ChCl:MA	721	[40]	ChCl:MA:15% water	1.192	1.203
ChCl:AA	49	[49]	ChCl:AA	1.105	1.111
ChCl:LA	320	[50]	ChCl:LA	1.132	1.150
ChCl:CA	2852	[37]	ChCl:CA:15% water	1.300	1.295

Figure 3 shows the molecular structures of the different DES components. As illustrated, AA has a short simple chain length, resulting in a straightforward molecular structure and low density. Furthermore, the interaction between AA and ChCl likely forms a moderate H-bond network, leading to a DES with low viscosity (Table 3). This property facilitates the retention of elements within the solution. On the contrary, MA has a medium chain length with two carboxylic acid functional groups, forming a moderate to high H-bond network that leads to a DES with high viscosity. LA, with a long molecular chain, and CA, with a complex structure with three carboxylic acid functional groups, also lead to high viscosity DESs (Table 3). Finally, despite EG having a short to medium chain length and forming a DES with low viscosity when mixed with ChCl (36 cP [40], Table 3), the resulting mixture exhibits a higher density than ChCl:AA and lacks acidic properties.

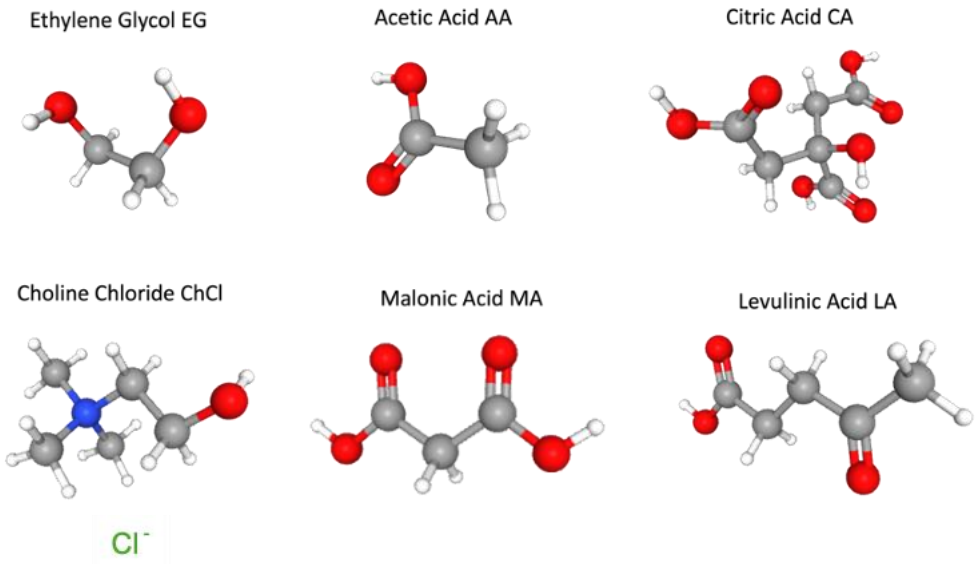

Figure 3. Molecular structures of EG, AA, CA, ChCl, MA, and LA reprinted from Ref. [51].

3.3. Leaching Performance Using ChCl-Based DES:I_2

Figure 4 presents the extraction efficiency of various DESs:I_2 in the leaching process. After 96 h, ChCl:AA:I_2 demonstrated the most selective and rapid leaching, extracting 99% of Cu, 92% of Ni, and 90% of Au. The extraction of Fe was 40%, while Al was below the detection limit. In contrast, ChCl:EG:I_2 exhibited the lowest extraction efficiency and selectivity compared with other DESs:I_2, with 96% of Cu and 50% of Ni, and no extraction of Au, Fe, and Al. This could be due to the lack of HBD acidity and the low affinity for certain metal ions [52]. Similarly, ChCl:LA:I_2 showed slow kinetics and low extraction efficiencies: no Au was extracted, while 86% of Cu, 66% of Ni, 45% of Fe, and 9% of Al were leached after 96 h. Finally, relatively low extraction efficiencies were obtained using ChCl:MA:I_2:15 wt.% water and ChCl:CA:I_2:15 wt.% water: 89% of Cu, 89% of Ni, 43% of Fe, and 7% of Al extracted in the former, and 99% of Cu, 94% of Ni, 93% of Au, 68% of Fe, and 29% of Al in the latter. Their performance was inferior to that of ChCl:AA:I_2, likely due to their higher viscosity, even after the addition of water. Therefore, ChCl:AA:I_2 emerged as the most effective DES for the selective extraction of Cu, Ni, and Au from the PCB powder [53].

