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An Environmentally Friendly Method for Recovery of Metals from Cathode Material of Lithium-Ion Batteries using L-Glutamic, Malonic, and Ascorbic acid

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Abstract

In this research work, with a simple, safe, and environmentally friendly approach to hydrometallurgy, a method for the recovery of lithium (Li), cobalt (Co), and nickel (Ni) from LIBs is suggested. The cathode materials are leached by malonic acid, as the leaching agent, and ascorbic acid, as the reducing agent in the first process, and by L-glutamic acid, as the leaching agent, and ascorbic acid, as the reducing agent in the second process. In order to optimize the leaching parameters including temperature, organic acid concentration, ascorbic acid concentration, type of organic acid, pulp density, and time, response surface methodology (RSM) of the experimental design process is used. According to the results, compared to L-glutamic acid in the second process, the leaching recovery increase considerably with malonic acid in the first process. This normally occurs due to the higher solubility of malonic acid in water, which results in a better complexation and a higher chelation rate. By contrast, as solubility of L-glutamic acid in water is low, metal-acid surface reaction and poor complexation are unavoidable. According to the statistical analysis of the results and validation testing, optimal experimental leaching occurs at the reaction temperature of 88 °C, organic acid concentration of 0.25 M, ascorbic acid concentration of 0.03 M, pulp density of 10 g/L, and leaching time of 2 h, via which metal recovery of 100% Li, 81% Co, and 99% Ni is achieved. Before and after acidic leaching, the sample active materials are qualitatively and quantitatively analyzed using X-ray diffraction, X-ray fluorescence, particle size analyzer, scanning electron microscope, energy dispersive spectroscopy, and atomic absorption spectroscopy.

1. Introduction

LIBs have excellent electrochemical properties, and are widely used in electronic devices and electric vehicles [1]. Spent LIBs are classified as the sub-group of e-waste, and are used in portable electronic devices including mobile phones, PCs, cameras, and more recently, in electrical vehicles, due to their desirable characteristics such as high energy density, high voltage, long storage, low discharge rate, and wide operating temperature range [2-6].

Today, thanks to developments and up-to-date electronic devices, the demand for LIBs is increasing. These batteries have a lifespan of about 3 to 8 years [7], before they are considered as waste, and are valuable sources of Li (5-8%), Ni (5-10%),

Co (5-20%), magnesium (Mg), aluminum (Al) and copper (Cu) but they are environmentally pollutant due to their heavy metal content and fluoride-containing electrolytes [4, 6, 8]. Consequently, serious problems may complicate proper disposal of LIBs that leads to environmental pollution and waste of resources [7]. Therefore, recovery of valuable metals from LIBs is both economically and environmentally cost-effective [9, 10]. Currently, 95% of e-waste is recycled unauthorizedly with little or no precautionary measures for the environment and human health.

According to a research work, global LIB cell production capacity was estimated to increase four to six times in 2021-2022 compared to 2017 [11].

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International Energy Agency (IEA) suggests that the global electric vehicle stock (excluding two/three wheelers) grows by 36% annually, reaching 245 vehicles in 2030 [11]. In spite of different estimations, which lack a clear and definite procedure, in order to achieve a safe future, in addition to economic and environmental reasons, recycling LIBs is a critical issue.

Generally, LIBs consist of cathode, anode, organic electrolyte with lithium solution compounds such as LiPF_6 , LiTFSI or LiBF_4 , a separator, and a metal shell. The cathode material of LIBs consists of Al foil coated with Li-based metal oxide (e.g. LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, and LiFePO_4), which make it highly capable of recycling valuable metals. Today, the research activities are focused on recycling metals from LIBs through mechanical techniques, pyrometallurgy, hydrometallurgy, and bioleaching [8, 12, and 13]. Meanwhile, due to a safer recycling process, more pure products, energy efficiency, diverse leaching solutions, and high leaching recovery, hydrometallurgy is preferred through which non-toxic waste and gases are produced and toxic substances are converted into safer forms such as salts, hydroxides, and metals [14, 15]. Hydrometallurgical recycling process includes pretreatment, acidic leaching, separation, purification, and synthesis of new products [16].

LiCoO_2 -based LIB waste consists of 33.5% LiCoO_2 , 24.5% metal shell, 14.5% Cu/Al, 16% carbon, 3.5% electrolyte, and 8% polymer [17-18]. Since cathode accounts for 30% of total battery manufacturing cost, most research works are focused on the development of cost-effective and environmentally friendly methods for recovery of valuable metals in cathodic materials [17].

In order to recycle battery cathodes, more research works were conducted on leaching of valuable cathodic metals using two types of acids. Mineral acids including HCl [19], H_2SO_4 [20], H_3PO_4 [21], and HNO_3 [22] are widely used for recycling metals from LIBs, and were found, according to research, more efficient in recycling metals from LIBs. However, dissolution at temperatures greater than 80 °C causes acid volatility and corrosion of laboratory equipment [23, 24]. Also if the residual leaching acid is absorbed by soil and groundwater, the environmental pollution by toxic emissions such as Cl_2 , SO_3 and NO_x [25] will happen.

In order to solve mineral acid-caused problems, the researchers widely utilize organic acids to recycle metals from LIBs. Using DL-malic acid, Li

et al. recovered 100% of Li and 90% of Co [26]. The researchers achieved the Co recovery of 98% and Li recovery of 99% using citric acid [23, 27]. 97.7% Li, 98.9% Co, and 98.2% Ni were recovered using lactic acid [28]. Nayaka et al. achieved the recovery of over 95% using a combination of ascorbic acid and tartaric acid [24]. Other researchers used formic acid for the recovery of 98.22% Li, 99.96% Co, and 99.96% Ni [29]. Using L-tartaric acid, they recovered 99.07% of Li, 98.64% of Co, and 99.31% of Ni [30]. Li et al. recovered about 100% of Co and about 96% of Li using 1.5 M succinic acid at 70 °C [31].

More recently, the researchers [25] used gluconic acid and lactic acid to recover 100% of Li and 97.36% of Co from LIBs, and indicated that lactic acid was more efficient than gluconic acid.

Reducing agents such as H_2O_2 [20-22, 26], NaHSO_3 [32], Na_2SO_3 [5], glucose [9], and ascorbic acid [2, 24] are added to increase recovery during leaching process. Because of less industrial equipment needed and non-toxic gas emissions, organic acid-based leaching is preferred [13].

A novel and efficient method of organic acid leaching for recovery of spent LIBs is proposed in this study. As a mild, non-volatile, non-toxic, and water-soluble organic acid, L-glutamic acid is biodegradable, edible, and environmentally friendly [33]. Malonic acid is another mineral acid that is found in many fruits and vegetables as a natural substance, and is considered as an appropriate leaching agent for two reasons: 1) it is water soluble and consequently less hazardous for the environment. 2) it is dicarboxylic, and has a high acidic strength, compared to other mineral acids, due to containing two carboxyl functional groups ($-\text{COOH}$). The two acids are well leached, have a low stability constant, which makes the complexes formed by them easily separated during the purification phase, do not damage the cathode system, and are less corrosive compared to mineral acids.

For the first time, the recovery of Li, Co, and Ni in LIBs was investigated using these two acids, and the optimum conditions were obtained. Also the effect of each acid on leaching and metal recovery rate were compared. Leaching recovery with malonic acid was significantly higher than L-glutamic acid. In this study, the effect of six qualitative and quantitative parameters during the leaching process including organic acids (L-glutamic and malonic), acid concentration (0.1-0.5 M), temperature (30-90 °C), ascorbic acid concentration as the reducing agent (0.01-0.05 M), pulp density (1-10g/L), and time (2-8 h) on the

recovery of Li, Co and Ni as well as the interaction of parameters were investigated.

2. Materials and Experiments

2.1. Materials

The spent LIBs used in this research work were laptop batteries collected from local electronics stores. Leaching agents included malonic acid ($C_3H_4O_4$), L-glutamic acid ($C_5H_9NO_4$), and ascorbic acid ($C_6H_8O_6$) as a reducing agent, which were all of analytical grade. All solutions were prepared in distilled water, and all analytical reagents were from the Merck Company.

