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RECYCLING OF PRINTED CIRCUIT BOARDS (PCBS) USING VARIOUS DEEP EUTECTIC SOLVENTS (DESS) AND INSIGHTS FROM DFT SIMULATIONS

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ABSTRACT – In this study, the dissolution of copper present in printed circuit boards (PCBs) was investigated using different choline chloride (ChCl) based deep eutectic solvents (DES) at a temperature of 100 °C for 24 h. According to the results, the two-component combinations ChCl-PTSA (p-toluene sulfonic acid) and ChCl-ACA (acetic acid) achieved nearly complete copper extraction efficiency. In contrast, ChCl-EG (ethylene glycol) showed less than 1% efficiency. The mechanism of copper dissolution in the ChCl-PTSA was examined using DFT simulations. COSMO analysis reveals a hydrogen bond between ChCl's chloride ion (negative potential) and PTSA's hydroxyl group. Mulliken charges show that DES formation causes charge redistribution, increasing polarization within the sulfonate group and stabilizing the DES structure via enhanced electrostatic interactions. In addition, COSMO analysis of DES with Cu(I) and Cu(II) reveals distinct interaction patterns: Cu(I) primarily interacts with chloride and sulfonate groups, disrupting the original hydrogen bonding network, while Cu(II) shows potential coordination with both chloride and sulfonate groups, influencing the electronic properties of the DES.

Keywords: Printed Circuit Board, Deep Eutectic Solvent (DES), Choline Chloride, Cu Recovery.

INTRODUCTION

The digitalization and upgrading of electronic gadgets generate significant amounts of Printed Circuit Boards (PCB)-containing e-waste. To conserve resources and protect the environment, the recycling of such waste is essential [1]. Waste PCBs contain more than 40 kinds of metals with a wide and variable range of concentrations, such as environmentally harmful metals (e.g. Pb, Cr, As, Cd and Hg) and others of economic value (e.g. Cu, Sn, Au, Ag and Pd) [2]. Methods for recycling metals from PCBs include pyrometallurgy, hydrometallurgy, and biometallurgy [2]. Among these methods, hydrometallurgy has been studied more due to its environmental compatibility compared to pyrometallurgy and higher production speed compared to biometallurgy [2]. Traditional leaching methods employ cyanide based or mineral acids chemicals (H_2SO_4, HCl and HNO_3) as major lixiviant [2,3]. potentially resulting in the generation of

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substantial quantities of toxic and corrosive waste [3]. However, further research is required to minimize the environmental impact of hydrometallurgy processes in rational kinetics [4]. Identifying environmentally benign solvents for sustainable chemistry applications has emerged as a crucial challenge, driving extensive research efforts in recent years. Deep eutectic solvents (DESs) have emerged as promising neoteric alternatives due to their advantageous properties, including low cost and high tunability [5–10]. In addition, DESs offer several advantages over conventional acid-based methods, including reduced environmental impact and carbon footprint [11,12]. DES was successfully used to extract Cu, Ni, Zn, and Sn from the PCBs. The leaching efficiency was impressive, with over 75.0% recovery of metals [3]. In addition, Choline chloride-based DESs have shown promising results in leaching various metals, including copper, zinc, and tin [13,14]. Considering the use of oxidants to achieve high efficiency in dissolving metals from PCBs and relatively low efficiency in some DESs, this study aims to achieve one-step dissolution of PCBs in DESs. In this regard, various DESs based on choline chloride were evaluated at a temperature of 100 °C and a duration of 24 h. In addition, the leaching mechanism was evaluated by DFT simulation.

