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Polycarboxylic Acid-Based Deep Eutectic Solvents for Critical Metal Recovery from Lithium-Ion Batteries: Kinetic and Efficiency Analysis

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Abstract

To meet the high demand for lithium-ion batteries (LIBs) and their corresponding challenges, effective and sustainable recycling methods are necessary. This research explores the use of deep eutectic solvents (DES) based on polycarboxylic acid to recover critical metals, such as lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn) from spent LIBs. The leaching efficiency of 3 DES was evaluated under various conditions by synthesizing them with succinic acid, malonic acid, and maleic acid using choline chloride. Optimal recovery was achieved with ChCl: Maleic acid, yielding 99.18 wt. % Li, 65.36 wt. % Co, 94.97 wt. % Ni, and 67.88 wt. % Mn at a S/L ratio of 20 g/L at 80 °C with constant stirring. Higher S/L ratios led to reduced recovery rates due to mass transfer limitations and solution saturation. Kinetic modeling revealed that the Jander model best described the leaching mechanism, suggesting a diffusion-controlled process. The activation energy calculation on DES ChCl: Maleic acid produces Li 38.57 kJ/mol, Co 63.09 kJ/mol, Ni 64.87 kJ/mol, and Mn 52.64 kJ/mol. The use of DES derived from eco-friendly polycarboxylic acids (succinic, malonic, and maleic acids) in this study represents an innovative way to recover critical metals from spent lithium-ion batteries (LIBs) in a sustainable and effective manner. Future studies are advised to examine the DES composition and investigate how agitation influences the recovery of specific metals.

Keywords: Lithium-ion batteries, DES, ChCl, Succinic acid, Malonic acid, Maleic acid

Introduction

The global energy crisis has significantly boosted the development of new vehicle energy sources. For example, the global energy crisis has driven advances in electric vehicles that aim to reduce dependence on fossil fuels and improve transportation sustainability [1]. This trend is expected to increase the production and demand for LIB used in vehicles. However, the widespread application of LIBs also raises several issues, including including the need for more critical resources and difficulties in processing spent LIBs [2]. The difficulty in processing used LIBs arises from their complex composition, presence of hazardous materials, challenges in efficient separation, economic concerns, and potential environmental impacts. These challenges emphasize the urgency of advancing recycling technologies in LIB waste management. Advances in recycling technologies and strategies are essential to address these challenges effectively. Piles of used LIBs contain high levels of toxic heavy metals and hazardous electrolytes, which can cause environmental damage [3]. Thus, efficiently recycling spent LIBs is crucial for addressing the shortage of metal resources while

minimizing environmental pollution. Recycling of LIBs is necessary not only to manage environmental and economic impacts but also to support sustainability and resource efficiency.

In recent years, the hydrometallurgical process is often used to recycle spent lithium-ion batteries. Compared to pyrometallurgical processes, hydrometallurgical processes offer benefits such as higher purity, greater metal recovery efficiency, and lower energy consumption. In traditional hydrometallurgical processes, such as nitric acid, sulfuric acid, and hydrochloric acid as inorganic acids are usually used because they can produce highly efficient leaching [4]. Finding alternative leaching agents is crucial to achieve a balance between efficient metal recovery and environmental sustainability when using inorganic acids. Still inorganic acids are relatively corrosive and can cause a lot of acidic wastewaters, which can cause environmental pollution [5]. Therefore, some researchers choose environmentally friendly and safe organic acids like citric and DL-malic acid over strong inorganic acids [6]. However, organic acids are generally less efficient in extraction, so it is necessary to incorporate reducing agents like H_2O_2, Na_2SO_3, or other similar agents into the process to enhance solubility and accelerate reaction rates [6]. Consequently, to recover critical metals from used lithium-ion batteries, it's miles essential to broaden solvents with better extraction efficiency, decrease fees, and which can be greater environmentally friendly. Deep eutectic solvents (DES) are emerging as leaching agents that show outstanding extraction efficiency for critical metals like a nickel, cobalt, and lithium, which is often found in lithium-ion [7]. DES are advantageous due to their customizable properties, which enhance metal solubility and extraction. DES synthesis generally involves easy and simple procedures, thus potentially reducing production costs.

Lately, DES has attracted worldwide attention. DES has advantages such as simple manufacturing process, biodegradability, low toxicity, good thermal and chemical stability, and environmental friendliness [8]. DES consists of 2 or more hydrogen donors and hydrogen acceptors which perform well in dissolving metallic oxides, with have much greater efficiency than aqueous solutions [9]. Wang *et al.* [10] obtained a high Li 94.7 % Co 97.9 % leaching efficiency at 180 °C for 12 h using DES choline chloride and urea. On the other hand, in Lu's study leaching LCO powder at an S/L ratio of 100 mg/ 5 mL with a temperature of almost 150 °C for 24 h using DES ChCl:Malonic acid resulting in a leaching efficiency of 96.4 % [11]. Deep eutectic solvents (DES) are crucial in efficiently recycling spent lithium-ion batteries (LIBs).

This research explores using Deep Eutectic Solvents (DES) to recycle lithium-ion batteries (LIBs). DES effectively dissolves metals and offers an eco-friendly alternative, making them an attractive solution for improving LIB leaching and recycling processes while addressing challenges associated with conventional solvents. Previous research indicates that achieving high recovery rates often necessitates elevated temperatures during the LIB leaching process. This research investigates an efficient leaching approach using DES based on polycarboxylic acids, with variations in Hydrogen Bond Donors (HBD), temperature, and solid-to-liquid ratios, aiming to enhance leaching efficiency.

