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Hydrometallurgical leaching and recovery of cobalt from lithium ion battery

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ABSTRACT

The main aim of this work was to test the ability of an amino acid (i.e. glycine) to leach cobalt from Li ion batteries (LiBs). The process parameters namely temperature, pulp density and concentration of glycine were optimized for maximizing the leaching efficiency of cobalt from the cathodic material. Response surface methodology (RSM) was applied for determining the experimental conditions instead of using the traditional one factor at a time (OFAT) approach in order to ascertain the interaction effects between the different factors. Thus, the optimal leaching value based on RSM and maximum cobalt leaching potential from LiBs was obtained. The optimum values for the parameters were as follows; temperature = 74 °C, pulp density = 19.9 g/L and glycine concentration = 0.936 M. Under this optimum condition, the cobalt leaching efficiency was 61.8%, while a maximum leaching of 89.7% was achieved at the following conditions: temperature = 100 °C, pulp density = 13.8 g/L and glycine concentration = 1.24 M. Oxalic acid was used for recovering cobalt from the leaching solution by varying the pH and molar ratio of oxalic acid and cobalt ions. Cobalt recovery efficiencies were ~88.0% at pH 7.0 and at oxalic acid to cobalt ion molar ratio of 2.5:1.0.

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1. Introduction

Lithium-ion batteries (LiBs) are widely used as power source in mobile phones, computers and other modern life gadgets. LiBs are preferred due to their unique characteristics, such as: (i) light weight, (ii) high energy density per unit weight, (iii) high operating voltage, (iv) ability to be recharged, and (v) performance life (Mylarappa et al., 2017; Dhiman and Gupta, 2021). The main constituent of LiBs is lithium cobalt oxide (LiCoO₂), present in the cathodic active material of the LiBs. The cathodic material makes up 20%–50% of the total content in the LiBs (Badawy et al., 2013; Yang et al., 2017; Bedekovic and Tenjer, 2021). Carbon graphite is usually used as the anode material (Jha et al., 2013). The electrolyte usually consists of lithium salt as an organic solvent (Mossali et al., 2020; Sethurajan and Gaydardzhiev, 2021). However, due to the development of newer technologies, the aging of LiBs with usage, and the user's desire to replace older devices, the service life of electronic devices containing LiBs is diminishing and their fraction in the waste stream is increasing

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(Kopacek, 2013). The LiBs market is increasing at a cumulative annual growth rate of 11% (Olivetti et al., 2017). LiBs are not directly hazardous to the environment but the toxic metal content (Li, Ni, Co) in LiBs has the potential to get leached from landfills and contaminate soils as well as the ground water bodies (Karnchanawong and Limpiteeprakan, 2009; Bedekovic and Tenjer, 2021; Saha et al., 2021).

In addition to the severe environmental hazards, the recovery of cobalt from LiBs is necessary due to its low abundance in nature. The abundance of cobalt is only 26 ppm of the earth's surface (Pourret and Faucon, 2017). Out of the total cobalt present on the earth's surface, the Democratic Republic of Congo contributes to 59% of the total cobalt production in the world (Investing News Network 2018). According to Binnemans et al. (2013), China is responsible for the export of 90% of electronic goods containing LiBs. Given the current economic scenario, there will be a supply risk to be dependent on traditional sources of cobalt. Currently, about 58% of the total produced cobalt is used in LiBs production, which was only 10% in 1999 (Dehaine et al., 2021). This trend is expected to increase in the next decades. An extreme shortage of lithium and cobalt is expected if recycling of equipment containing them is not initiated at the industrial scale (Meshram et al., 2015; Choubey et al., 2016).

Due to the intricacy of LiBs, there are essentially no generic recycling systems or processes (Gaines, 2018). Currently, pyrometallurgical processes are being practiced in some industries like Umicore and Batrec (Zhao et al., 2021). However, these processes have disadvantages like non-selectivity, release of harmful gases and chemicals, and high energy expenditures, among others (Zhao et al., 2021). Several companies, like Accurec (Germany), Recupyl (France), Sony/Sumitomo (Japan), etc., have adopted a combination of hydrometallurgical and pyrometallurgical processes (Meshram et al., 2014). Due to its complexity and economic benefits, recycling of waste LiBs is minimal, i.e. only 5% of the total LiBs generated (Harper et al., 2019). Hence, several lab-scale investigations on recovering cobalt and lithium from LiBs utilizing industrial acids such as sulphuric acid, nitric acid, and hydrochloric acid have been reported to address the drawbacks (Tanong et al., 2016; Boxall et al., 2018; Guo et al., 2018; Sethurajan et al., 2019; Lin et al., 2021). However, these acids could cause secondary pollution by releasing toxic gases during the leaching process in addition to polluting wastewater streams by increasing their acidity. Hence, the focus of this research is on recovering cobalt using mild amino acids like glycine which have no reported pollution concerns. There are very few studies that report the Co hydrometallurgy from spent LiBs using unconventional mild acids (Li et al., 2013; Nayaka et al., 2016). But most of those studies employed the commonly used one factor at a time (OFAT) approach. This method neglects the interaction of the factors when they are changed simultaneously (Golmohammadzadeh et al., 2017). Response surface methodology (RSM) approach is useful to not only deduce the optimal conditions but also instrumental to understand the interaction between the process variables. There are a lot of instances where the selective recovery of the soluble Co from the industrial acid leachates have been reported (Shuva and Kurny, 2013; Torkaman et al., 2017). However, the recovery of the dissolved Co from the amino acid leachates are still not well understood.