2.2. Sample preparation

First, the spent LIBs were immersed in a saturated NaCl solution (5 wt%) for 24 hours to be discharged in order to prevent associated hazards including fire or explosion caused by unwanted short circuiting [15, 34]. Next, after full discharging, the batteries were washed with distilled water and dried at 60 °C for 8 hours. Then the metal shell of the batteries was removed by scissors, and their cathode and anode were separated manually [35].

In order to separate the coated cathodic material, the Al sheet was removed from curvature, and cut into small pieces (about 1 cm*1 cm), and dried at 60 °C in oven for 24 h. The crushed parts of cathode were powdered by a ceramic-walled ball mill for 2 h to avoid impurities enter cathodic material. At the next step, the powder was separated and categorized through wet and dry sieve. First, using 200 µm mesh, passing particles were smaller than 75 µm, and then the remaining particles were wet sieved in order for particles smaller than 75 µm to pass. The solution obtained from wet sieve was filtered, and after drying, the powder remained from two sieves was combined and divided similarly by riffle splitter for leaching. Finally, the black cathode powder was heated to 700 °C in a furnace for different lengths of time. Carbon and Polyvinylidene Fluoride (PVDF) were best removed from the powder after 2 h of heating.

2.3. Analytical methods

Following the mechanical treatment, in order to quantify Co, Li, and Ni in the basic compound and the material obtained from leaching, an AAS (Atomic Absorption Spectrometer, Australia, Varian AA220FS) was used. To set the basic cathodic compound, cathodic waste was dissolved

with Aqua regia (HNO_3 : HCl = 1:3, v/v) and 5.86% Li, 32.21% Co, and 12.73% Ni were quantified in the cathode. Leaching efficiency was calculated as follows:

$$R(\%) = \left(1 - \frac{W_w \times G_w}{W_f \times G_f}\right) \times 100 \quad (1)$$

where R is the leaching efficiency (%), W_w is the residual leached powder weight (g), G_w is the element grade in residual leached powder (%), W_f is the battery cathode weight (g), and G_f is the element grade in battery cathode (%).

X-ray diffraction (XRD, Philips-3040/60 PW) measurement with Cu-K α in the range $5 < 2\theta < 100$ was used to investigate the phases present in pre- and post-leaching samples and also carbon content or its elimination after calcination. The source voltage and current were set at 40 kV and 40 mA, respectively. The size of 80% of cathodic powder particles passing through Particle Size Analyzer (Analysette 22 MicroTec plus) was 20.2 µm. To determine the content of chemical compound in pre- and post-sieve cathode powder and for different calcination times, an X-ray sequential fluorescence spectrometer (XRF, ARL™ PERFORM'X) was used. Scanning electron microscopy and energy dispersive spectroscopy (SEM and EDS map, Hitachi, s-4160) were utilized to analyze the surface morphology of the active materials before and after leaching.

2.4. Design of Experiment (DoE)

In order to optimize the leaching process, 2-level fractional factorial design technique was used to remove the statistically insignificant parameters. Then the experiments were optimized using Central Composite Design (CCD) in Demo version of Design Expert 12 (State-Ease Inc., Minneapolis, MN, USA). The parameters and range of parameters are potentially effective on leaching efficiency. These parameters include reaction time, reaction temperature, pulp density, acid type, organic acid concentration, and reducing agent concentration (ascorbic acid), determined based on paper reviews [7, 36-38]. Using DoE, the number and cost of tests decrease. Screening and optimization are two main applications of DoE software [39].

In order to remove insignificant parameters, 16 experiments were designed using 2-level fractional factorial design (2^{6-2}). Their parameters and specifications for DoE are displayed in Table 1.

Table 1. Parameters and their specifications in 2-level fractional factorial design.

Symbol	Factor name	Unit	Type	Low level	High level
A	Temperature	°C	Numeric	25	90
B	Organic acid concentration	mol/L	Numeric	0.05	0.5
C	Ascorbic acid concentration	mol/L	Numeric	0	0.05
D	Acid type	-	Categoric	Malonic	Glutamic
E	Time	h	Numeric	2	8
F	Pulp density	g/L	Numeric	1	10

After the experiments, using Half-Normal Plot and Pareto Chart, the effective parameters were identified, and leaching time and pulp density were set as the insignificant parameters. Ergo, in optimization experiments, leaching time of 2 hours, and pulp density of 10 g/L were considered to prevent analysis errors by atomic absorption device.

In the next step, due to its high accuracy, RSM was used to optimize the effective parameters in the recovery of Co, Li, and Ni. Despite the high accuracy of the software, some errors associated with atomic analysis, unwanted evaporation during

leaching process, volumetric measurements, and dilution coefficient affect the test results, and cannot be ignored.

Two insignificant parameters were removed using 2-level fractional factorial method. Then optimization experiments were designed through the remaining 4 parameters (temperature, organic acid concentration, reducing agent concentration, and type of acid) using CCD in RSM. Table 2 displays the parameters and their level. Table 3 reports on 36 experiments designed based on the quadratic model with parameters and responses in standard mode.

Table 2. Selected parameters and their levels for DoE.

Symbol	Factor name	Unit	Type	Low actual	High actual
A	Temperature	°C	Numeric	30	90
B	Organic acid concentration	mol/L	Numeric	0.1	0.5
C	Ascorbic acid concentration	mol/L	Numeric	0.01	0.05
D	Acid type	-	Categoric	Malonic	Glutamic

Leaching tests

All the experiments were conducted using a PYREX Flask Erlenmeyer 500 mL (ISO Lab, Germany) containing 100 mL of test solution. To control the temperature of the test environment, the Erlenmeyer was placed inside a water bath, and the temperature was kept at ± 5 °C range by a glass thermometer. In order to reduce the evaporation, a glass condenser was attached to the Erlenmeyer. A magnetic stirrer was also used to stir and mix the solution. All the experiments were conducted in 2 hours, and the pulp density of all tests was 10 g/L. At the end of each experiment, the solution was filtered using a filter paper (150 mm, Whatman international Ltd Maidstone, China), and washed with distilled water.

3. Results and Discussion

3.1. Characteristics of cathodic materials in LIBs

Table 4 shows the results of XRF analysis. Before and after sieving, there is a significant change in the amount of Al in the sample, and compounds such as CuO, MgO, and CaO, present in insignificant amounts in some analyses, are ignorable impurities resulting from the environmental and laboratory conditions. According to Table 4, due to the removal of carbon as the impurity, the main elements including Li, Co, Ni, and manganese (Mn) increased following seizing and calcination. However, XRF is limited by the atomic number of elements, and those with low atomic number and low energy such as Li, carbon, and oxygen could not be detected in XRF.

Table 3. Design and responses of CCD experiments.