Materials and methods

Materials and instrumentation

The chemicals used in this research include choline chloride ($C_5H_{14}C_1NO$) sourced from Himedia, maleic acid ($C_4H_4O_4$), succinic acid, malonic acid as well as nitric acid and hydrochloric acid, all get from Merck.

Table 1 The main chemical composition of LIB.

Element	LE	Ni	Mn	Al	Co	Si	Fe	Cu	P	Hf	S	Sb	Sn
Mass fraction (wt.%)	63.137	14.817	14.571	0.340	5.926	0.355	0.467	0.142	0/094	0.054	0.058	0.026	0.013

*LE: Light elements

The first process for the battery is to disassemble the lithium-ion battery to separate its internal components manually. Next, the battery cathode is collected, and a ball mill is used to grind it finely. It is

then sieved through a 270 mesh (53 μm) sieve. Used lithium-ion batteries that have passed through the 270-mesh sieve are called black mass and can be used in the next process. Portable XRF characterization was conducted to determine the main chemical components in the black mass (**Table 1**). Meanwhile, an XRD tool (Panalytical, Expert3 Powder) is used to show the main phase in the raw material. Elemental analysis of black mass was done by digesting the black mass with aqua regia. Then, ICP-OES characterization (Analytic Jena, Plasma Quant 9000 Elite, Germany) was used to determine the initial metal content analyzed.

Deep eutectic solvent preparation and analysis

This DES synthesis utilizes a hydrogen bond donor (HBD) that is choline chloride and various hydrogen bond acceptors (HBAs) namely succinate, malonic acid, and maleic acid. DES synthesis was done by mixing HBD and HBA at 70 °C for 2 h with constant stirring at 1000 rpm. Then, a homogeneous transparent solution was obtained. The synthesized deep eutectic solvent (DES) was measured for pH value and density. In addition, the deep eutectic solvent (DES) was analyzed using FT-IR.

Leaching and analysis

In the leaching process, DES was first heated in a 3-neck round flask to a predetermined temperature and then a certain amount of LIB that had passed the 270-mesh sieve was added. In this process, solvent variations were conducted (DES ChCl:Succinic acid, DES ChCl:Malonic acid and DES ChCl:Maleic acid), and solid/liquid variations (10,20,30,40 and 50 gr/L). After the leaching experiment, the DES containing the metal was centrifuged to separate the filter and residue. Then, the leach solution was diluted with a 2 % nitric acid solution to determine the metal concentration using ICP-OES. The recovery of Li, Co, Ni, and Mn is characterized by ICP-OES analysis and can be calculated using the following Eq. (1) [12].

$$\eta = \left(\frac{CE \times v}{C \times m}\right) \times 100\ \% \quad (1)$$

where: CE is a final concentration of (Li, Co, Ni and Mn) in solution (mg/L),

V is the volume of the solution resulting in the initial (L)

C is the mass fraction of (Li, Co, Ni and Mn) content in the sample (mg/g)

m is the total mass of the sample used in the leaching process (g).

Results and discussion

Characterization of lithium-ion batteries

The X-ray diffraction (XRD) analysis provides a comprehensive characterization of the active materials in the lithium-ion battery (LIB). The primary phases identified in the raw materials (**Figure 1**) are $Li_1Ni_{0.45}Mn_{0.4}Co_{0.15}O_2$ (ICSD 98-005-5374) and graphite (ICSD 98-007-6767) as confirmed by their corresponding ICSD patterns.

Blue squares for graphite and red circles for NMC (Nickel Manganese Cobalt) are highlighted in the XRD spectra, which show distinct diffraction peaks for both phases. The positions of these peaks correspond to specific diffraction angles (2 theta), providing evidence of the crystalline structure of these materials. Furthermore, the intensity and clarity of these peaks validate the sample's high degree of crystallinity. The absence of significant amorphous background or extraneous phases suggests high purity of the raw materials, crucial for battery performance. The primary phase, $Li_1Ni_{0.45}Mn_{0.4}Co_{0.15}O_2$, is characteristic of NMC lithium-ion batteries. This composition, with a nickel-to-manganese-to-cobalt ratio of 45:40:1. The presence of graphite further supports its role as the anode material, widely used for its excellent lithium intercalation and deintercalation properties. Together, these phases form the foundation of a high-performance LIBs.

Then, the initial metal content was analyzed using ICP-OES. The chemical composition of crucial base metals in black mass, as determined by aqua regia digestion, is summarized in **Table 2**.

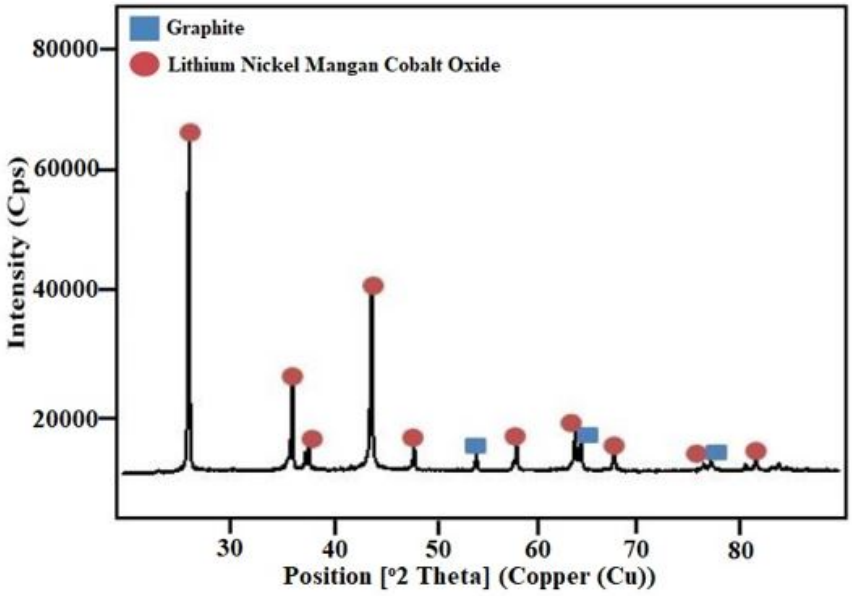

Figure 1 XRD spectrum of the spent LIB cathode.