EXPERIMENTAL

Material

The sequential process for PCB preparation process, starting with dismantling personal computers to extract PCBs. Next, electronic chipsets are removed from the PCBs, followed by shredding. Finally, the PCB samples are screened to achieve a particle size of less than 1 mm. This sample was used to evaluate dissolution in different DESs. Two-component DES was synthesized by mixing of a fixed component: choline chloride (ChCl) ($(CH_3)_3NCH_2CH_2OH)Cl$ (>98%, Merck) as the hydrogen bond acceptor (HBA) along with a second variable component including: formic acid (FA, HCOOH, >99%, Merck), lactic acid (LA, $C_3H_6O_3$, >98%, Merck), fructose (F, $C_6H_{12}O_6$, >98%, Merck), acetic acid (ACA, CH_3COOH, >99%, Merck), thiourea (T, CH_4N_2S, >98%, Merck), oxalic acid (OA, $C_2H_2O_4$, >95%, Merck), ethylene glycol (EG, $C_2H_6O_2$, >99%, Merck), p-toluene sulfonic acid (PTSA, $C_7H_8O_3S.H_2O$, >98%, Merck), urea (U, CH_4N_2O, >99%, Merck), malonic acid (MOA, $C_3H_4O_4$, >99%, Merck), maleic acid (MA, $C_4H_4O_4$, >99%, Merck), with mentioned mol ratio mentioned in Table 1. This mixture was heated at 70 °C for one hour in a 15-ml glass vial within an oil bath. To obtain a completely transparent mixture, the temperature was increased to 80 °C, and continuously stirred with a magnet. It is worth mentioning that, in order to reduce experimental error due to the significant moisture absorption by these substances, the materials were thoroughly dried in an oven at 70 °C for 3 h before the synthesis.

Table 1 The characteristics of different DES and their mol ratio

ChCl: FA	ChCl: LA	ChCl:F	ChCl:A CA	ChCl: T	ChCl :OA	ChCl: EG	ChCl:P TSA	ChCl :U	ChCl: MOA	ChCl :MA
2:1	1:1	1:1	1:1	1:2	2:1	1:2	2.4:1	1:2	1:1	1:1

Analysis and characterization

The PCB was characterized using XRD, Philips PW-3710 diffractometer equipped with a Cu K_α radiation source (λ = 1.54056 A). The analysis of metals was conducted by dissolving 1 g of PCB in a 20 ml aqua regia, and then, it was made up to 100 ml with deionized water. Finally, the concentration of Cu in the filtrate was determined using atomic adsorption spectroscopy (Varian 240AA). In addition, the solution after the leaching process was subjected to AAS analysis for calculating the Cu recovery.

Leaching in DES

During the leaching stage, 0.1 g of PCB was added to 5 g of DES. All experiments were conducted in a 15 ml glass vial placed in an oil bath at 100 °C for 24 h, with uniform stirring using a magnet (400 rpm). After the leaching process, the solution was filtered immediately, the solution was used for metal analysis and leaching residue used for further analysis. The flowchart for leaching process is summarized in Fig. 2. The Cu recovery was calculated using the following equation:

$$R_{Cu}(\%) = \frac{C_{Cu} \times V}{m \times A} \times 100 \quad (1)$$

where C_{Cu} is the concentration of Cu (g/l), V is the volume of the leaching solution (l), m is the mass of powders of PCB (g), and A is the grade of metal in the mixture of PCB.

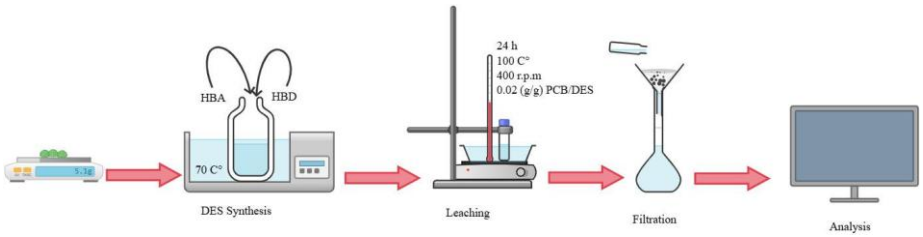


Figure 2 Flowchart of PCB leaching in different DESs

DFT simulation

The simulation utilized Materials Studio's DMol3 module for density functional theory (DFT) calculations to analyze a ChCl and PTSA DES, both in pure form and after copper leaching. The computational approach involved systematic geometry optimization and electronic structure analysis under varying conditions. Initially, a coarse geometry optimization was performed using the GGA-BLYP functional with TS dispersion correction, a DN basis set, and coarse integration accuracy. This was followed by a refined optimization using the GGA-PBE functional, a DNP basis set, medium integration accuracy, and a medium k-point grid. Solvation effects were simulated using the COSMO (Conductor-like Screening Model) with DMol3-PBE parametrization. Analyses included evaluating the COSMO surface and Mulliken charge distribution for ChCl, PTSA, DES, and