Run	Temperature (°C)	Organic acid concentration (mol/L)	Ascorbic acid concentration (mol/L)	Acid type	Recovery (%)					
					Li	Li predicted	Co	Co predicted	Ni	Ni predicted
1	60	0.3	0	Malonic	72.96	67.14	22.62	27.38	86.7	80.31
2	60	0.56	0.03	Malonic	87.63	88.42	63.26	63.29	92.7	88.57
3	60	0.56	0.03	Glutamic	92.85	86.78	63.1	50.1	85	73.33
4	20.52	0.3	0.03	Malonic	74.39	75.98	46.64	48.85	64.4	63.39
5	60	0.3	0.06	Glutamic	99.3	90.64	67.97	65.04	82.6	83.86
6	30	0.5	0.05	Malonic	98.5	90.82	64.63	64.48	75.9	80.71
7	90	0.5	0.05	Malonic	100	100	98.49	93.31	100	100
8	30	0.1	0.01	Malonic	45.69	43.43	8.94	6.23	30.3	26.19
9	90	0.1	0.05	Malonic	96.43	95.11	76.38	74.6	86.7	82.72
10	99.48	0.3	0.03	Malonic	99.27	100	85.32	86.79	96.5	100
11	60	0.3	0.03	Glutamic	83.72	78.80	56.89	53.45	82.6	78.15
12	60	0.3	0	Glutamic	40.36	46.51	13.59	13.01	26.8	39.06
13	90	0.1	0.01	Malonic	75.15	65.38	40.24	35.06	77.8	68.67
14	30	0.5	0.01	Glutamic	45.13	49.46	12.16	10.57	19.6	30.63
15	90	0.5	0.01	Malonic	93.47	83.04	65.92	53.78	89.9	88.36
16	30	0.1	0.05	Glutamic	57.09	61.52	26.24	31.39	49.4	49.77
17	60	0.3	0.03	Glutamic	84.51	78.8	59.86	53.45	84.8	78.15
18	30	0.1	0.01	Glutamic	36.22	31.79	12.23	10.15	23.6	15.94
19	30	0.1	0.05	Malonic	80.39	73.15	54.93	45.76	77.8	68.02
20	60	0.04	0.03	Glutamic	50.24	53.54	22.18	24.28	37.9	47.41
21	20.52	0.3	0.03	Glutamic	55.38	64.35	24.55	34.47	45.4	48.15
22	60	0.3	0.03	Glutamic	84.78	78.80	57.71	53.45	84.6	89.56
23	60	0.3	0.03	Malonic	85.96	86.1	70.8	67.82	92.8	93.39
24	60	0.04	0.03	Malonic	57.79	65.17	26.31	36.66	47.3	50.66
25	60	0.3	0.06	Malonic	99.54	100	80.37	79.42	91.3	99.1
26	60	0.3	0.03	Glutamic	84.18	86.54	56.26	53.45	83.6	86.52
27	90	0.5	0.05	Glutamic	99.53	100	81.36	78.94	89	87.16
28	90	0.1	0.01	Glutamic	48.53	53.75	14.96	20.68	40.2	50.42
29	30	0.5	0.01	Malonic	53.36	61.09	14.62	24.94	39	45.88
30	90	0.5	0.01	Glutamic	62.64	71.41	19.06	28.4	78.1	73.11
31	60	0.3	0.03	Malonic	91.49	90.43	68.72	67.82	87.6	90.34
32	99.48	0.3	0.03	Glutamic	96.08	93.24	75.27	72.42	87	87.75
33	90	0.1	0.05	Glutamic	81.25	83.47	51.01	60.22	72.5	67.47
34	60	0.3	0.03	Malonic	88.46	90.43	65.97	67.82	91.2	93.39
35	30	0.5	0.05	Glutamic	75.26	79.18	40.79	45.11	70.7	69.46
36	60	0.3	0.03	Malonic	85.96	90.43	59.77	67.82	89.8	93.39

Table 4. Determination of elements in cathodic material of LIBs (before and after seizing and for different calcination durations).

Element (wt%)	Retained particles	Passed particles	1 h furnace	2 h furnace	4 h furnace	6 h furnace
Al ₂ O ₃	44.84	1.12	1.08	1.11	0.88	1.26
K ₂ O	0.09	-	-	0.09	-	0.1
NiO	10.63	18.21	18.22	19.11	16.8	20.21
SiO ₂	0.31	0.2	0.18	0.24	0.63	0.25
CaO	0.13	-	-	-	0.22	-
P ₂ O ₅	0.21	0.42	0.25	0.39	0.39	0.45
MnO	7.72	10.46	15.49	13.58	15.6	12.5
SO ₃	0.06	0.19	0.22	0.16	0.12	0.16
Co ₃ O ₄	21.53	47.21	50.55	49.4	47.5	57.31
MgO	-	-	-	0.19	0.35	-
CuO	-	-	0.22	-	-	-
L.O.I	8.18	9.35	0.45	1.9	1.21	1.34

Calcination was performed at 700 °C and for 1, 2, 4, and 6 hours to determine the optimum calcination time, which was 2 hours due to less energy and almost the same efficiency as other times. Based on the results [40] obtained from TG-MS analysis of LIBs, during heat treatment, low levels of temperature promote weight loss. First, at 500 °C, PVDF is thermally decomposed. Second weight loss occurs at 500-650 °C. CO₂ peak in the gas phase is achieved at about 550 °C, and may be associated with redox reactions between acetylene black and cathode active substances during metal transfer. The results [40] show that heat treatment separates cathode active materials from collectors in the battery, and completely removes binders and carbon conductors. It also changes the molecular structure and partially reduces transition metals, which facilitates the recovery of transition metals by leaching.

Figure1 shows the layered crystal cathode sample pattern before and after calcination at 700 °C for 2 h and residual material of leaching by malonic acid and L-glutamic acid. In Figure1a, XRD analysis of the sample before calcination indicates a carbon peak that was not detected in Figure1b after carbon peak calcination, which is burned in the carbon calcination process. This proves the efficiency of the process in the removal of impurities. Figure1b indicates that the cathodic material is mainly LiCoO₂. Figure1c and Figure1d are XRD analysis of the residual material of leaching by malonic acid and L-glutamic acid. Most peaks are indicators of insoluble Co₃O₄ species. They also confirm that LiCoO₂ reacts with malonic acid and glutamic acid during leaching, and LiCoO₂ is leached and new species are created.

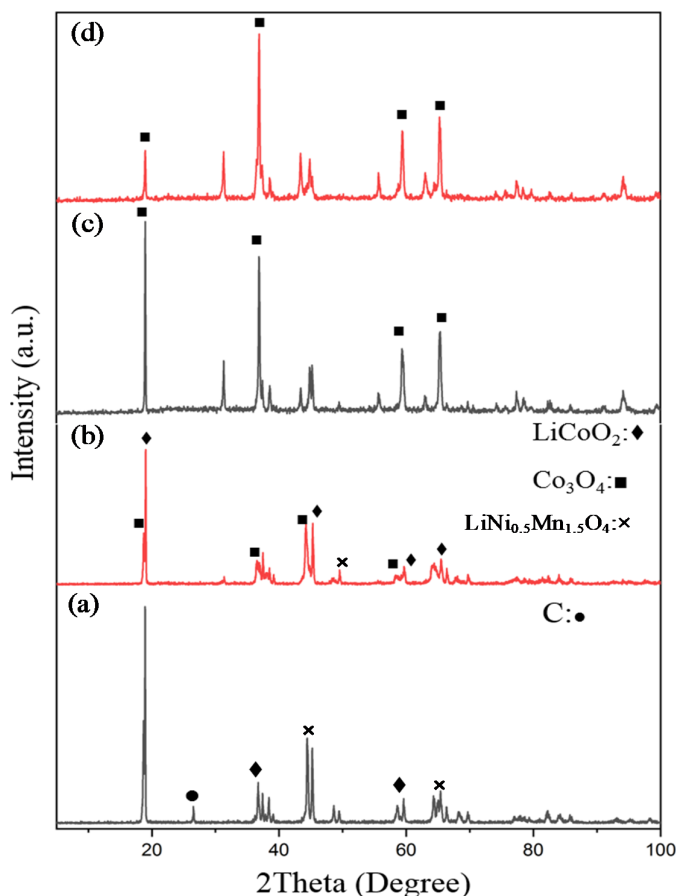


Figure1. XRD pattern of cathodic material before and after leaching (a) before calcination (b) after calcination at 700 °C for 2 h (c) residual materials after leaching by malonic acid (d) residual material after leaching by glutamic acid.

Figure2 shows the particle size distribution of cathodic material before and after leaching. Accordingly, 90% of the particles were larger than

1 µm, the diameter of 80% of the particles (before leaching) was 20.2 µm and the diameter of 80% of the particles (after leaching by malonic acid) was

13.3 μm . The average particle diameter before and after leaching was 11.2 μm and 9.1 μm , respectively. This means that particle size

decreased during leaching, which confirms the maximum recovery of Li, Co, and Ni by reduced particle size.