Table 2 Chemical composition of critical base metals in LIB (after aqua regia digestion).

Sample code	Concentration (wt.%)			
	Li	Co	Mn	Ni
LIB	3.79	8.22	15.74	14.31

Synthesis and characterization of deep eutectic solvents (DES)

The data on the results of making DES with several variations of HBD (hydrogen bond donor) are shown in **Table 3**. In **Table 3**, each DES has an acidic pH and ChCl:Maleic acid DES has the most acidic pH among others. A lower pH (more acidic) can increase the solubility of certain metals, and at low pH, metals can form soluble complexes with acids. In addition, this DES also has a higher density than to water solvents. DES density that is too high can hinder the movement of the leaching solution, thereby reducing the contact between the solution and the leached material. Thus, the density and pH of DES have an essential role because they can affect the extraction reaction rate and the metals' solubility in the leaching process [13].

Table 3 The data on the results of making DES with several variations of HBD

DES	HBD	HBA	Density (gr/mL)	pH	Physical properties
ChCl: SA	Choline chloride (ChCl)	Succinic acid (SA)	1.2168	1.91	Clear liquid
ChCl: MA	Choline chloride (ChCl)	Maleic acid (MA)	1.2148	0.18	Clear liquid
ChCl: MAA	Choline chloride (ChCl)	Malonic acid (MAA)	1.2128	0.68	Clear liquid

The first DES synthesis, namely ChCl: Succinic acid, was characterized by FTIR in the wave number range 4000 - 500 cm^{-1}, as shown in **Figure 2**. Choline chloride has a wide band at wave numbers 3219.57, 3026.01, and 3005.48 cm^{-1}, which illustrates a hydroxide group (–OH) [49]. Meanwhile, the carboxyl group (–CO) absorption from succinic acid is 1195.88 cm^{-1}, and in DES ChCl:Succinic acid it shifted to 1209.65 cm^{-1}. This implies that the presence of hydrogen bonds generally results in a decrease in

vibrational frequency due to the weakening of the C=O bond strength in the carboxyl group [14]. Then the wave number range 892.81 - 953.12 cm^{-1} show the presence of quaternary ammonium ions from choline chloride. The shift of the OH group from 3026.01 cm^{-1} in ChCl to 3021.09 cm^{-1} in ChCl:Succinic acid indicates the presence of hydrogen bonds.

Figure 2(b) shows the FTIR spectrum of DES ChCl: Malonic acid. The FTIR spectrum reveals strong absorption at wave numbers 3219.57 and 2990.91 cm^{-1}, characterized by a broad absorption band, indicating the presence of hydroxide groups (–OH) in both choline chloride and malonic acid. Furthermore, after the formation of DES ChCl:Malonic acid, the intensity of the peak associated with the hydroxide group (–OH) in DES expanded and shifted to the wave number area around 3320.83 and 2919.68 cm^{-1}. At wave number 1694.09 cm^{-1}, the C-O stretching vibration of the carboxyl group in malonic acid is observed, while in the DES ChCl: Malonic acid, it is slightly shifted to the region of 1717.06 cm^{-1}. This change indicates the involvement of O-H groups in hydrogen bonding interactions with Cl [15].

Furthermore, **Figure 2(c)** shows the FTIR spectrum of the last DES, namely DES ChCl:Maleic acid. The absorption peak corresponding to the hydroxide group (–OH) in maleic acid is at a wave number of around 3057.66 cm^{-1}. Meanwhile, there is a strong absorption indicating the presence of a carboxyl group in maleic acid at wave number 1632.69 cm^{-1}. Furthermore, there is an absorption at 1481.55 cm^{-1}, which shows that there is a –NH bond in choline chloride shifted to 1476.61 cm^{-1} in ChCl: Maleic acid. Then, there is an amine group at wave number 1084.16 cm^{-1}, which shifts to 1082.07 cm^{-1} on choline chloride. Additionally, absorption at 953.12 cm^{-1}, corresponding to the –CN group in choline chloride, shifts slightly to 953.50 cm^{-1} in DES ChCl acid. Shifts in wavenumbers can be influenced by various factors, including hydrogen bonding, which weakens the electrostatic forces and causes absorption shifts. Furthermore, hydrogen bonding can lead to a decrease in absorption intensity and broadening of the absorption band [16].

Based on FTIR analysis of the 3 synthesized DES, each has different chemical characteristics and functional groups. All 3 DES contain carboxylic acid groups, but maleic acid shows a characteristic peak of C=C unsaturated double bond (around 1600 cm^{-1}). The unsaturation of maleic acid provides a unique reactivity, which may enhance its ability to form complexes with metal ions. This characteristic may improve its solvency properties compared to the other 2 DESs [17].