In the present study, Co hydrometallurgy using glycine as the lixiviant and oxalic acid as the recovery agent from waste Li ion batteries were investigated. The main objective of this study was to study the Co leaching characteristics and the effect and interaction of different leaching parameters on the leachability of Co from LiBs. The leaching process parameters such as (i) glycine concentration (0.3–1.0 M), (ii) pulp density (20–40 g/L) and (iii) temperature (40–85 °C) were optimized for the maximum Co leaching. This study also tested the effectiveness of Co-oxalate precipitation to selectively recover Co from the poly metallic leachate.

2. Materials and methods

2.1. LiBs samples and pre-treatment

Mobile phone batteries (Li ion batteries) were procured from SIMS recycling solutions, based in Eindhoven, the Netherlands. The batteries were immersed in sodium chloride solution (5% wt.) for a period of 30 min (He et al., 2016). This insured that the batteries were completely discharged, and also reduced the likelihood of a short circuit occurring. The batteries were dismantled using screwdrivers, pliers with necessary safety gears such as safety glasses, gas masks, nitrile gloves and lab coat. All the dismantling operations were undertaken in the fume hood with extreme care. The cathode material (black colour) which is attached to the aluminium film was separated from polyvinylidene fluoride (PVDF) and graphite anode manually.

The cathodic material obtained post dismantling had an approximate dimension of 12 mm × 12 mm. Hence it was necessary to reduce the size of the particles at least to a size of 3 mm × 3 mm (Badawy et al., 2013; Nayaka et al., 2016). The dismantled samples were size reduced using a household grinder. Water was used as the cooling agent to avoid overheating of the grinder. The wet sample generated post grinding was incubated at a temperature of 105 °C for a period of 24 h. The sample was weighed before and after drying to check for loss in weight of the sample. The post dried sample was calcinated in a furnace (Thermo scientific M110 muffle furnace, The Netherlands) at a temperature of 600 °C for 4 h (Zheng et al., 2016). This was done to assure the combustion of PVDF and any other contaminants in the sample and to improve cobalt recovery from the sample. This pre-treated sample was used for performing the leaching experiments.

Table 1
Coded levels and range of leaching variables for the RSM-CCD experimental design.

Sl. No.	Parameters	$-\alpha$	-1	0	1	$+\alpha$
1	Temperature ($^{\circ}\text{C}$)	25	40	63	85	100
2	Pulp density (g/L)	13	20	30	40	46
3	Glycine concentration (M)	0.06	0.3	0.65	1	1

2.2. Leaching experiments

All the experiments were conducted in a temperature-controlled water bath, at 150 rpm. The experiment was conducted in 100 mL Erlenmeyer flasks which were sealed with a rubber cork to avoid any moisture or water intrusion from the water bath. All the leaching experiments were conducted using 25 mL of the leaching medium. Glycine was used as the lixiviant. Hydrogen peroxide (5%) was added to the lixiviant in all the experiments. Prior optimization studies, a preliminary experiment was conducted to ascertain the optimal leaching time for the dissolution of Co under fixed operating conditions (temperature: 62.5 $^{\circ}\text{C}$, pulp density: 30 g/L, glycine concentration: 0.65 M).

2.3. Optimization of the leaching parameters using response surface methodology

Response surface methodology (RSM) was used for designing the experiments instead of the traditional one factor at a time approach. The factors considered were temperature (40–85 $^{\circ}\text{C}$), pulp density (20–40 g/L) and glycine concentration (0.3–1.0 M). The experiment design was generated by the MINITAB 18 (USA) software. A full factorial central composite design (CCD) (face centred, unblocked) was used. Table 1 presents the generated coded levels and range of leaching variables for the experimental design.

Further leaching experiments were also conducted at the optimum conditions based on the results of experimental design. Another leaching study was conducted to determine the effect of pH control on the leaching of Co from LiBs at the following conditions, temperature: 100 $^{\circ}\text{C}$, pulp density: 13.8 g/L and glycine concentration: 1.24 M.

2.4. Selective recovery of cobalt from the leachate

Cobalt oxalate precipitation experiments were conducted using oxalic acid as the precipitating agent. The initial pH and molar ratio of the precipitating agent (oxalic acid) to cobalt were chosen as the important parameters to be optimized for maximum Co recovery. The leachate was centrifuged to separate the impurities from the supernatant. The precipitate was filtered using 0.45 μm filter paper and the cobalt content of the supernatant was measured. The pH of the solution was adjusted using 1 M HCl for pH values lower than 7.0 and using 0.5 M NaOH for pH 8.0. After determining the optimal pH value for the precipitation, the next step was to determine the optimal molar ratio. In order to determine the optimum pH, the precipitation experiments were conducted at a constant molar ratio (1:1) and by varying the pH (pH 4.0, 5.0, 6.0, 7.0 and 8.0). The molar ratio was defined as the ratio of the moles of oxalic acid used to the number of moles of cobalt ions in the solution. After determining the optimum pH value where the extraction is maximum, the molar ratio was investigated at ratios of 2:1, 3:1 and 4:1.