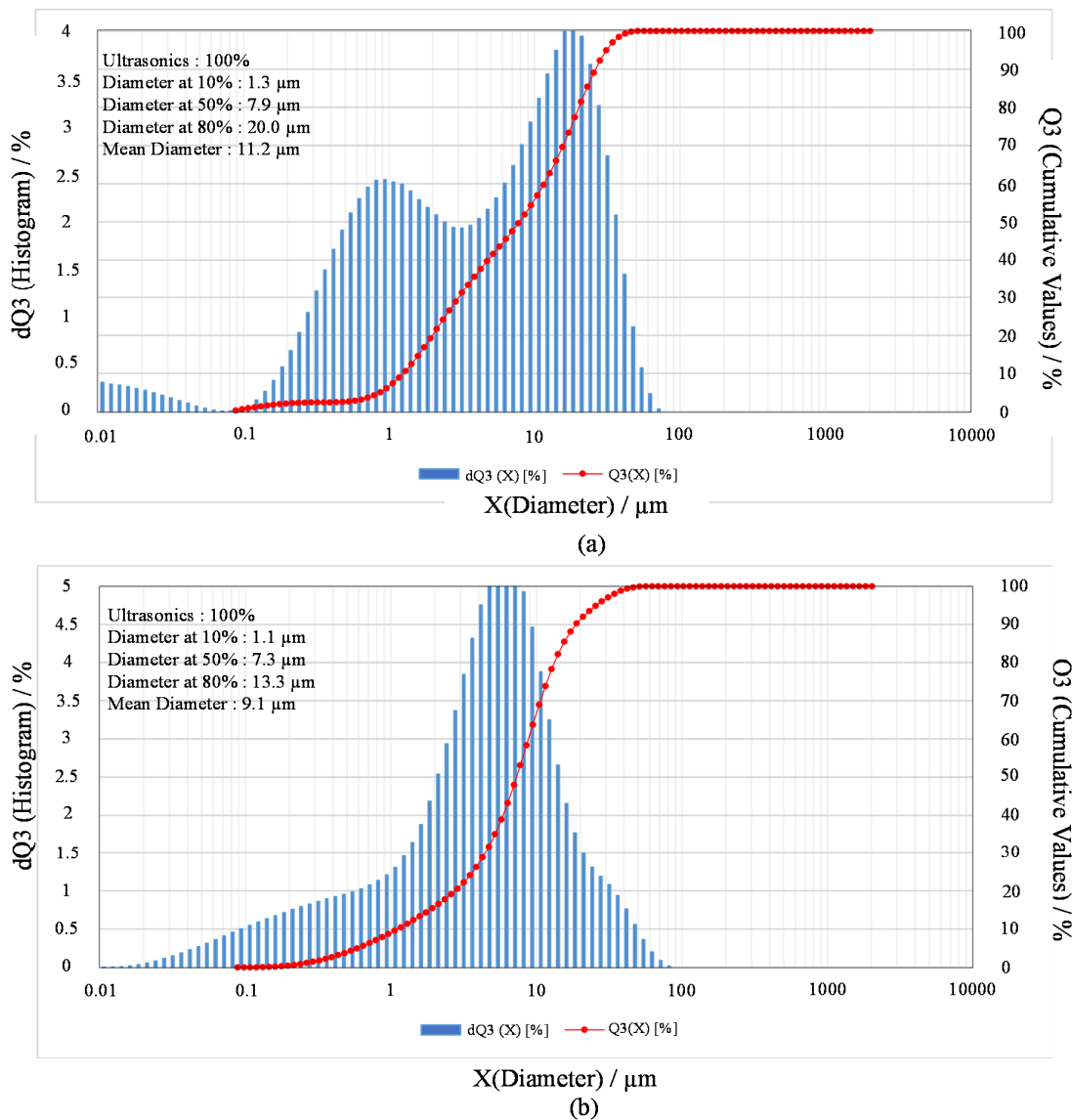


Figure 2. Particle size distribution of cathodic material (a) after degradation and calcination at 700 °C for 2 hours and (b) after leaching at 88 °C, with 0.25 M malonic acid, pulp density of 10g/L, and ascorbic acid concentration of 0.03 M.

SEM shows significant changes before and after leaching to evaluate waste cathode and leaching residues. According to Figure 3a, before leaching, the cathode has layered crystals of a relatively regular structure, while crystalline cathode powder after leaching by malonic acid and glutamic acid is converted into smaller pieces with irregular structure. In malonic acid leaching, under optimum

conditions, rod-shaped and spherical particles with irregular and porous structure are observed after leaching. In addition, hollow-structure spherical and elliptical particles can be observed after leaching with glutamic acid under optimum conditions. This indicates proper leaching performance for the recovery of cathodic materials.

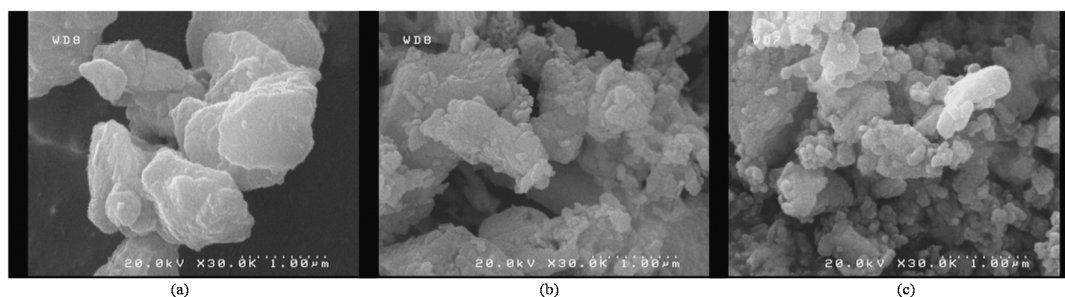


Figure3. SEM images (a) LIB cathode remained in furnace at 700 °C for 2 hours. (b) residual cathodic material from leaching by malonic acid (c) residual cathodic material from leaching by L-glutamic acid.

Figure4 is the EDS map images of cathodic materials after calcination at 700 °C for 2 hours, before and after leaching. Figure4a indicates scattered and extendedly distributed Co and Ni particles on cathode surface. According to Figure4b and Figure4c, as confirmed by EDS,

some Co was detected in the leaching residues. This means the residues had some Co_3O_4 and CoO , which was also confirmed by XRD analysis. According to Figure4b and Figure4c, Ni was dissolved during leaching and its value in the residue decreased.

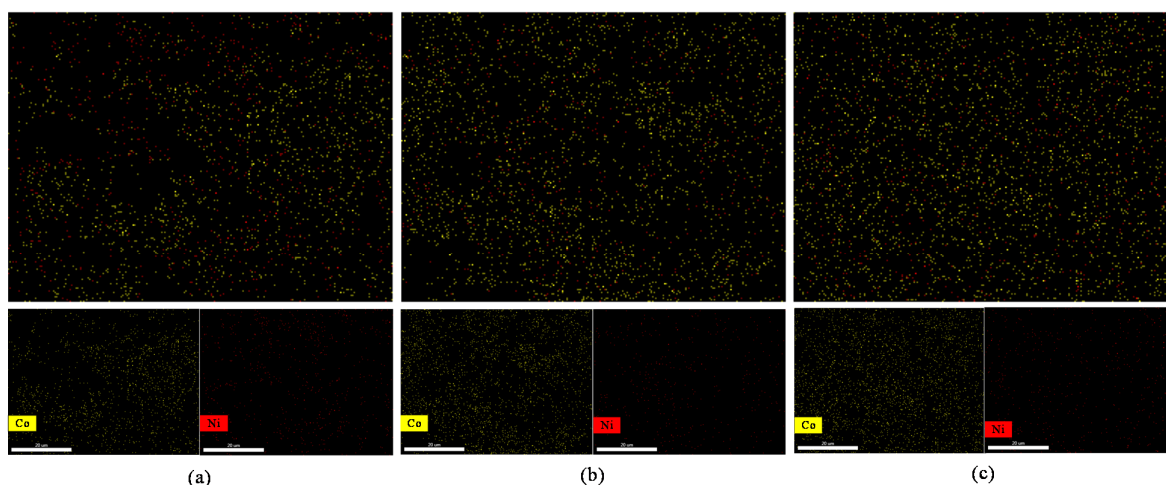


Figure4. EDS map image (a) cathodic material after leaching at 700 °C for 2 hours (b) cathodic material after leaching by malonic acid (c) cathodic material after leaching by L-glutamic acid.