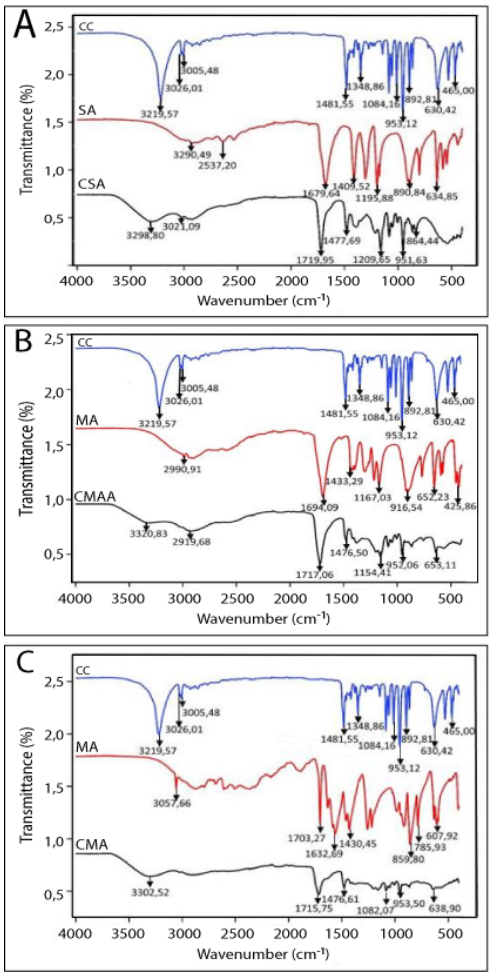

Figure 2 FTIR spectra of (A) DES ChCl: Succinic Acid, (B) DES ChCl:Malonic Acid, (C) DES ChCl: Maleic Acid.

Leaching of lithium-ion batteries

In this leaching process, DES variations, temperature variations, and solid/liquid variations were used to find efficient temperature conditions and solid/liquid ratios. The effect of leaching temperature studied was 30, 55 and 80 °C on DES variations ChCl: Succinic acid, ChCl: Maleic acid, and ChCl: Malonic acid with a constant solid/liquid variable of 20 gr/L and continuous stirring of 1000 rpm. **Table 4** shows an increase in the yield of Li 20.57, Co 1.39, Ni 11.53, and Mn 3.32 % (30 °C) to Li 48.85, Co 16.75, Ni 23.76, and Mn 15.86 % (80 °C). However, Ni experienced a decrease at a temperature of 55 °C and increased again at 80 °C. Meanwhile, **Table 4** shows an increase in recovery from Li 22.81, Co 4.85, Ni 6.56, and Mn 7.44 % (30 °C) to Li 84.86, Co 45.82, Ni 68.42 and Mn 67.88 %. The recovery of Li, Co, Ni, and Mn in the leaching process increases with increasing temperature. This is in line with the hypothesis that there increase in the kinetic energy of molecules and ions and an increase in collisions between reactants due to an increase in temperature. In addition, increasing the temperature can cause more active molecules, accelerating the reaction rate [18].

In the 3 temperature variations in the 3 DES used in the leaching process, it is observed that the highest leaching percentage occurs for the element lithium rather than for the elements cobalt, manganese, and nickel. In metal oxide structures such as $LiNi_xMn_yCo_zO_2$, lithium has weaker bonds and is more easily released from the oxide structure compared to Co, Ni and Mn. This makes Li easier to dissolve and extract than other metals. In addition, lithium is an alkali group, where the alkali group has high reactivity Zhang *et al.* [19], and lithium has higher solubility or solubility properties compared to cobalt, manganese, and nickel. This shows that the percentage of lithium in the leaching process is more significant than cobalt, manganese and nickel.

Table 4 Leaching recovery with temperature variation at various deep eutectic solvents (20 gr/L, constant stirring 1000 rpm for 2 h).

DES	Temperature (deg.C)	Recovery			
		Li (wt.%)	Co (wt.%)	Mn (wt.%)	Ni (wt.%)
ChCl: Succinic acid	30	20.57	1.39	3.32	11.53
	55	23.38	3.82	5.04	5.18
	80	48.85	16.75	15.86	23.76
ChCl: Malonic acid	30	22.77	4.85	7.44	6.56
	55	77.69	31.95	47.56	52.37
	80	84.83	45.91	62.18	68.42
ChCl: Maleic acid	30	56.69	11.50	17.87	22.99
	55	85.74	37.31	40.03	56.17
	80	99.18	65.36	67.88	94.98

The leaching process of NMC used DES ChCl: Succinic acid, DES ChCl: Maleic acid, and DES ChCl: Malonic acid involved several steps. The first stage is protonation, where protons (H^+) in DES are replaced by metal ions (Me^+). [20]. Then the next stage is the reduction of high-valence metals with succinic acid, maleic acid and malonic acid [2]. For example, in NMC Co^{3+}, has been reduced to Co^{2+}, and Mn^{4+} has been reduced to Mn^{2+}. Subsequently, chloride anions are added to create chloro (chlorometalate) metal complexes [21]. Furthermore, Co^{2+} can form a cobalt chloride complex with Cl from ChCl to be more soluble in DES and can be extracted. Cobalt (II) tends to form complexes with ligands that can form strong and stable bons. In this case, chloride (Cl^-) is a ligand that can coordinate well with metal ions, while polycarboxylic acid may not provide the same stability [22]. Thus, it can be assumed that the presence of succinic acid, maleic acid and malonic acid as reducing agents.