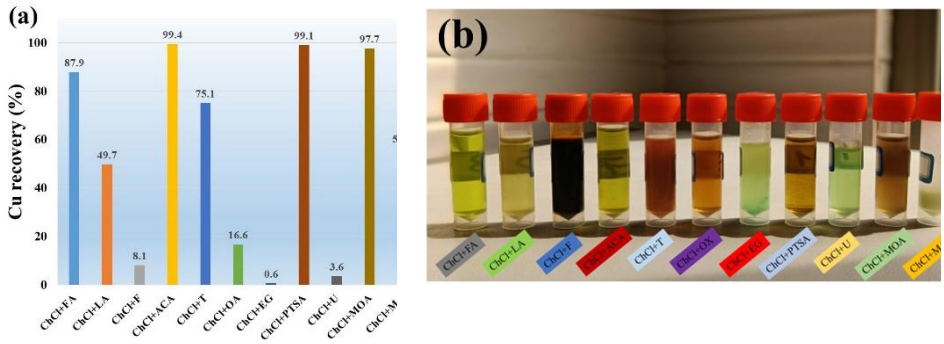
DES containing monovalent and divalent copper species, ensuring a comprehensive understanding of ionic interactions and solvation effects in the DES environment.

RESULTS AND DISCUSSION

Results of leaching experiments

Copper recovery from different DESs varies significantly, as shown in Fig. 3, with ChCl+ACA and ChCl+PTSA demonstrating the highest recovery rates at 99.10% and 99.40%, respectively. ChCl+MOA (97.70%) and ChCl+FA (87.93%) also exhibit high recovery percentages, while ChCl+T shows a moderate recovery of 75.12%. DES such as ChCl+MA and ChCl+LA result in recoveries of 56.40% and 49.71%, respectively. In contrast, ChCl+F and ChCl+U have much lower recovery rates at 8.14% and 3.56%, and ChCl+EG shows the lowest Cu recovery at 0.61%. Finally, ChCl+OA has a recovery rate of 16.64%.

Recently, ChCl-based DESs with various hydrogen bond donors have demonstrated significant potential in selectively leaching copper from PCBs [11,13]. Reported recovery rates for copper using DESs are approximately 75%, showcasing their efficiency compared to traditional methods [13,15]. For example, Liu et al. utilized a ChCl-ethylene glycol DES in combination with 5 wt.% hydrogen peroxide as an oxidizing agent to efficiently extract copper under mild conditions (25 min, 20 °C), highlighting the method's practicality and environmental benefits [11]. Additionally, Abbott et al. investigated the leaching mechanism and found that metal complexes, particularly MCl_x^- species, form extensively in choline chloride-based DESs, contributing to their high selectivity and efficiency in metal recovery [16].



Figre 3 (a) Cu recovery in different DESs and **(b)** their color

DFT results

DFT of ChCl and PTSA

The COSMO surface of ChCl, as shown in Fig. 4a, reveals a clear charge separation with negative potential around the chloride ion and positive potential near the choline moiety, particularly around the hydroxyl groups. This distribution highlights the molecule's polar nature and role in interacting with hydrogen bond donors (HBD) to form

a DES. The Mulliken charge distribution (Fig. 4b) further emphasizes this separation, with the chloride anion carrying a significant negative charge (-0.669) and the nitrogen atom in the choline cation having a positive charge (+0.171). The oxygen atom of the hydroxyl group is also negatively charged (-0.502). In contrast, carbon atoms bonded to nitrogen have slight negative charges and hydrogen atoms exhibit positive charges, indicating delocalization of positive charge across methyl and methylene groups.