3.2. DoE-based leaching of Li, Co, and Ni

3.2.1. DoE results

ANOVA was used for graphical analysis of the data after the experiments. The F-value obtained from ANOVA indicates the importance of the mentioned factor. According to the experiments for Li, Co, and Ni, the highest F-value is for independent variables including temperature and ascorbic acid, indicating the high effect of these variables on the recovery of Li, Co, and Ni in leaching process. In this study, the variables A, B, C, D, B^2 , and C^2 were significant terms, and insignificant factors with low and limited effect such as AB, AC, AD, BC, BD, CD, and A^2 in Li and Co recovery were removed from the model. The variables A, B, C, D, AC, A^2 , B^2 , and C^2 were important factors of Ni recovery, and other

insignificant factors were excluded in order to improve the model. A, B, C, and D were temperature, acid concentration, ascorbic acid concentration, and type of acid, respectively.

The proposed model for the recovery of Li, Co, and Ni is based on quadratic model of CCD. Following is the quadratic equation for predicting optimal conditions:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i \cdot X_i + \sum_{i=1}^k \beta_{ii} \cdot X_i^2 + \sum_{i \leq j}^k \sum_{j=1}^k \beta_{ij} \cdot X_i \cdot X_j + \dots + e \quad (2)$$

where "i" is the linear coefficient, "j" is the quadratic coefficient, β is the regression coefficient, "k" is the number of factors studied and optimized in the experiment, and "e" is the random error.

The correlation coefficient should be at least 0.8 to obtain a good fit. The high value of R^2 indicates a good match between the calculated and observed

results in experiment range. According to Table (5), the R^2 value of the quadratic regression model for Li, Co, and Ni was 0.8796, 0.9037, and 0.8634, respectively, and the difference between $Pred.R^2$ and $Adj.R^2$ was less than 0.2, indicating the model's remarkable validity. Also Adeq Precision, with acceptable values of greater than 4, has significant values in all models.

Table 5. Response surface model.

Model	Recovery Li	Recovery Co	Recovery Ni
Mean	76.76	49.14	71.19
Std. Deviation	7.54	8.57	10.01
Model Degree	Quadratic	Quadratic	Quadratic
R^2	0.8796	0.9037	0.8634
$Adj.R^2$	0.8547	0.8838	0.8229
$Pred.R^2$	0.8023	0.8460	0.7356
Adeq Precision	24.370	26.837	18.400

3.2.2. Results of model fitting

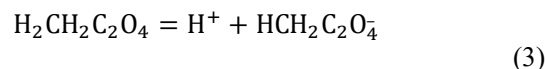
3.2.2.1. Effect of type of acid

After determining the appropriate model by software to investigate the effect of each parameter on recovery process, the graph diagrams were examined. The slopes indicate the importance of each parameter, as steeper lines are more effective, and vice versa.

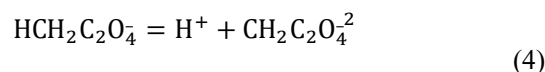
Figure 5a shows the effect of type of acid (malonic and L-glutamic acid) on the recovery of Li, Co, and Ni leaching at 88 °C, acid concentration of 0.25 M, ascorbic acid concentration of 0.03 M, and pulp density of 10 g/L for 2 h in optimum conditions. Changing organic acid from L-glutamic to malonic, the recovery of Li, Co, and Ni increased from 84.80% to 96.20%, from 64.16% to 78.53%, and from 80.01% to 94.53%, respectively.

Therefore, malonic acid was more effective than L-glutamic acid for the above-mentioned cases. Malonic acid is a suitable leaching agent due to its easy dissolution in water.

The reaction of malonic acid decomposition is explained as follows [41]:



$$pK_1^o = 2.85 \pm 0.03$$



$$pK_2^o = 5.69 \pm 0.03$$

and reaction by decomposition of L-glutamic acid, which is an amino acid, is explained as follows[42]:



$$pK_1 = 2.19$$



$$pK_2 = 9.67$$

Amino acid molecules have at least one acid and one base group, and amino acids have at least two decomposition constants. pK_1 in L-glutamic molecules is associated with the release of hydrogen in carboxyl group, and pK_2 is associated with the release of hydrogen from the amine group[42].

The above equations show that malonic acid and L-glutamic acid have a two-step separation reaction, from which two moles of H^+ are produced. According to the studies, malonic acid was more efficient than L-glutamic acid. There are two carboxylic groups in the structure of both acids but the amine group existing in the structure of L-

glutamic acid reduces its acidic strength. On the other hand, increasing the carbon chain length in the structure of L-glutamic acid reduces its acidic strength. Furthermore, in L-glutamic acid, the intracellular hydrogen bonds between the amine and the acid group reduces the acidic properties of the substance [41, 42].

Complexation better occurs with malonic acid due to its higher solubility compared to L-glutamic acid. Also at low temperatures, it has more chelation power and more extraction of Li, Co, and Ni, compared to L-glutamic acid. At low temperatures, due to low solubility of L-glutamic acid, metal-acid reaction occurs only on its surface and complexation is weak. As the temperature increases and the dissolution of L-Glutamic acid increases, the chelation power and the extraction of Li, Co, and Ni increases [41, 42].

3.2.2.2. Effect of temperature

The higher the temperature, the more the solubility of malonic acid and L-glutamic acid because the temperature dependence of the separation coefficient in the acidic form is reversed by increasing ion strength [41].

Figure 5b shows the effect of temperature on the recovery of Li, Co, and Ni using 0.25 M of malonic acid, 0.03 M of ascorbic acid, pulp density of 10 g/L, and duration of 2 h. As the temperature increased from 30 °C to 90 °C, the recovery of Li, Co, and Ni increased from 76.75% to 98.71%, from 50.46% to 79.29%, and from 69.36% to 99.45%, respectively. Temperature was one of the parameters affecting leaching, and at higher temperatures, the dissolving power of acids and the recovery of Li, Co, and Ni increased. Increasing the leaching temperature improves leaching efficiency and results in an endothermic reaction [15]. The average kinetic energy of molecules and the rate of ion transfer increase with temperature. Consequently, frequent and more energetic encounters accelerate leaching reaction [28, 43].

Chemical reaction rate and ion transfer rate are significantly affected by temperature. At lower temperatures, leaching reaction is controlled by chemical reaction, and when temperature increases, chemical reaction rate increases as well and the leaching process is determined by ion transfer [26].

3.2.2.3. Effect of organic acid concentration

Figure 6a shows the effect of organic acid concentration on the recovery of Li, Co, and Ni using malonic acid at 88 °C, ascorbic acid

concentration of 0.03 M, and pulp density of 10 g/L for 2 h. A higher acid concentration increased Li recovery gradually from 80.89% to 97.87%. Increase in acid concentration from 0.1 M to 0.5 M increased Co recovery from 62.39% to 81.11%, and the increase in concentration led to the increase in Ni recovery from 78.33% to 97.09%.

Li and Ni leaching were dependent on H^+ concentration and acidic strength, so the higher the acid concentration, the higher the recovery level. However, in Co recovery process, despite the significant effect of H^+ concentration on Co mobility, chelation, conversion of Co^{3+} to Co^{2+} , and complexation occur in order for its extraction [2]. Chelation depends on the type of anion produced by leaching agent. However, it occurs at higher pH levels. Therefore, increased acidity of the solution delays the chelation.

At low temperatures, because glutamic acid is insoluble, the leaching power of malonic acid is higher but at optimum temperatures, because glutamic acid is completely dissolved, it has more power to chelate Co than malonic acid.

With increasing organic acid concentration to optimum concentration, the recovery increases significantly but due to the nonlinear effect of increasing organic acid, after the optimum point, there is no evident significant change in the recovery of Li, Co, and Ni. This is because at the optimum point, the environment meets saturation in terms of H^+ concentration and adding more organic acid will not affect the dissolution of the metal. The effect of increasing the concentration of organic acid on Li and Ni to the optimum point is greater than Co because Li and Ni can recover by adding organic acid but Co needs a reductive in the environment to recover.

3.2.2.4. Effect of ascorbic acid concentration

Figure 6b shows the effect of ascorbic acid concentration on the recovery of Li, Co, and Ni using malonic acid at 88 °C, 0.25 M acid concentration, pulp density of 10 g/L, and duration of 2 h.