Table 5 presents the percentage recovery of leaching with varying solid/liquid (S/L) ratios for different deep eutectic solvents (DES) used. High recovery percentages for Li, Co, Mn, and Ni were achieved at an S/L ratio of 20 gr/L with both DES ChCl: Malonic acid and ChCl: Maleic acid. Beyond this ratio, recovery rates declined, likely due to an increased concentration of the solid sample, which could negatively impact the mass transfer coefficient and reduce leaching recovery [23]. In the case of DES ChCl acid, a high recovery of Co, Mn, and Ni was similarly observed at an S/L ratio of 20 gr/L, while Li achieved a high recovery only at an S/L ratio of 40 gr/L. Thus, selecting the appropriate S/L ratio is critical for maximizing recovery and optimizing the leaching process. In addition, excessive amounts of DES will cause reagent wastage and be detrimental to subsequent metal separation [24]. Overall, 20 gr/L was considered as the optimal S/L ratio. It can be seen in **Table 5** that Mn recovery using ChCl: Malonic acid and ChCl: Maleic acid DES does not occur efficiently at high solid/liquid ratios due to insufficient solubility, complexation, and reduction issues for Mn. Differences in chemical reactivity, product stability, and viscosity effects also contributed to the lack of Mn recovery compared to Li, Co, and Ni as the solid/liquid ratio increased [25]. The solid/liquid ratio increases, Li recovery does not decrease when using ChCl: Succinic acid DES because it may have a higher solvent capacity for lithium. This means that ChCl: Succinic acid DES can dissolve more lithium in its solution, so its effectiveness remains high even at higher solid/liquid ratios [26].

Table 5 Leaching recovery with S/L variation at various deep eutectic solvents (Temperature 80 °C, constant stirring 1000 rpm for 2 h).

DES	Ratio Solid/Liquid (gr/L)	Recovery			
		Li (wt.%)	Co (wt.%)	Mn (wt.%)	Ni (wt.%)
ChCl: Succinic acid	20	48.85	16.75	15.86	23.76
	30	28.71	11.99	11.99	17.13
	40	55.31	6.93	7.52	10.02
	50	48.49	7.51	7.65	11.15
ChCl: Malonic acid	20	84.83	45.91	62.18	68.42
	30	76.80	40.78	54.99	60.49
	40	84.30	44.16	0.60	61.63
	50	70.83	37.70	0.52	50.91
ChCl: Maleic acid	20	99.18	65.36	67.88	94.98
	30	91.01	55.25	57.02	78.93
	40	85.87	48.54	0.49	67.59
	50	77.57	48.19	0.48	66.61

This research showed that Co, Ni and Mn recovery from LIB leaching used DES ChCl: Succinic acid was lower than ChCl: Malonic acid, and ChCl: Maleic acid. This may be because succinic acid has a different ability to form complexes with metals. Malonic acid and maleic acid may be more effective in forming more soluble complexes with Ni, Mn, and Co compared to succinic acid. This is due to differences in the chemical structure and relative acidity of the 3 acids [27]. Malonic acid and maleic acid have 2 carboxylic groups (-COOH) in their structure, while succinic acid has 2 carboxylic groups but is connected by a methylene group (-CH_2-). These carboxylate groups are responsible for complex formation with metals. The presence of 2 carboxylic groups in malonic acid and maleic acid allows for the formation of more stable and soluble complexes than succinic acid. The carboxylate groups in succinic acid are connected by methylene group, causing the distance between the 2 carboxylate groups to be slightly larger. This significant distance can impact the carboxylate group's ability to form a stable complex with the metal, leading to lower solubility and consequently affecting metal recovery.

Table 6 Leaching recovery with variation deep eutectic solvent (Temperature 80 °C, 20 gr/L constant stirring 1000 rpm for 2 h).

DES	Recovery			
	Li (wt.%)	Co (wt.%)	Ni (wt.%)	Mn (wt.%)
ChCl: Succinic acid	48.85	16.75	23.76	15.85
ChCl: Maleic acid	99.18	65.36	94.97	67.88
ChCl: Malonic acid	84.83	45.91	68.42	62.18

Table 6 presents a comparison of the percentage recovery of leaching using various deep eutectic solvents (DES) under optimal conditions, specifically at a solid/liquid (S/L) ratio of 20 gr/L with a temperature of 80 °C for 2 h, where DES consists of choline chloride (ChCl) and maleic acid had high leaching recovery. The better performance is attributed to the greater acid strength of maleic acid in comparison to succinic and

malonic acids. At low pH, metal ions are more likely to exist as free cations or form complexes with anions from the added acid, enhancing the solubility of metals like lithium, cobalt, manganese, and nickel due to ion-ion strong interactions with the solvent. It has been demonstrated in prior research that acid-based DES exhibit strong capability in efficiently extracting valuable metals from spent LIB cathodes [28]. Consequently, the optimal leaching recovery using the ChCl acid DES was achieved at 80 °C and S/L ratio of 20 gr/L for 2 h, resulting in recovery rates of 99.18 wt.% for Li, 65.36 wt.% for Co, 67.88 wt.% for Mn, and 94.97 wt. % for Ni. Previous research conducted leaching under more intensive conditions, at 105 °C for 5 h using DES choline chloride and lactic acid resulted in 100 % recovery for Li, Mn, Co, and Ni [29]. When compared to these results, this study has much lighter leaching conditions with quite good results when compared to previous literature.