The COSMO surface of PTSA (Fig. 4c) shows negative potential concentrated around the sulfonate group (-SO3H) and positive potential across the aromatic ring and methyl group, reflecting its acidic nature and capacity to act as an HBD in DES formation. The Mulliken charge distribution (Fig. 4d) highlights significant charge localization within the sulfonate group, with the sulfur atom having a substantial positive charge (+1.373) and oxygen atoms exhibiting negative charges (-0.624 and -0.541). The hydroxyl oxygen is also negatively charged (-0.624), while carbon atoms in the aromatic ring have varying charges, and hydrogen atoms exhibit positive charges.

These complementary electrostatic characteristics drive the interaction between ChCl and PTSA. ChCl, acting as a hydrogen bond acceptor (HBA), has a concentrated negative potential around the chloride ion, facilitating strong electrostatic attraction with the positively polarized hydrogen atoms of PTSA's sulfonic acid group. PTSA, as an HBD, features a highly positive sulfur atom and acidic hydroxyl hydrogen, enabling effective hydrogen bonding with ChCl's chloride ion. The negative potential on sulfonate oxygens stabilizes the interaction by attracting ChCl's positive regions. These charge and potential complementarities suggest that strong hydrogen bonding and electrostatic interactions between ChCl and PTSA facilitate the formation of a stable DES.

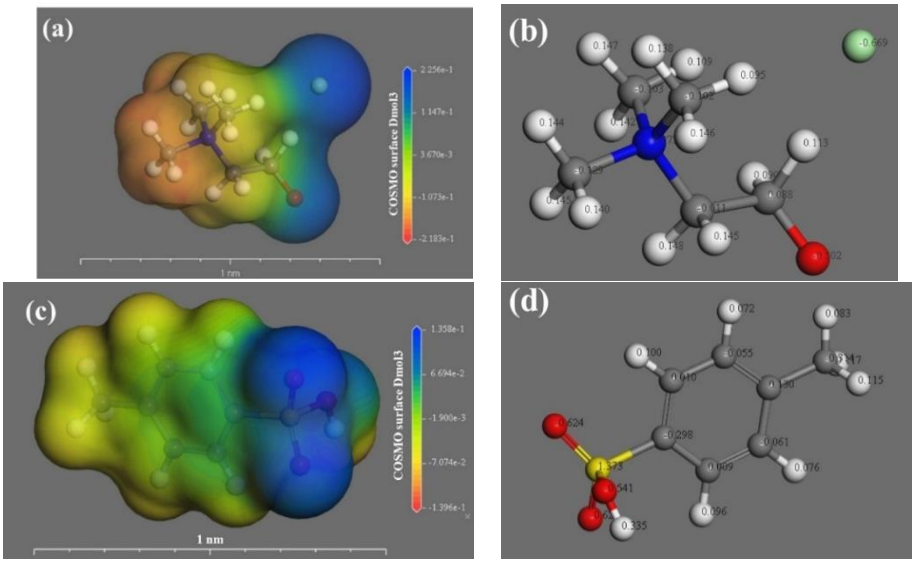


Figure 4 DFT-calculated COSMO surfaces **(a, c)** and Mulliken charges **(b, d)** for ChCl and PTSA

DES

Fig. 5 illustrates the COSMO surface and Mulliken charges of the DES composed of ChCl and PTSA. The ChCl component shows a prominent negative potential around the chloride ion, indicating its role as a hydrogen bond acceptor, and positive potential around the methyl groups bonded to nitrogen. The PTSA component exhibits negative potential around the sulfonate group and transitions from near-neutral to slightly positive potential on the aromatic ring. The spatial arrangement of the negative chloride ion near the positive hydroxyl group of PTSA confirms the formation of a hydrogen bond, which is crucial for DES stability. The Mulliken charge distribution reveals key electrostatic features: the chloride ion carries a significant negative charge (-0.618), the sulfur atom in PTSA bears a large positive charge (+1.403), and the sulfonate oxygens exhibit substantial negative charges (-0.605 to -0.645). These charges facilitate stabilizing electrostatic interactions and hydrogen bonds within the DES.