The effectiveness of ChCl:AA:I_2 might be attributed to the interactions between ChCl and AA, which likely form a moderate H-bond network, resulting in a DES with a low to average viscosity around 49 cP [49] (Table 3). This low viscosity is crucial, as it strikes a balance between efficient metal ion diffusion and effective complexation, facilitating the selective extraction of valuable metals. The ability of ChCl:AA:I_2 to extract significant amounts of Cu, Ni, and Au while minimizing the co-extraction of Fe and Al, compared with other DESs, could be attributed to the presence of specific chemical functionalities that exhibit a strong affinity for Cu, Ni, and Au. This phenomenon could also be related to the hole theory, as described by Ramon et al. [38]. According to this theory, a vacant electron orbital generates a positive charge or electrophilic site, also known as a hole. This electrophilic site actively attracts and interacts with electron-rich species, facilitating selective leaching mechanisms. The unique characteristics of ChCl:AA:I_2 may enable the creation of such electrophilic sites, enhancing the DES's ability to target and extract specific metals effectively. Furthermore, one possible explanation for this selectivity is the presence of acetate ions that may engage in unique chemical interactions. Smith et al. [40] emphasized that, in DESs, the solvent species with anionic characteristics predominantly govern complexation reactions. In ChCl:AA:I_2, the acetate ions may act as electrophilic sites

that can be complex with metals from the PCBs by attracting and accepting electrons from the metal ions. This electron transfer could drive specific chemical processes, including oxidation and complexation, contributing to the high extraction efficiencies observed for Cu, Ni, and Au. Further, the addition of I_2 plays a crucial role in enhancing the extraction kinetics, primarily by increasing the solubility of metal oxides in the DES matrix through complexation [41]. Jenkin et al. [41] proved that the use of DES:I_2 is favourable for dissolving precious metals, such as Au, even compared with traditional methods like cyanidation (Reaction (R1)):