2.5. Analytical methods

Scanning electron microscopy (SEM) analysis of the sample was done using JEOL JSM-6010LA (Japan). Atomic absorption spectrometer (Perkin Elmer Analyst 200, USA) was used for the quantitative analysis of all the metals present in the sample. A Hach DR/890 colorimeter (USA) was used for measuring the total aluminium content.

2.6. Statistical analysis

The leaching and recovery studies were conducted in triplicate, and the mean value and standard deviations are displayed in the figures. In this study, 2-way ANOVA and Pareto effect analysis of the experimental data was performed. The *P*-value and *F*-value of the experimental data was checked, and the significance of the parameters were established by comparing their standardized effect values.

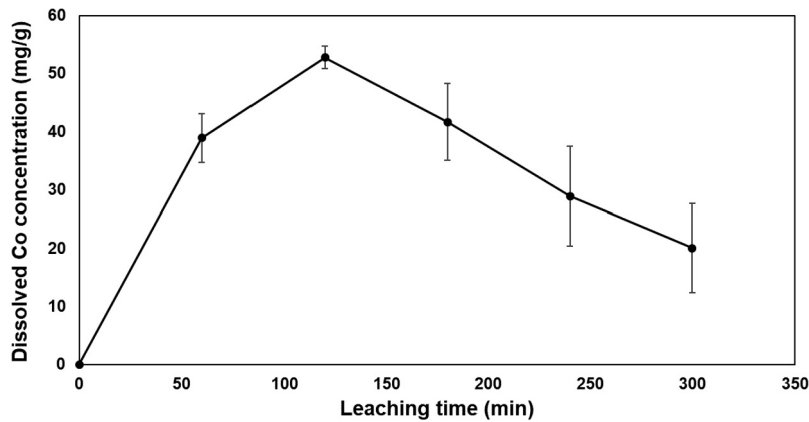
3. Results

3.1. Total metal characterization of the cathodic materials (LiBs)

The results of the total metal characterization of the LiBs sample are mentioned in Table 2. The spent LiBs contain a very high concentration of Al (55%) Co (30%) and minor amounts of Li (5%) and Ni (4%) and trace amounts of Fe. The total metal content of the sample was 991.9 ± 54.39 mg/g of cathodic sample, which suggests the presence of impurities despite performing the calcination step. The high aluminium content in the samples can be explained by the ineffective separation of the residual aluminium foil from rest of the cathodic material.

Table 2
Bulk chemical composition of the investigated LiBs.

Metal	Concentration (mg/g)
Cobalt	298.48 ± 23.72
Aluminium	557.58 ± 28.27
Lithium	50.70 ± 1.99
Nickel	3.82 ± 0.36
Iron	0.41 ± 0.05

**Fig. 1.** Effect of glycine concentration on the leaching rate of Co from spent LiBs (experimental conditions: temperature: 62.5 °C, pulp density: 30 g/L, glycine concentration: 0.65 M).**Table 3**
ANOVA results from the data of the RSM-CCD experiments.

Parameter	F-value	P-value	Note
Temperature (°C)	0.27	0.616	
Pulp density (g/L)	27.92	<0.05	Significant
Glycine concentration (M)	3.68	0.084	
Squared effects			
Temperature (°C) × Temperature (°C)	8.62	0.015	Significant
Pulp density (g/L) × Pulp density (g/L)	7.58	0.020	Significant
Glycine concentration (M) × Glycine concentration (M)	1.21	0.297	
2-Way interaction			
Temperature (°C) × Pulp density (g/L)	1.30	0.280	
Temperature (°C) × Glycine concentration (M)	0.70	0.422	
Pulp density (g/L) × Glycine concentration (M)	0.29	0.599	

3.2. Leachability of Co from LiBs

3.2.1. Optimum time for Co leaching

The results of the preliminary leaching study are shown in Fig. 1. The results reveal that the maximum leaching of Co from the LiBs can be obtained within 120 min. However, beyond 120 min, a decrease in the soluble concentration of Co was observed. Hence, 120 min was chosen as the optimum leaching time for further RSM experiments.

3.2.2. Optimization of the leaching parameters

Table 3 summarizes the effects and interaction of the process variables. Table 3 clearly shows that the pulp density is the statistically significant parameter for the leaching of Co from LiBs. The squared effects of the temperature and pulp density were also statistically significant for the Co leaching. However, the interaction between the process parameters (temperature, pulp density and glycine concentration) were to be found insignificant.

The main effects plot (Figure S2 of the supplementary material) further reveals that pulp density is the most influential parameter affecting the leachability of Co from LiBs. When the pulp density was low (i.e. 10 g/L), the leaching efficiency was high and when the pulp density was 40 g/L, the Co leaching efficiency decreased significantly. Concerning the concentration of glycine, the Co leaching trend was contrast to the effect observed in the case of pulp density. Generally, an increase in the glycine concentration results in an increase in the Co leaching efficiency.

Table 4
Composition of the Co-oxalate precipitate.