Compared to the individual components, the Mulliken charge distribution in the DES shows a redistribution of charge density. The chloride anion's charge decreases from -0.669 to -0.618, and the hydroxyl oxygen's charge changes from -0.502 to -0.450, reflecting its involvement in hydrogen bonding. In PTSA, the sulfur charge increases from +1.373 to +1.403, and the sulfonate oxygens' charges adjust, indicating increased polarization and charge localization. These shifts enhance electrostatic interactions with the choline cation and confirm the establishment of intermolecular forces and hydrogen bonding that stabilize the DES structure.

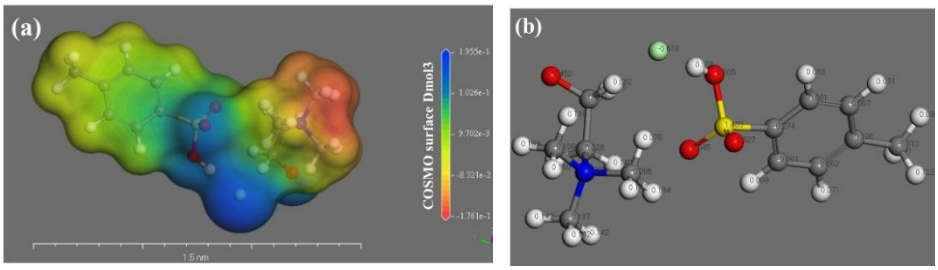


Figure 5 DFT-calculated COSMO surfaces **(a)** and Mulliken charges **(b)** for DES.

DES containing metal ions

Fig. 6 illustrates the COSMO surface of the DES with monovalent (Cu(I)) and divalent (Cu(II)) copper. For Cu(I), the ChCl portion shows strong negative potential around the hydroxyl oxygen, indicating high electron density and no involvement in copper complexation. The chloride ion exhibits a reduced potential, nearing neutral, while the PTSA sulfonate group shows negative potential, and the aromatic ring transitions from near-neutral to slightly positive. Incorporating Cu(I) alters the electronic structure and intermolecular interactions, with the chloride ion and sulfonate group potentially interacting with Cu(I), disrupting the original hydrogen bonding network.

In the Cu(II) system, the COSMO surface reveals a charge distribution with the ChCl hydroxyl oxygen having strong negative potential, suggesting it does not participate in

Cu(II) complexation. The methyl groups bonded to nitrogen show positive potential. The PTSA component displays negative potential around the sulfonate group and a transition to slightly positive potential on the aromatic ring. The presence of negative potential around the sulfonate group and the chloride ion indicates potential complexation sites for Cu(II), influencing the electronic properties and reactivity of the DES-Cu(II) system. Overall, these visualizations highlight varying electrostatic potentials and potential interaction sites within the DES-Cu(II) system.

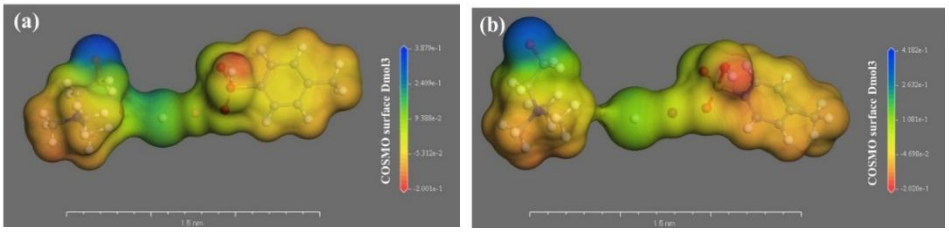


Figure 6 COSMO surface analysis ChCl:PTSA DES containing **(a)** Cu(I) and **(b)** Cu(II).

CONCLUSION

In conclusion, this study highlights the significant variability in Cu recovery rates among different DESs, with ChCl+ACA and ChCl+PTSA demonstrating the highest recoveries, about 100 %. The COSMO and Mulliken charge distributions provide valuable insights into the molecular interactions driving DES formation, particularly between ChCl and PTSA. These interactions are characterized by strong HBD and HBA as well as electrostatic attractions, which stabilize the DES structure. Incorporating Cu(I) or Cu(II) alters the electronic structure and intermolecular interactions within the DES, with potential complexation sites identified around the Cl ion and the -SO_3H group.

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