$$2Au + I_2 \rightleftharpoons 2Au^+ + 2I^- \quad \text{(R1)}$$

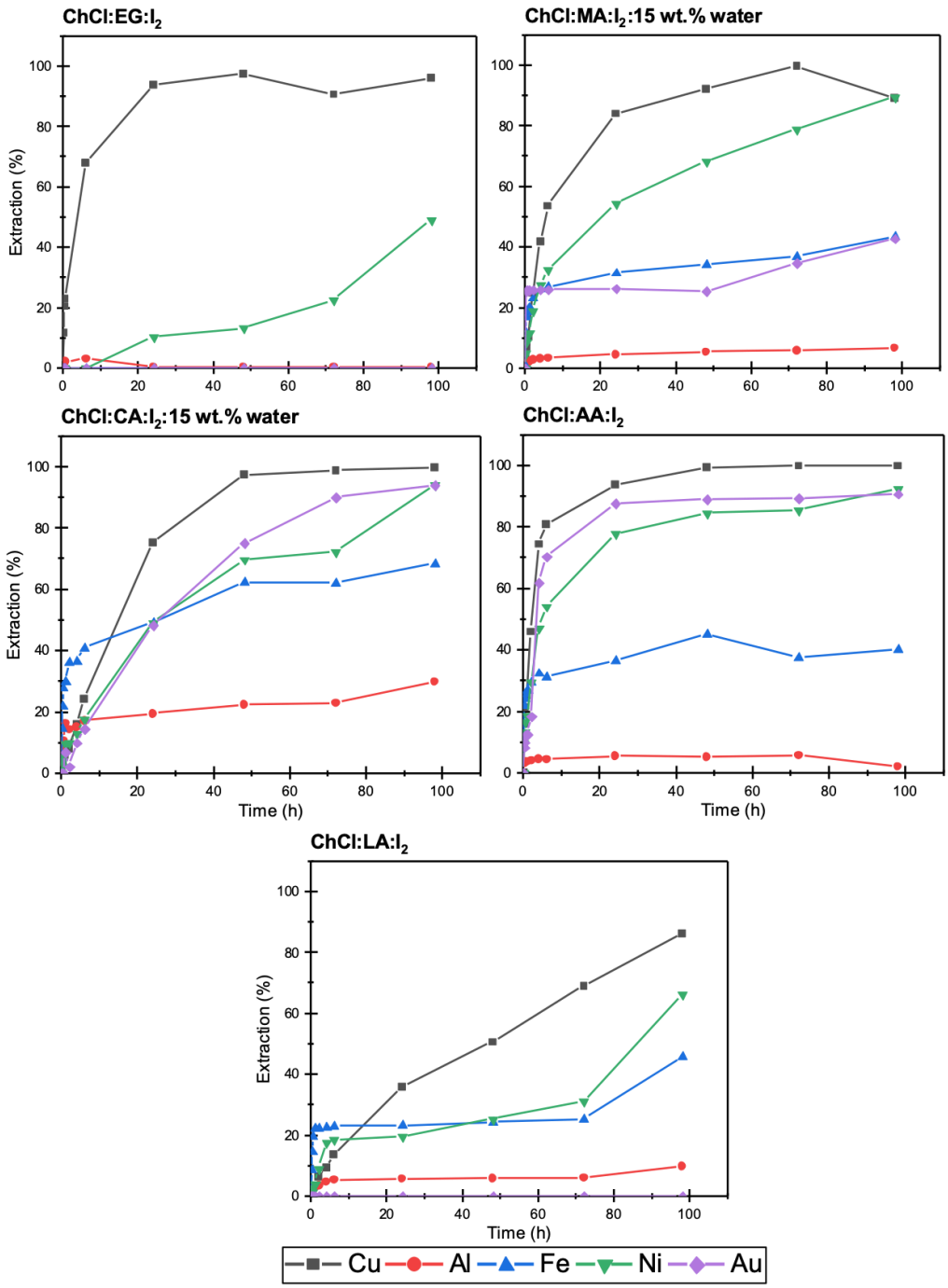

Figure 4. Leaching PCB powder by the DESs with I_2: ChCl:EG:I_2, ChCl:MA:I_2:15 wt.% water, ChCl:LA:I_2, ChCl:CA:I_2:15 wt.% water, and ChCl:AA:I_2, respectively, at 65 °C.

This approach is considered environmentally friendly and safe, reducing the toxic impact associated with cyanide-based processes. The balanced combination of low viscosity, efficient metal leaching, and high selectivity makes ChCl:AA:I_2 a promising choice for sustainable and eco-friendly metal extraction applications.

3.4. The Effect of the HBA and EG on Leaching

Previous studies have demonstrated that DESs containing EG show lower Fe extraction [54,55]. Therefore, the capacity of EG in reducing Fe extraction was investigated by adding 15 wt.% of EG to the ChCl:AA:I_2 DES used. However, as shown in Figure 5, the addition of EG in the ChCl:AA:I_2 DES did not lead to a significant reduction in Fe extraction, which implies that EG primarily acted as a diluting agent rather than enhancing selectivity against Fe extraction. For instance, ChCl:AA:I_2:15 wt.% EG yielded extraction results that closely resembled those of ChCl:AA:I_2, with values of 99% for Cu, 95% for Ni, 99% for Au, 55% for Fe, and 5% for Al after 96 h of leaching at 65 °C. Therefore, the addition of EG did not significantly influence the performance of the DES in terms of selectivity against Fe extraction.

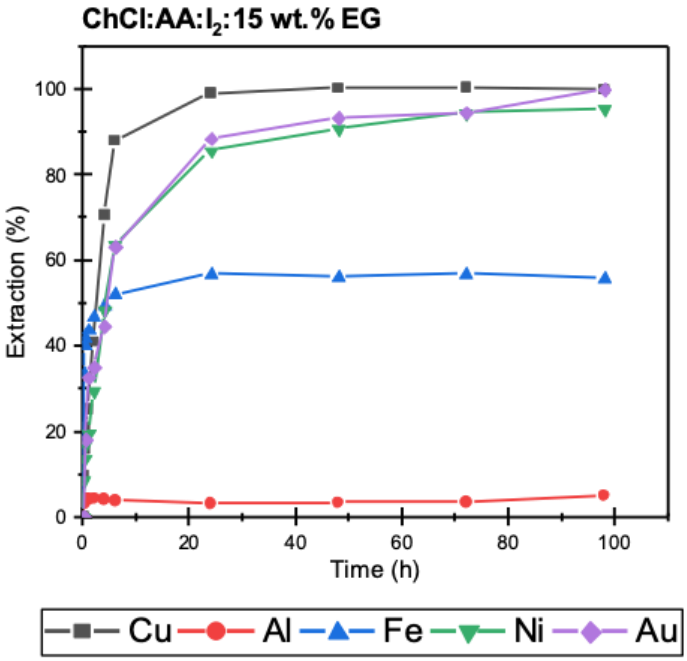

Figure 5. Leaching PCB powder by using ChCl:AA:I_2:15 wt.% EG at 65 °C.

Finally, the use of AA without the addition of the HBA (ChCl) was tested. Leaching tests were conducted using pure AA solutions, both with and without I_2. Figure 6 shows the result after 96 h, revealing that metal extraction in pure AA, with or without I_2, was not as effective as in ChCl:AA:I_2 DES. Using AA in the absence of I_2, the extraction efficiencies dropped to 70% for Cu, 64% for Ni, 0% for Au, 36% for Fe, and 7% for Al compared with ChCl:AA:I_2 in Figure 4. When I_2 was added to AA, the extraction efficiencies obtained were 27% Cu, 81% Ni, 0% Au, 65% Fe, and 13% Al. By contrast, as shown in Figure 4, the ChCl:AA:I_2 DES achieved significantly higher extraction efficiencies for Cu, Ni, and Au, regardless of the extraction levels for Fe and Al. This improved performance is likely attributed to the chemical interactions and the physiochemical and thermal properties of DESs, which enhance the leaching process, as previously discussed [38]. It is important to note that AA alone cannot be classified as a DES because it lacks the H-bond network that forms when combined with ChCl. This hydrogen network is essential for increasing extraction efficiency, as supported by prior studies [35,40,56].