Higher ascorbic acid concentration increased the recovery of Li, Co, and Ni from 72.30% to 99.57%, from 50.44% to 89.97%, and from 83.49% to 97.90%, respectively.

This increase in the efficiency is because the added ascorbic acid reacts very quickly at zero moment [13].

With the increase of reducing agent, leaching efficiency of Li is higher than Co and Ni because Li-O bond energy is poor and ascorbic acid has a

great ability to absorb molecular oxygen (O), and is therefore considered as a strong reducing agent [9, 44]. The chemical bond between Co and O is very strong, therefore, acid leaching of lithium cobalt oxide (LiCoO_2) is difficult [26]. Adding ascorbic acid is more effective on the recovery of Co than Ni, as the reducing agent converts insoluble Co^{3+} into soluble Co^{2+} in leaching

environment and helps accelerate Co recovery. In general, oxidation-reduction factors in the system contribute to leaching of metal species [2, 26]. Reduction of Co can lead to an unstable crystalline structure in the cathode, which is important for improving the leaching efficiency of Co and simultaneously accelerating the dissolution of other metals in the crystalline structure [16].

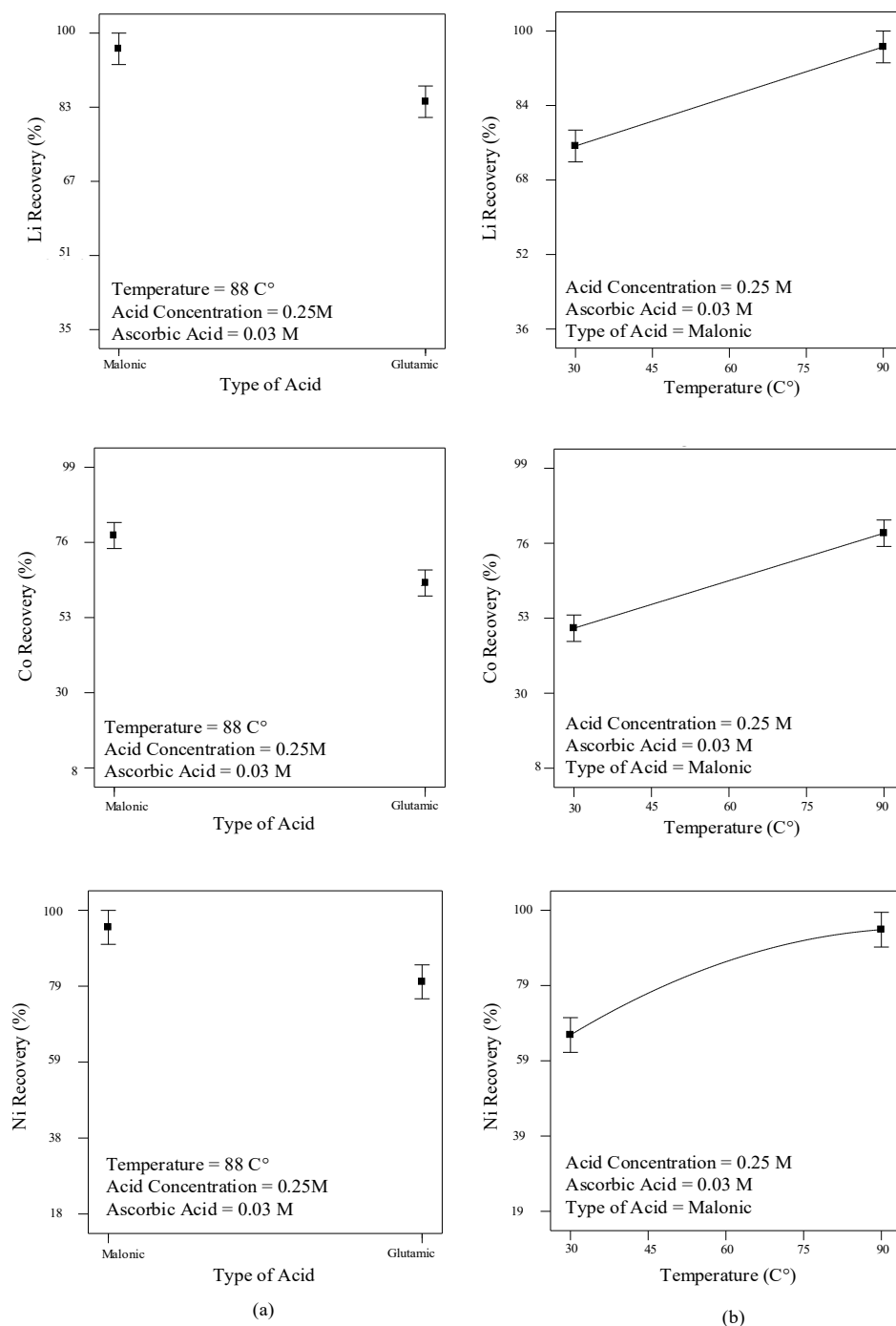


Figure 5. Effect of type of acid and temperature on the recovery of Li, Co, and Ni (a) Effect of type of acid on the recovery of Li, Co, and Ni at 88 °C, malonic acid concentration of 0.25 M, and ascorbic acid concentration of 0.03 M (b) Effect of temperature on recovery of Li, Co, and Ni at malonic acid concentration of 0.25 M and ascorbic acid concentration of 0.03 M.