Kinetic study

Various kinetics models can explain the mechanism of solid-liquid reactions. Based on experimental data, 5 different kinetic models can be applied, namely DTPL (diffusion through a product layer) Prasetyo *et al.* [12], SCR (shrinking core reaction) Prasetyo *et al.* [30], SPM (shrinking particle model) Aryani *et al.* [31], Jander and Kroger and Ziegler [32]. DTPL is based on diffusion through the product layer formed at the particle surface. Whereas SCR it is based on the reaction occurring at the particle surface, and over time the unreacted core shrinks. In SPM, the reaction occurs due to the diffusion of reactants through the formed product layer [12]. Furthermore, the Jander kinetics model assumes that the reaction occurs on the particle surface, with the reaction rate controlled by diffusion through the product layer. While Kroger and Ziegler kinetics model is an advancement of the Jander model, in which the diffusion coefficient varies with time. Temperature is crucial in demonstrating its effect on Li, Co, Ni, and Mn recovery kinetics in the kinetic model. Temperature is related to reaction rates, where high temperatures generally increase chemical reaction rates because the high kinetic energy of particles accelerates the interaction between DES and target materials. Besides that, temperature is used to calculate activation energy and determine how much temperature affects the reaction rate. The x and t data for the kinetics equation are shown in **Table 7**.

Table 7 Leaching kinetics equation.

Model	Equation	Plot created
DTPL	$kt = 1 - 3(1-x)^{2/3} + 2(1-x)$	$1 - 3(1-x)^{2/3} + 2(1-x)$ vs t
SCR	$kt = 1 - (1-x)^{1/3}$	$1 - (1-x)^{1/3}$ vs t
SPM	$kt = 1 - (1-x)^{2/3}$	$1 - (1-x)^{2/3}$ vs t
Jander	$(1-(1-x)^{1/3})^2 = kt$	$(1-(1-x)^{1/3})^2$ vs t
Kroger and Ziegler	$(1-(1-x)^{1/3})^2 = k \ln t$	$(1-(1-x)^{1/3})^2$ vs ln t

The apparent rate constant (min^{-1}) is k, time (min) is t, recovery of Li, Co, Mn and Ni is x.

The coefficient of determination (R^2) is a statistical metric that indicates how effectively the regression model accounts for data variation in regression analysis. It assesses which independent variable can explain the dependent variable. A higher coefficient of determination signifies a greater capacity of the independent variables to account for variations in the dependent variable. The data regarding the coefficient of determination is provided in **Table 8**.

According to the coefficient of determination (R^2), the Jander model is deemed superior because its coefficient is close to 1. The kinetic modelling used to analyze the leaching mechanism of lithium-ion batteries with ChCl: Maleic acid is depicted in **Figure 3**. In addition, the k values obtainable from the slope of the DES kinetics plots of ChCl: Succinic acid, ChCl: Maleic acid, and ChCl: Malonic acid can be found in **Table 9**.

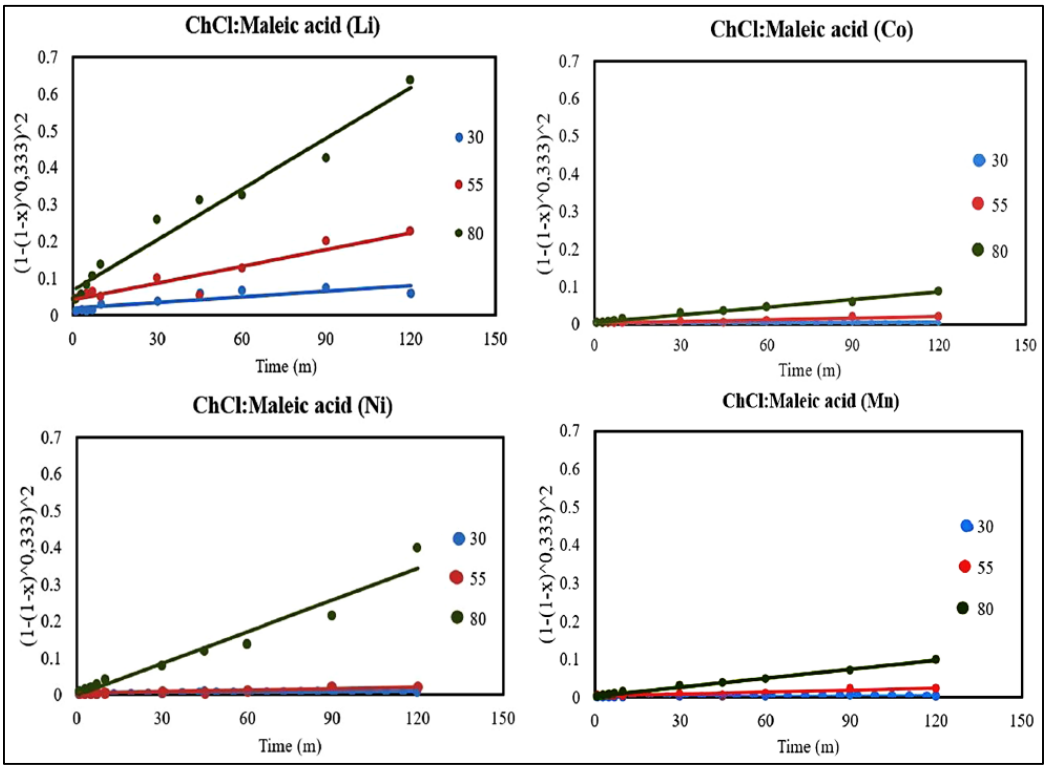

Figure 3 Kinetics plot of DES ChCl: Maleic acid at different temperatures.

Table 8 Coefficient of determination (R^2).