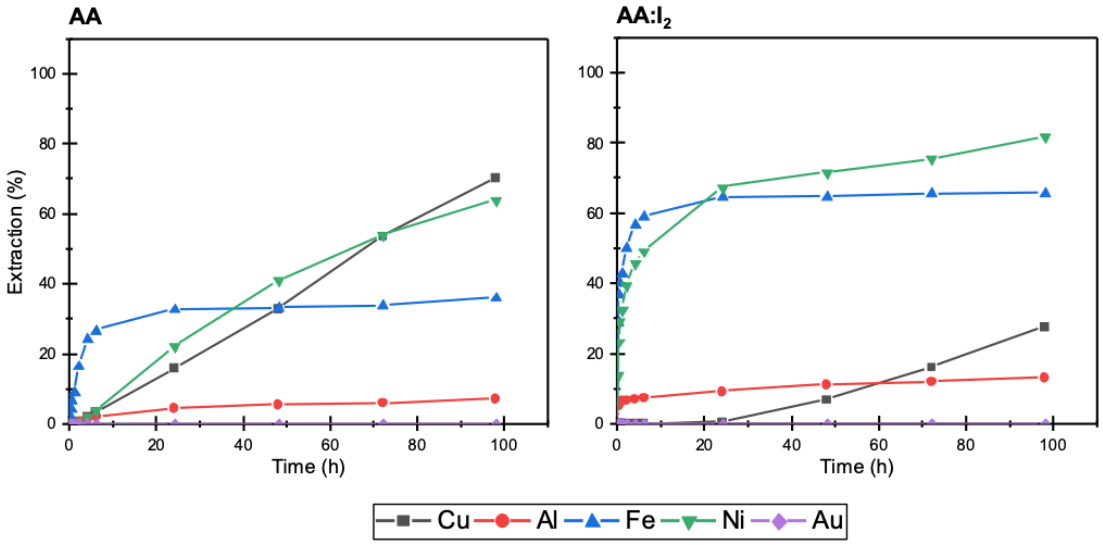

Figure 6. Leaching PCB powder by using AA-based solvents: pure AA and pure AA:I_2 at 65 °C.

4. Conclusions

The investigated DESs demonstrated substantial potential in the selective leaching of CSMs and precious metals, including Cu, Ni, and Au, while aligning with sustainable development principles. The environmentally benign and cost-effective nature of these solvents makes them attractive alternatives to conventional aqueous leaching reagents such as sulfuric acid and hydrochloric acid. This study successfully identified an efficient DES formulation for the selective extraction of Cu, Ni, and Au from PCB waste, also providing valuable insights for future applications in sustainable solvometallurgy. Specifically, ChCl:AA:I_2 emerged as the most effective and selective DES under relatively mild experimental conditions, such as low temperature (65 °C) and moderate stirring speed (300 rpm). This DES:I_2 combination not only exhibited superior performance in extracting Cu (99%), Ni (92%), and Au (90%) but also minimized the co-extraction of undesirable elements like Al (0%) and Fe (40%). Such selectivity is important for optimizing the purity and efficiency for further metal recovery steps. The use of ChCl as an HBA in combination with AA and I_2 proved essential for achieving high extraction yields, as it facilitated the formation of a sufficient H-bond network conducive to metal dissolution. These findings underscore the importance of careful DES selection in the overall leaching performance.

Author Contributions: Conceptualization, S.S., D.M. and G.K.; methodology, S.S., D.M. and G.K.; validation, S.S.; formal analysis, S.S.; resources, G.K.; writing—original draft preparation, S.S.; writing—review and editing, G.K. and D.M.; visualization, S.S.; supervision, G.K.; funding acquisition, G.K. All authors have read and agreed to the published version of the manuscript.

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

Abbreviations

Abbreviation	Definition
E-waste	Electronic waste
PCB	Printed circuit board
CSM	Critical strategic metal
DES	Deep eutectic solvent
IL	Ionic liquid
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
H-bond	Hydrogen bond
ChCl	Choline chloride
EG	Ethylene glycol
MA	Malonic acid
LA	Levulinic acid
CA	Citric acid
AA	Acetic acid
PLS	Pregnant leach solution
S/L ratio	Solid/liquid ratio
MP-AES	Microwave plasma atomic emission spectroscopy

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