Metal	Concentration (mg/g)
Cobalt	480.00 \pm 24.49
Aluminium	23.33 \pm 1.88
Lithium	24.67 \pm 1.89

3.2.3. Contour plots

The results from Pareto (Fig. S1) and ANOVA analysis (Table 3) show that the pulp density ($F = 27.92$; $P < 0.001$) is the most influential factor affecting Co leaching followed by the glycine concentration ($F = 3.68$; $P \geq 0.05$) and temperature ($F = 0.27$; $P \geq 0.05$). Among the interaction effects between the parameters, none of the interactions were statistically significant because of their high P values (>0.1). As shown in Fig. 2a, at a constant glycine concentration of 0.65 M, increasing the values of both temperature and pulp density from low to high levels, decreased the amount of Co leached. However, at a constant temperature of 65 °C, the maximum amount of Co leached was observed at the highest level of glycine concentration and the lowest pulp density (Fig. 2b). Similarly, at a constant pulp density of 30 mg/L, the amount of Co leached was the highest at low temperature and high glycine concentration (Fig. 2c). These results clearly show that the optimum conditions of the process parameters were not within the range of experimental conditions tested in this study. Nevertheless, maximum Co leaching (~ 160 – 260 mg/g) was achieved at either high or low values of the process parameters, while at their respective intermediate levels, the Co leaching was found to be the lowest ($\sim <55$ mg/g).

3.2.4. Co leaching under the optimum conditions

Fig. 3 shows the amount of Co leached from LiBs under the computed optimum conditions, i.e. Temperature: 74 °C, pulp density: 19.9 and g/L, glycine concentration: 0.94 M. It can be seen that a maximum of 180 mg/g of Co can be leached at the optimum conditions. However, it can also be observed, that after 120 min, the soluble Co concentration in the leachate starts to decrease.

3.2.5. Effect of pH control on the Co dissolution

The effects of the uncontrolled and controlled pH of the glycine leachate is shown in Fig. 4a and b. The results shown in Fig. 4a confirms that, when the pH is uncontrolled, the soluble Co concentration decreases after a threshold value (approximately 250 mg/g or 89% of total Co and pH 7.0–7.5). From Fig. 4b, it is evident that when the pH is controlled (using HCl) during leaching, the decrease in the soluble Co concentration can be overcome. It is evident from Fig. 4a and b that the pH of the leaching system is an important factor for the solubility of Cobalt.

3.3. Recovery of Co from the glycine mediated LiBs-leachates

The effect of the initial pH on the Co-oxalate precipitation by oxalic acid is shown in Fig. 5a. The effect of molar ratio of oxalic acid to dissolved Co concentration on the Co-oxalate precipitation is shown in Fig. 5b. It can be noted from Fig. 5a that the pH is an important parameter for the Co-oxalate precipitation from the LiB leachates. For instance, when the initial pH is in the mild acidic range (pH 4.0–6.0), the precipitation is low (45%–50%). However, when the initial pH is in the neutral to mild alkaline range (pH 7.0–8.0), the Co precipitation efficiency increased from 50% to 65%. Therefore, pH 7.0 was selected for further precipitation studies. It is evident from Fig. 5b that the ratio of the dosage of oxalic acid to soluble Co concentration is another important factor for the Co precipitation from LiB leachates. In this study, oxalic acid to dissolved Co molar ratios of 1:1, 2:1, 2.5:1, 3:1 and 4:1 were investigated. The results revealed that at a molar ratio of 1:1, the precipitation was as low as 60%. However, when the molar ratio was maintained at 2:1, 2.5:1, 3:1 and 4:1, the precipitation efficiency ranged between 85 and 90%. At a molar ratio of 2.5:1 of oxalic acid to dissolved Co concentration, a maximum of 88% of soluble Co was precipitated from the LiB leachates. The composition of the Co-oxalate precipitation is displayed in Table 4.

4. Discussion

4.1. Spent lithium ion batteries, a potential resource of Co

This study shows that spent LiBs can be used as a potential resource of critical metals, particularly Co. These waste LiBs can be hydrometallurgically reprocessed to produce Co and thereby, the depletion of natural resources of Co can be resolved to some extent. It can be noted that the spent LiBs contain 298 mg/g of Co, which is in line with the values reported in the literature (Heydarian et al., 2018). On the other hand, cobalt is not evenly dispersed geologically and is also found in very low concentrations in the Earth's crust (Junhui and Yushu, 2020; Sethurajan and Gaydardzhiev, 2021). Only a minimum of Co (2%) is produced from independent Co mines and a recent data from China mining federation states that Co will be one of the nine seriously endangered metals in the near future (Junhui and Yushu, 2020). This problem