Element	Kinetics model	R^2								
		DES ChCl: Succinic acid			DES ChCl: Maleic acid			DES ChCl: Malonic acid		
		Temperature (deg.C)								
		30	55	80	30	55	80	30	55	80
Li	SCR	0.6442	0.834	0.9064	0.7182	0.877	0.9182	0.5325	0.8362	0.8798
	SPM	0.6448	0.8328	0.895	0.7132	0.8631	0.8234	0.5351	0.8257	0.8371
	DPTL	0.6247	0.8446	0.9541	0.7302	0.8865	0.9202	0.4998	0.8485	0.9227
	Jander	0.6214	0.845	**0.9583**	0.7312	0.893	**0.9693**	0.4954	0.8569	**0.9491**
	Kroger	0.6255	0.7928	0.776	0.8533	0.6079	0.8333	0.5171	0.7258	0.9048
Co	SCR	0.3125	0.8859	0.9378	0.6738	0.8553	0.938	0.5217	0.8264	0.9297
	SPM	0.3122	0.8859	0.9348	0.8726	0.8547	0.9191	0.5224	0.904	0.9192
	DPTL	0.4202	0.8718	0.98	0.6931	0.8547	0.9837	0.4542	0.8309	0.9783
	Jander	0.4434	0.8697	**0.9799**	0.6924	0.854	**0.9863**	0.4954	0.8299	**0.981**
	Kroger	0.1288	0.5111	0.7329	0.8021	0.5297	0.8071	0.5344	0.6706	0.8076
Ni	SCR	0.3475	0.8681	0.9413	0.6936	0.8299	0.9573	0.5335	0.8556	0.9243
	SPM	0.3451	0.8686	0.9366	0.7333	0.8743	0.9354	0.5346	0.8252	0.9083
	DPTL	0.437	0.815	0.9879	0.7012	0.8411	0.9862	0.4538	0.865	0.9675
	Jander	0.8115	0.4413	**0.988**	0.7	0.854	**0.9531**	0.449	0.8647	**0.9731**
	Kroger	0.1132	0.5398	0.7369	0.8162	0.5007	0.6662	0.4957	0.6749	0.8138
Mn	SCR	0.68	0.918	0.9	0.735	0.8739	0.954	0.394	0.847	0.93
	SPM	0.6796	0.9185	0.8967	0.8921	0.8258	0.9488	0.3941	0.8443	0.9108

Element	Kinetics model	R^2								
		DES ChCl: Succinic acid			DES ChCl: Maleic acid			DES ChCl: Malonic acid		
		Temperature (deg.C)								
		30	55	80	30	55	80	30	55	80
	DPTL	0.7133	0.8907	0.9651	0.7555	0.8668	0.9935	0.3689	0.8551	0.9711
	Jander	0.7149	0.8883	**0.9664**	0.7557	0.8653	**0.9961**	0.367	0.8546	**0.9767**
	Kroger	0.3578	0.5203	0.7524	0.8399	0.5366	0.7928	0.4848	0.6704	0.8166

Table 9 k values for valuable metals (Li, Co, Ni, and Mn) in existence ChCl: Succinic acid, ChCl: Maleic acid, and ChCl: Malonic acid.

Temperature (deg.C)	DES	k			
		Li	Co	Ni	Mn
30	ChCl: Succinic acid	0.0000442	0.0000001	0.0000092	0.0000008
55		0.0000379	0.0000011	0.0000025	0.0000022
80		0.0003176	0.0000309	0.0000644	0.0000263
30	ChCl: Maleic acid	0.0005186	0.0000193	0.0000738	0.0000398
55		0.0015097	0.0001399	0.0003814	0.0016381
80		0.0045594	0.0006681	0.0028825	0.0007753
30	ChCl: Malonic acid	0.0000555	0.0000040	0.0000078	0.0000072
55		0.0011753	0.0001422	0.0004376	0.0003540
80		0.0015823	0.0002758	0.0006361	0.0008511

Jander kinetics is a model applied to describe the reaction rate, where the reaction occurs at the surface of solid particles, and the rate is controlled by the diffusion of reactants through the shrinking solid or ash layer [32]. The Jander model describes 2 stages: The diffusion of solvent ions into the pores of the particle and chemical reactions at the surface, and diffusion of products from the surface [32]. In the initial stage, reactants in solution diffuse towards the solid surface, which is influenced by the concentration gradient, temperature, and physical properties of the reactants and the solid material. At the solid-liquid interface, chemical reactions allow the reactants to interact with the solid material and lead to the dissolution of the desired components. During the process, a product layer is formed on the solid surface, which can affect the reaction rate and inhibit the diffusion of reactants. The leaching efficiency depends on managing the thickness and permeability of this layer and the diffusion of products into the solution to keep the reaction going. The Jander mechanism emphasizes the importance of the interaction of diffusion and reaction kinetics in improving leaching efficiency.

In this research, the activation energy (Ea) was determined using the Arrhenius equation (Eq. (2)). In this equation, A is a temperature-independent constant, the temperature in Kelvin (T), gas constant (R = 8.314 J/mol) and k is the rate constant where the value of k is taken from **Table 9**.

$$\ln k = \ln A - \frac{Ea}{R}\ x\ \frac{1}{T} \quad (2)$$

Figure 4 shows the Arrhenius plot between ln (k) vs (1/T) for the recovery of crucial metals (Li, Co, Ni, and Mn) from active materials by leaching using DES ChCl: Maleic acid. Calculation of activation energy (Ea) in DES ChCl: Maleic acid obtained Li 38.57 kJ/mol, Co 63.09 kJ/mol, Ni 64.87 kJ/mol and Mn 52.64 kJ/mol. When compared with previous research, the activation energy for all elements in the leaching process using

DES ChCl: Maleic acid is more significant than that of the activation energy in the leaching process using DES ChCl: EG, namely Li 19.8 kJ/mol, Co 24.4 kJ/mol, Ni 36.5 kJ/mol and Mn 41.6 kJ/mol [2].