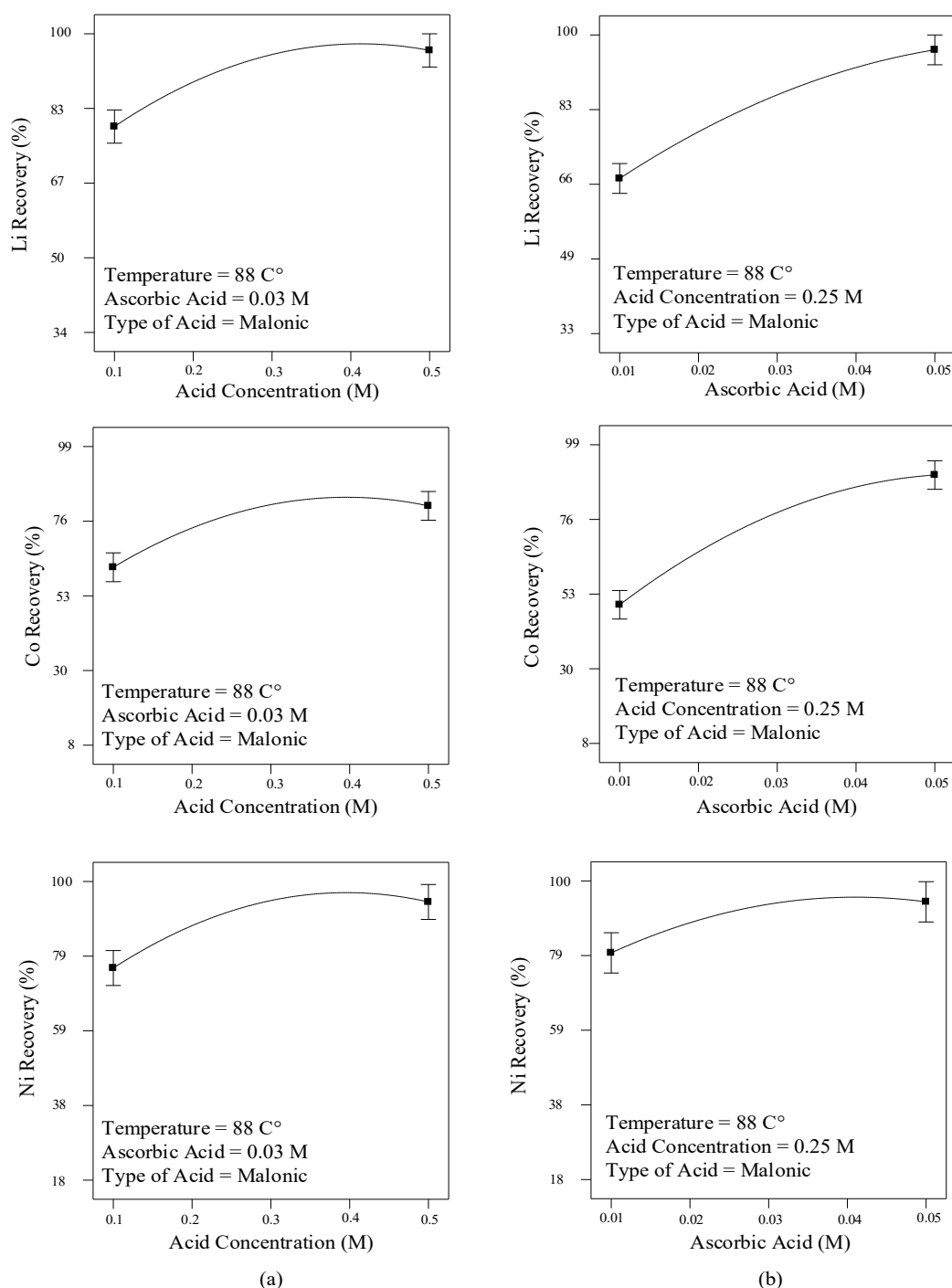


Figure6. Effect of acid concentration on the recovery of Li, Co, and Ni (a) effect of malonic acid concentration on the recovery of Li, Co, and Ni at 88 °C, and ascorbic acid concentration of 0.03 M. (b) effect of ascorbic acid on the recovery of Li, Co, and Ni at 88 °C and acid concentration (malonic) of 0.25 M.

3.2.2.5. Effect of parameter interaction on metals recovery

3D response surface diagrams are graphical representations of the regression equation used to determine the optimal values of variables in the

intended ranges [45]. The fitted model shows the contribution of each factor to the response

Figure7 shows the effect of operational parameters on the recovery of Li, Co, and Ni from cathode materials and the interaction between the relevant parameters in optimum conditions. Figure7a and Figure7b indicate the relationship

between the effect of acid concentration (malonic) and temperature with pulp density of 10 g/L and leaching time of 2 h and ascorbic acid concentration of 0.03 M on Li and Co recovery. According to Figure7, maximum Li recovery occurred at the temperature range of 30 °C to 90 °C, as highest temperature, and acid concentration of 0.1 to 0.5 M at the average level of organic acid concentration.

When acid is consumed between two solid-liquid phases, the H^+ concentration gradient between common point of solid-liquid and solution increases gradually, leading to higher diffusion speeds. After the leaching reaction reaches equilibrium, maximum Li leaching efficiency is achieved. This is because the rate of diffusion does not change with increasing acid concentrations and enough Li is replaced. By adding more acid, the effect of diffusion rate and viscosity weakens, which does not change the leaching efficiency significantly [19].

Higher temperatures can improve the kinetics of leaching reaction and solid-liquid diffusion [12]. In Figure7b, maximum Co recovery occurred at the maximum temperature and the average acid concentration. After the average acid level was reached, leaching recovery decreased with increasing recovery concentration. The increasing rate of recovery of Li and Co is due to the large amount of H^+ available for leaching, while chelation occurs at high pH. Therefore, the increase in acid concentration greater than a certain point complicates chelation [25].

Figure7c illustrates the relationship between the effect of acid concentration (malonic) and temperature at pulp density of 10 g/L, leaching time of 2 h and ascorbic acid concentration of 0.03 M on Ni recovery. The results show that higher temperature increased Ni recovery at average acid concentration, after which there was no noticeable change in Ni recovery. Ni leaching efficiency is

higher than Co, this probably occurs due to the divalent state of Ni in the battery cathode, thus Ni is leached easier than Co [13].

Figure7d also shows the interaction between temperature and concentration of ascorbic acid in the optimum conditions defined for Li recovery. This indicates that maximum recovery is at the highest temperature and high level of ascorbic acid. Dissolution mechanism probably starts with the dissolution of active cathode in the presence of ascorbic acid, followed by the chelation of Co^{2+} and reaction of Li with malonate and glutamate. Figure7e shows the interaction between temperature and ascorbic acid concentration of 0.25 M for Co recovery. According to Figure7e, the highest Co recovery occurred at maximum temperature and acid ascorbic concentration. In Figure7f, the interaction between temperature and ascorbic acid concentration at the acid concentration (malonic) of 0.25 M and pulp density of 10 g/L and duration of 2 h is investigated. The highest Ni recovery was observed at the high temperature level and the average level of ascorbic acid concentration. When temperature increased, Ni recovery increased considerably so that the highest Ni recovery occurred at the highest temperature. Also according to the diagram, with increase in ascorbic acid concentration, Ni recovery increased. The process continued until the average concentration of ascorbic acid was obtained after which there was no noticeable change in Ni recovery. Accordingly, most Ni recovery occurred at the highest temperature and the average level of ascorbic acid.

3.2.3. Process optimization

To optimize the recovery of Li, Co, and Ni from LIBs, response surface regression equations were used. The obtained equations for Li, Co, and Ni are as follows:

$$\text{Lithium recovery} = +84.62 + 10.98 \times A + 8.83 \times B + 14.86 \times C - 5.82 \times D - 7.87 \times B^2 - 4.46 \times C^2 \quad (6)$$

$$\text{Cobalt recovery} = +60.64 + 14.42 \times A + 9.36 \times B + 19.77 \times C - 7.19 \times D - 9.73 \times B^2 - 8.33 \times C^2 \quad (7)$$

$$\text{Nickel recovery} = +85.77 + 15.04 \times A + 9.85 \times B + 13.22 \times C - 7.62 \times D - 6.20 \times A \times C - 5.89 \times A^2 - 10.26 \times B^2 - 6.75 \times C^2 \quad (8)$$

where A, B, C, and D are the parameters including temperature, acid concentration, ascorbic acid concentration, and type of acid, respectively.

To transfer actual values to code values, the following equation is used [25]:

$$\text{Code values} = \frac{2 \times (\text{actual value} - \text{actual mean value})}{\text{the range of actual value}} \quad (9)$$

Desirability of the quadratic model is estimated for Li recovery of 0.99, Co recovery of 0.80 and Ni

recovery of 1. Generally, the overall model recovery for Li, Co, and Ni is estimated to be 0.93.