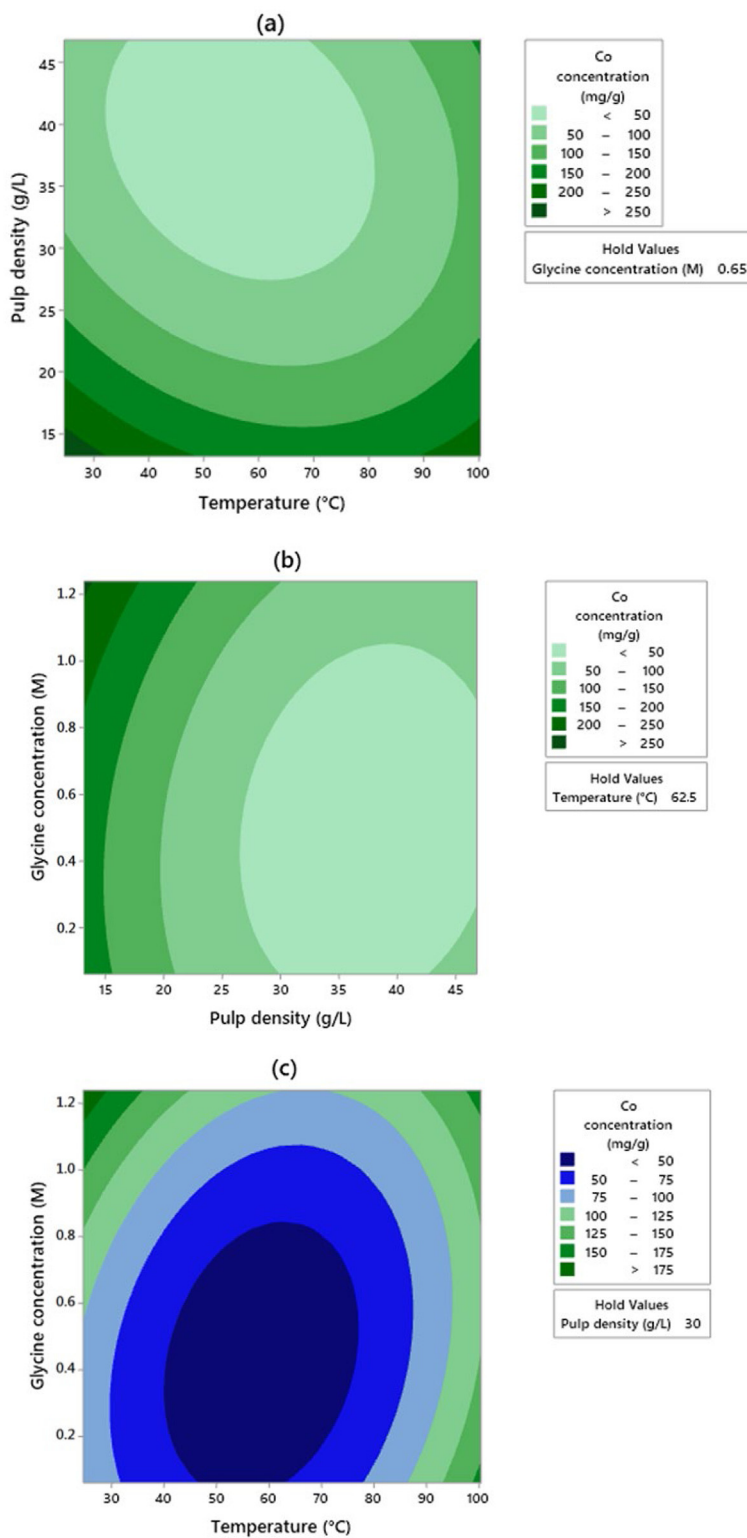


Fig. 2. Contour plots for the optimization of Co leaching from spent LiBs as a function of: (a) pulp density vs. temperature, (b) glycine concentration vs. pulp density and (c) glycine concentration vs. temperature.

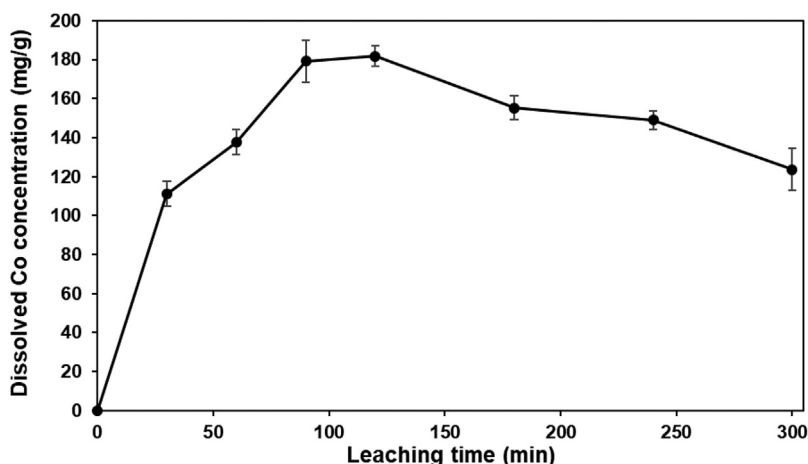


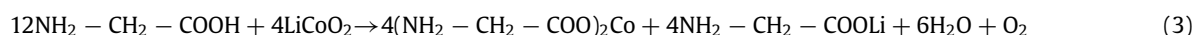
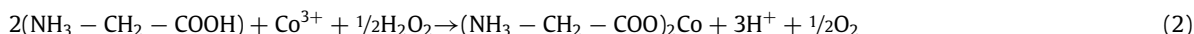
Fig. 3. Co leaching rate from the spent LiBs using glycine (optimum experimental conditions: temperature - 74 °C, pulp density - 19.9 g/L and glycine concentration - 0.94 M).

(Co primary reserves shortage) can be addressed by proper recycling of LiBs because it contains 30% by weight of Co per gram of waste LiBs. Apart from Co, Li is also seen in significant concentration along with Al and Ni.

The results of this study showed that more than 60% of Co can be leached by amino acid i.e. glycine, under optimum conditions of temperature: 74 °C, pulp density: 19.9 g/L and glycine concentration: 0.94 M. Furthermore, a maximum of 88% Co can be recovered as Co-oxalate from the glycine mediated LiB leachates (Fig. 6). The results of this study in terms of leaching and recovery efficiency, are comparable to the previous studies (Chen et al., 2011; Nayaka et al., 2016; Chen et al., 2021). The Co-oxalate can be used as a precursor for the production of cathode active materials (LiCoO₂) of LiBs (Nayaka et al., 2016).