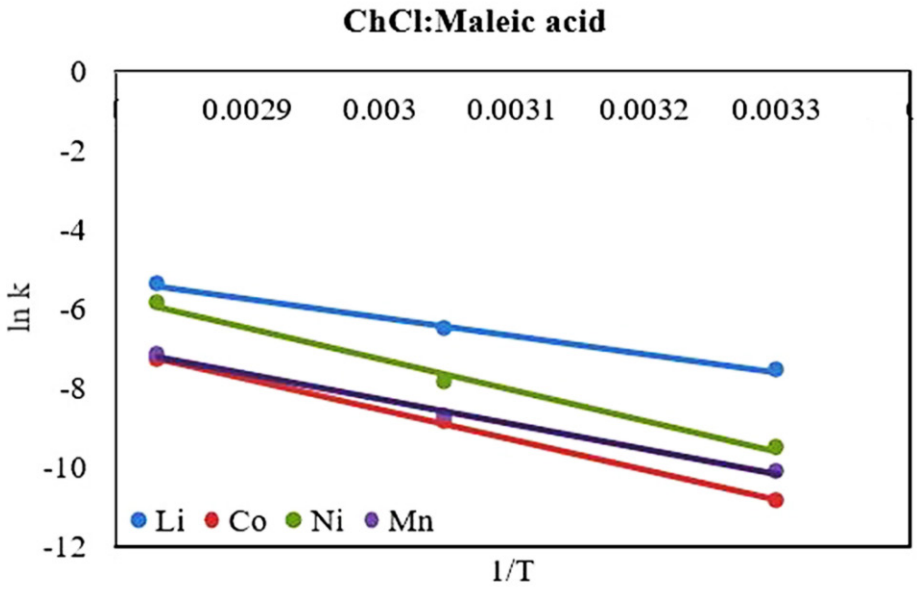

Figure 4 Arrhenius plot for the extraction of Li, Co, Ni, and Mn from LIB using DES ChCl: Maleic acid.

Table 10 The activation energy for valuable metals (Li, Co, Ni, and Mn) extraction by ChCl: Succinic acid, ChCl: Maleic acid, and ChCl: Malonic acid.

DES	Li (kJ/mol)	Co (kJ/mol)	Ni (kJ/mol)	Mn (kJ/mol)
ChCl: Succinic acid	33.95	96.10	32.38	60.23
ChCl: Maleic acid	38.57	63.09	64.87	52.64
ChCl: Malonic acid	60.68	76.02	79.59	85.97

Based on the activation energy shown in **Table 10**, the reaction that occurs is an endothermic reaction, where the kinetic energy of molecules increases so that the frequency and strength of collisions between molecules increases. This rise in energy enhances both the frequency and strength of collisions among the molecules, resulting in a faster reaction rate as more molecules possess sufficient energy to surpass the activation energy. The results suggest that activation energies lower than 40 kJ/mol indicate the dominance of physical interactions between bulk volumes and the solid phase, while activation energies exceeding 40 kJ/mol point to the dominance of surface chemical processes [15].

Table 10 shows that the different activation energies of Li, Ni, Mn, and Co during the leaching process are due to variations in metal binding energy, the need for reduction, diffusion, complex formation, and chemical reactions and interactions with the solvent [33]. Each metal has unique characteristics that affect how much energy is required to start and continue the leaching process. Metal binding energy refers to the energy required to break a bond between a metal and a ligand or other material in a compound or complex. The binding energy of metals varies depending on the ion charge, ion size, electron configuration, and other chemical properties. Where smaller metal ions tend to have higher binding energies because the electrostatic attraction between the ion and the ligand is stronger. For example, the Ni^{2+} ion is smaller than the Li^{+} ion, so the Ni^{2+} ion has a higher binding energy because of the large charge in a smaller volume. The unique characteristics of metal refer to the specific traits that differentiate one metal from another, that can affect their behavior during the leaching process. The unique characteristics of metals, such as their tendency to form complexes,

chemical reactivity, an interaction with solvents, determine how the behave in the leaching process.

Moreover, the activation energy is also different between DES ChCl:Succinic acid, ChCl:Malonic acid, and ChCl:Maleic acid for each element. This can be due to several factors: differences in chemical structure, complexation ability, bond energy, reaction mechanism, and interaction with DES. All these factors may hinder the leaching process and require more energy to achieve the same reaction rate compared to other DES. The highest activation energy is found in DES ChCl:Malonic acid, this may be due to the inability of malonic acid to form stable complexes with metals, high viscosity, and less efficient reaction mechanism [34]. All these factors may hinder the leaching process and require more energy to achieve the same reaction rate compared to other DES.

Conclusions

This research effectively showcased an efficient approach for leaching spent lithium-ion batteries using deep eutectic solvents (DES) with solid/liquid (S/L) variations to recover valuable metals. The optimal conditions use DES ChCl: Maleic acid at an S/L ratio of 20 g/L, 80 °C, and continuous stirring at 1000 rpm for 2 h, achieving high recovery rates: 99.18 wt.% for Li, 65.36 wt.% for Co, 67.88 wt.% for Mn, and 94.97 wt.% for Ni. Notably, Li exhibited the highest recovery, outperforming Co, Mn, and Ni. Kinetic analysis using the Jander model confirmed that temperature significantly influenced the recovery process, with the Arrhenius equation revealing that surface chemical processes dominate in the leaching process of Co, Mn, and Ni, while physical interactions are more prominent for Li. These findings dish up a promising method for efficiently recovering critical metals from spent batteries, contributing to more sustainable recycling processes. Further research should focus on investigating the composition of DES and studying the effect of agitation on specific metal recovery.

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