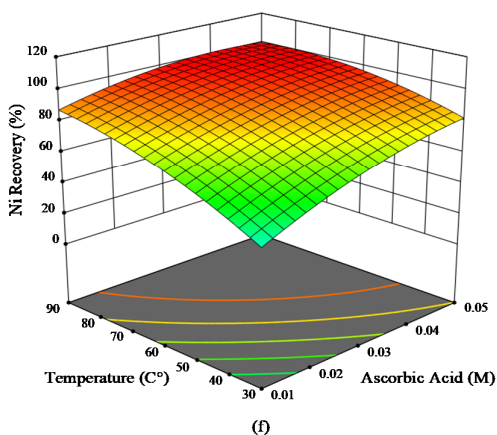
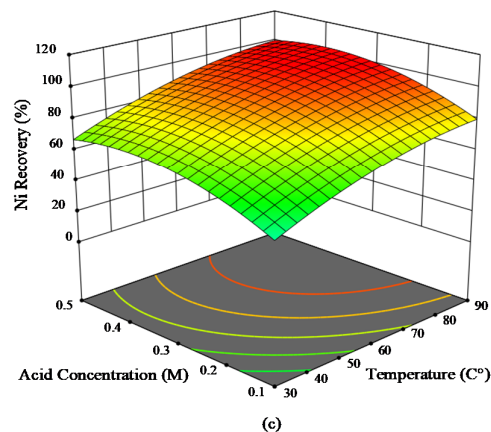
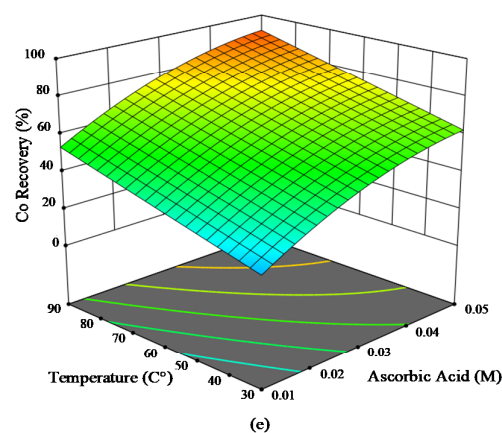
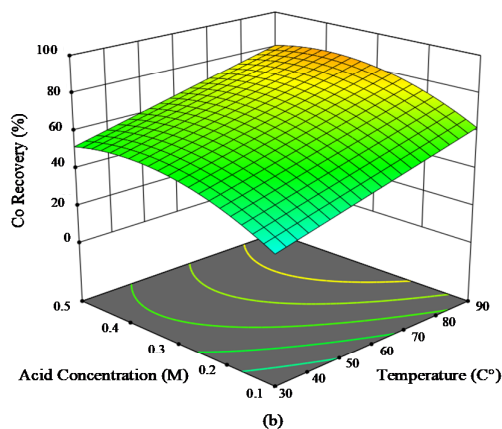
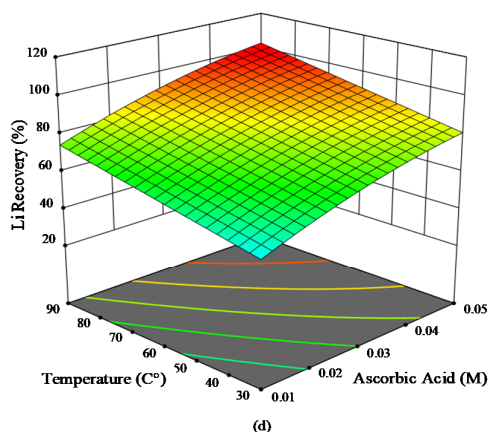
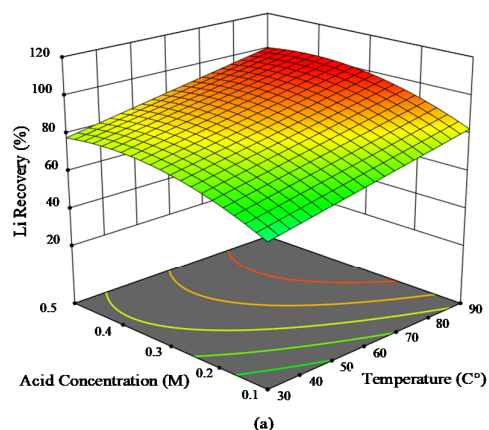


Figure 7. 3D response diagrams (a), (b), and (c) interaction of temperature-acid concentration on recovery of Li, Co, and Ni at ascorbic acid concentration of 0.03 M, pulp density of 10 g/L, and duration of 2 h. (d), (e), and (f) interaction of temperature-ascorbic acid concentration on the recovery of Li, Co, and Ni at organic acid concentration of 0.25 M, pulp density of 10 g/L, and duration of 2 h.

Table 6. Predicted and experimental optimized conditions for two acids.

Temperature (°C)	Organic acid concentration (mol/L)	Ascorbic acid concentration (mol/L)	Acid type	Recovery (%)					
				Li	Li predicted	Co	Co predicted	Ni	Ni predicted
88	0.25	0.03	Malonic	97.54	99.9	80.17	80.98	95.11	100
90	0.39	0.04	Glutamic	98.63	100	81.06	79.51	90.24	91.35

According to process optimization and validation of optimal points, optimal values of independent variables for maximum recovery in optimum conditions were specified. Temperature of 88 °C, organic acid concentrations of 0.25 M (malonic acid), ascorbic acid concentration of 0.03 M are the parameters in optimum conditions (Table 6).

4. Conclusions

An environmentally friendly method for the recovery of Li, Co, and Ni using two organic acids was provided in this work, and the following results were obtained:

- 1- Independent parameters including temperature, organic acid concentration, ascorbic acid concentration (as reducing agent), type of acid, pulp density, and time were investigated. Pulp density and time were considered as the insignificant parameters, which were constant in optimization testing. Temperature and concentration of reducing agent (ascorbic acid) were suggested as two significant parameters for the recovery of Li, Co, and Ni. According to RSM, the optimal condition was obtained at the temperature of 88 °C, acid concentration of 0.25 M, ascorbic acid concentration of 0.03 M, pulp density of 10g/L, and duration of 2 h.
- 2- According to the results provided in this research work, when the type of acid changed from L-glutamic to malonic, the recovery of Li, Co, and Ni increased from 84.8% to 96.2%, from 64.16% to 78.53%, and from 80.01% to 94.53%, respectively. Due to low acidity and solubility, glutamic acid is less effective.
- 3- According to the analytical results, when temperature increases from 30° to 90°, leaching recovery increases. The procedure improves kinetics of leaching process and solid-liquid diffusion. With the increase in the concentration of reducing agent from 0.01% M to 0.05% M, the recovery of Li, Co, and Ni increased from 72.30% to 99.57%, from 50.44% to 89.97%, and from 83.49% to 97.90%. The increase in the concentration of reducing agent mostly affected Co solubility, resulting from reduced Co^{3+} to Co^{2+} , which is easily dissolved. However, using SEM-EDS and XRD analyses, the remainder of some Co, in cobalt oxide form, in the powder remained from leaching was detected.

Considering high leaching efficiency and avoiding environmentally damaging effects, this approach can prove useful in the recovery of valuable metals from LIBs.

Conflict of Interest:

The authors declare that they have no conflict of interest.

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بازیافت فلزات از کاتد باتری های یونی لیتیومی با استفاده از اسیدهای آلی ال گلوتامیک، مالونیک و اسید آسکوربیک به روش سازگار با محیط زیست

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چکیده:

در این تحقیق، با رویکردی ساده، ایمن و سازگار با محیط زیست به روش هیدرومیتالورژی روشی برای بازیابی لیتیوم، کبالت و نیکل باتری‌های یونی لیتیومی پیشنهاد شده است. مواد کاتد با استفاده از اسید مالونیک به عنوان عامل لیچینگ و اسید آسکوربیک به عنوان عامل احیاکننده در فرآیند اول و اسید ال گلوتامیک به عنوان عامل لیچ و اسید آسکوربیک به منظور احیا کنندگی در فرآیند دوم لیچ شدند. به منظور بهینه سازی، پارامترهای لیچینگ شامل دما، غلظت اسید آلی، غلظت اسید آسکوربیک، نوع اسید آلی، چگالی پالپ و زمان از طراحی آماری آزمایش ها، روش سطح پاسخ، استفاده گردید. نتایج لیچینگ نشان می دهد که بازیابی لیچینگ با اسید مالونیک در فرآیند دوم به طور قابل توجهی بیشتر از ال گلوتامیک اسید در فرآیند اول بود. این امر به دلیل قدرت حلالیت بالاتر اسید مالونیک نسبت به ال گلوتامیک اسید است، که کمپلکس سازی بهتر انجام شده و قدرت چلاته کردن بیشتر آن در دمای پایین بوده است. در مورد ال گلوتامیک اسید، به دلیل انحلال کمتر در آب واکنش فلز-اسید فقط در سطح انجام شده و کمپلکس سازی ضعیف تری صورت می پذیرد. تحلیل آماری نتایج و تست های اعتبار سنجی، موید این است که شرایط بهینه لیچینگ در شرایط آزمایشگاهی در دمای واکنش ۸۸ درجه سانتیگراد، غلظت اسید آلی ۰.۲۵ مولار، غلظت اسید آسکوربیک ۰.۰۳ مولار، چگالی پالپ ۱۰ گرم بر لیتر و زمان لیچینگ ۲ ساعت می باشد که در این شرایط بازیابی لیتیوم ۱۰۰٪، بازیابی کبالت ۸۱٪ و بازیابی نیکل ۹۹٪ می باشد. مواد فعال کاتد قبل و بعد از لیچینگ اسیدی توسط Scanning, Particle Size Analyzer, X-Ray Fluorescence, X-Ray Diffraction و Atomic Absorption Spectroscopy, Energy Dispersive Spectroscopy, Electron Microscope به صورت کمی و کیفی آنالیز شدند.

کلمات کلیدی: بازیافت باتری یونی لیتیومی، ال گلوتامیک اسید، مالونیک اسید، بهینه سازی لیچینگ.