4.2. Glycine mediated leaching of Co from LiBs

The leaching of Co from LiBs can be explained using Eqs. (1)–(3):



Nayaka et al. (2016) also investigated and reported the leachability of Co from LiBs using glycine containing lixiviant solution. It was noted that 0.5 M of glycine (in combination with ascorbic acid) was able to leach more than 95% of Co from LiBs, which is almost half of the glycine concentration used in this study (Table 5). This could be because of the lower pulp density used by Nayaka et al. (2016), i.e. 2 g/L, which is 10 times lower than the pulp density reported in this study (20 g/L). Nayaka et al. (2016) also used ascorbic acid (0.2 M) in combination with glycine to achieve the high leaching efficiency (95%). Chen et al. (2021), investigated the leaching efficiency of glycine lixiviant (in combination with H₂O₂) and it was reported that very high concentration of glycine (4 M) could leach more than 95% of Co from LiBs (temperature: 80 °C, pulp density: 10 g/L, time: 7 h) (Table 5). The leaching efficiency achieved by Chen et al. (2021) is also higher than the efficiency reported in this study (Table 5). This is also because of the different leaching conditions employed by Chen et al. (2021), i.e. 4 times higher glycine concentration and 2 times lesser solid to liquid (S/L) ratio compared to this study (Table 5).

Pulp density and temperature generally play an important role in the leaching of metals from primary ores or waste materials. An increase in pulp density results in a decrease in the unit volume of lixiviant per unit volume of material to be leached and it also results in an increase in the system pH. The system pH is an important parameter for the leaching of Co, because the dissolved Co was observed to decrease at higher pH in the pH uncontrolled systems (Fig. 4a). The temperature (74 °C) reported in this study is comparable to that of the temperature (80 °C) reported in Nayaka et al. (2016) and Chen et al. (2021) (Table 5). The statistical analysis of the optimization studies also supported the fact that pulp density and temperature are the most important parameters that influence the amount of Co that can be leached from the LiBs.

Apart from glycine, there are few studies that have reported the use of amino acids such as aspartic acid (Li et al., 2013) and iminodiacetic acid (Nayaka et al., 2016). A maximum of 60% Co was leached by 1.5 M aspartic acid at a S/L ratio of 10 g/L within 2 h (Li et al., 2013). The leaching efficiency of Co from LiBs by aspartic acid (60%) is comparable to the leaching efficiency reported in this study. Co dissolution from LiBs by organic acids like citric (Golmohammadzadeh et al., 2017,

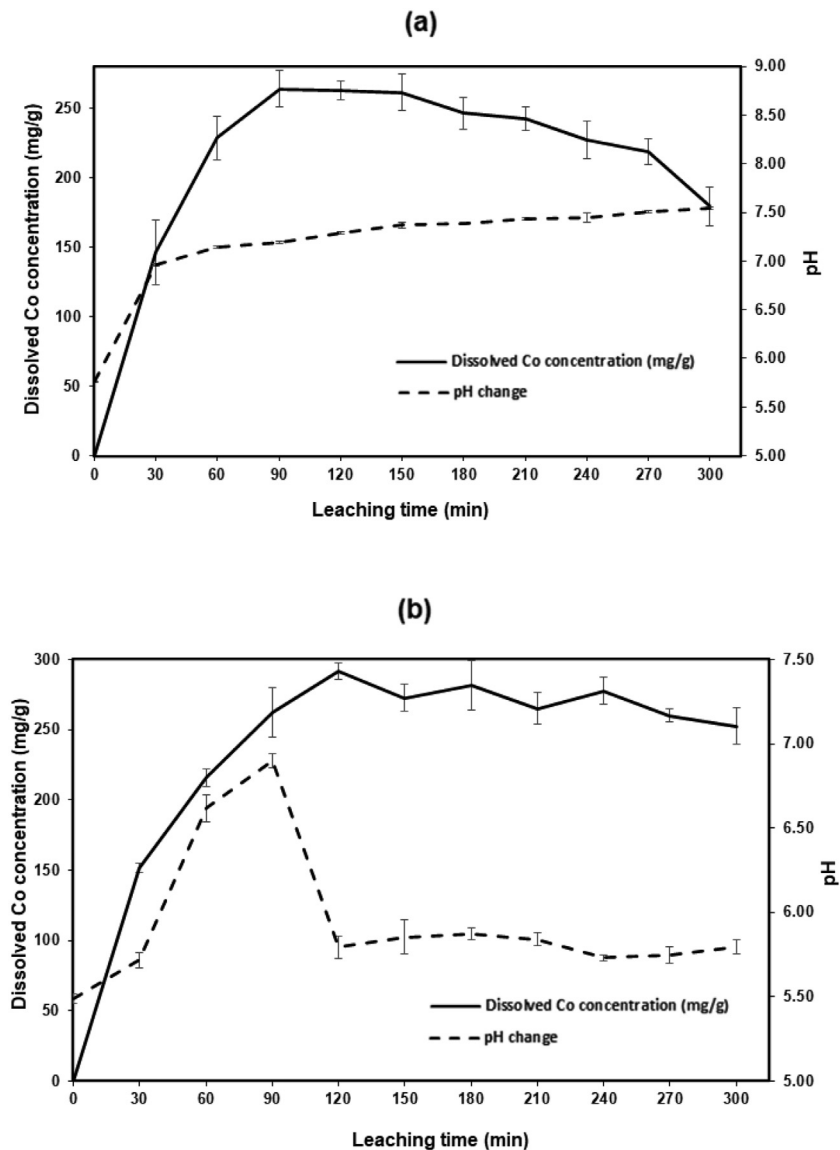


Fig. 4. Leaching rate of Co from LiBs: (a) uncontrolled pH and (b) controlled pH (experimental conditions: temperature - 100 °C, pulp density - 13.8 g/L and glycine concentration - 1.24 M).

2018), malic (Li et al., 2013), Succinic (Li et al., 2015) and oxalic acids (Zeng et al., 2015) are higher when compared to the leaching efficiency of amino acids such as glycine and aspartic acid. This is due to the fact that the sequence of organic acids has a higher acidity than the sequence of amino acids (Li et al., 2013).

4.3. Selective Co recovery from glycine mediated LiB leachates

This study demonstrated that more than 75% of dissolved Co can be precipitated from the LiBs mainly as Co-oxalate (Fig. 6). LiBs can thus be seen as an important secondary resource for Co. The Co-oxalate precipitation from leachates can be explained by Eq. (4):



The precipitation of metal ions from leachates is pH dependent (Lewis, 2010). It can be observed from Fig. 5a that Co oxalate precipitation is higher in the mild alkaline pH range (pH 7.0–8.0) when compared to the mild acidic pH range (pH 4.0–6.0). For the selective precipitation of metals, it is also crucial to examine the molar ratio between the precipitating agent and the concentration of the target metal (Chen et al., 2011; Nayaka et al., 2016). It can be seen

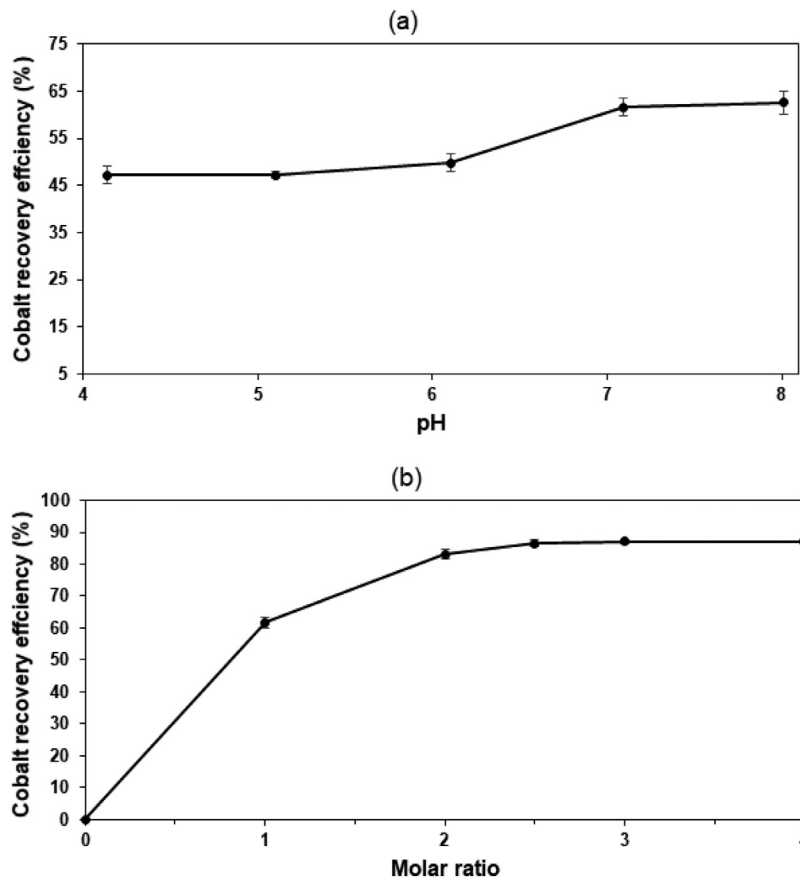


Fig. 5. Effect of: (a) initial pH and (b) molar ratio of oxalic acid to dissolved Co concentration on Co-oxalate precipitation from LiB leachates.

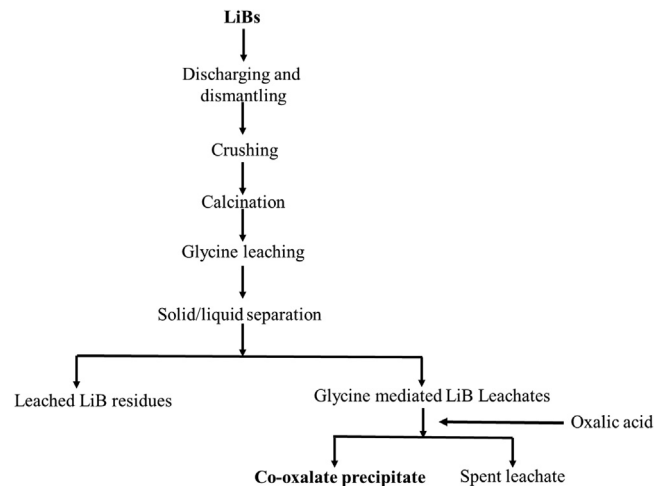


Fig. 6. Schematic of the hydrometallurgical flow chart for the selective recovery of Co from spent LiBs.

from Fig. 5b, more than 75% of Co can be precipitated from the LiB leachate at a molar ratio of 2.5:1.0. Nayaka et al. (2016) demonstrated the selective Co recovery from glycine mediated leaching of LiBs; however, their study did not investigate the effect of molar ratio of precipitating agent (oxalic acid) to the dissolved Co concentration (Nayaka et al., 2016) (Table 4). Chen et al. (2011) demonstrated a process for the selective recovery of Co (Co-oxalate) from LiBs via alkaline leaching followed by roasting and reductive acid leaching and finally precipitation using ammonium oxalate. The

Table 5

Comparison of the results of this study with other amino acid-based studies.

Li battery type	Leaching agent used	Reducing agent	Optimum leaching conditions			Leaching efficiency (%)	Recovery from the pregnant leachates (%)	References
			Temperature (°C)	Pulp density (g/L)	Time (min)			
Laptop batteries	1.5 M Aspartic acid (C ₄ H ₇ NO ₄)	4% H ₂ O ₂	NA	10	120	60	Not studied	Li et al. (2013)
Mobile phone batteries	0.1 M Iminodiacetic acid (C ₄ H ₇ NO ₄)	0.02 M ascorbic acid	80	2	360	91	Oxalic acid precipitation was attempted but no other details were mentioned	Nayaka et al. (2016)
Mobile phone batteries	0.5 M Glycine (C ₂ H ₅ NO ₂)	0.02 M ascorbic acid	80	2	360	95	Oxalic acid precipitation was attempted but no other details were mentioned	Nayaka et al. (2016)
Not mentioned	4 M Glycine (C ₂ H ₅ NO ₂)	10% H ₂ O ₂	80	10	420	97	Not studied	Chen et al. (2021)
Mobile phone batteries	1.24 M Glycine (C ₂ H ₅ NO ₂)	5% H ₂ O ₂	100	13.8	120	89	88% using ammonium oxalate precipitation at 2.5:1 molar ratio	This study

Note: *NA – not available.

study showed that 1.15:1 is the optimum molar ratio of ammonium oxalate to Co. It is noteworthy to mention that, the leachate was earlier subjected to the removal of impurities (by pH adjustment using NaOH) and solvent extraction prior to oxalate precipitation (Chen et al., 2011). Bulk chemical analysis of the precipitates reveal that Co ions form the bulk of the particle (56%). Trace amounts of Al and Li co-precipitation were also observed in the precipitates. The precipitates could be in the form of Co-oxalate (Nayaka et al., 2016); however, mineralogical characteristics of the precipitates were not studied by the authors.

4.4. Future research prospects

This study demonstrated that both the leaching of cobalt and the selective recovery of cobalt from LiBs is technically feasible. However, additional rigorous laboratory experiments are required before deploying the technology at a larger scale or for commercial purposes. Prior to the actual leaching and recovery stage, pretreatment of the waste batteries should be carried out in order to achieve an efficient Co hydrometallurgy process. For example, a simpler, yet effective pretreatment technique (mix of physical and thermal treatments) might be preferable to chemical treatment (e.g. N-Methyl-2-Pyrrolidone, NMP). It is critical that, during the pretreatment stage, no intrinsic metal values are lost but only impurities (aluminium and anode materials) and harmful pollutants are removed (e.g. PVDF and electrolytes). The results of this study indicate that glycine-mediated leaching is successful at removing Co from waste LiBs and that temperature and pulp density have a significant effect on Co leaching. However, a second level optimization research utilizing a response surface methodology - central composite design (RSM - CCD) with a broader process parameter range is needed in order to determine the optimum values for maximum Co leaching. This study sought and optimized the selective recovery of Co using oxalic acid. The results indicate that a significant amount (>75%) of the dissolved Co may be recovered selectively from pregnant leachates. As a follow-up, the mineralogy of the precipitates can be examined, as well as the process optimization necessary to precipitate the desired size particles. It will be interesting to conduct a feasibility study on the usage of the precipitates (Co-oxalate) in the production of new Li ion batteries. Before beginning industrial applications, a techno-economic study integrating the inherent metal values of the waste LiBs, the materials cost and energy required for the hydrometallurgical process, and the resale values of the precipitates would be necessary.

5. Conclusions and recommendations

The results of this study show that the critical metal (Co) can be leached and recovered from the end-of-life lithium ion batteries (LiBs). The spent LiBs contain a substantial concentration of critical metals like Co and Li. Pre-treatment techniques like separation of impurities and contaminants from the cathodic material could facilitate the extraction of the desired metal (Co). The study proved that high concentration of Co (89%) can be leached from the cathodic materials of LiBs, using mild amino acid like glycine under optimum leaching conditions. Pulp density and temperature are the significant parameters for the leaching of Co from LiBs (among the investigated variables). The dissolved Co present in

the glycine leachates can be recovered using suitable precipitating agent such as oxalic acid in the form of Co-oxalate precipitate, which can be used to produce new LiBs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2022.102915>.

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