Article

Material and Waste Flow Analysis for Environmental and Economic Impact Assessment of Inorganic Acid Leaching Routes for Spent Lithium Batteries' Cathode Scraps

Yi-Chin Tang *, Jian-Zhi Wang, Chih-Ming Chou and Yun-Hwei Shen

Department of Resources Engineering, National Cheng Kung University, Tainan 70101, Taiwan
* Correspondence: n48091500@gs.ncku.edu.tw

Abstract: With the development trend and technological progress of lithium batteries, the battery market is booming. This means that the demand for lithium batteries has increased significantly, resulting in a large number of discarded lithium batteries. The consumption of plenty of lithium batteries may lead to the scarcity and expending of relevant raw material metal resources, as well as serious heavy metal environmental pollution. Therefore, it is of great significance to recycle valuable metal resources from discarded lithium batteries. The proper recycling of these valuable metals can reduce the shortage of mineral resources and environmental hazards caused by a large number of scrapped vehicle batteries. Recently, different systematic approaches have been developed for spent lithium battery recovery. However, most of these approaches do not account for the hidden costs incurred from various processing steps. This work is determined by the concept of material flow cost accounting (MFCA). Hence, in this research, a MFCA-based approach is developed for the leaching process of spent lithium batteries recovery, taking into consideration the hidden costs embedded in process streams. In this study, hydrochloric acid had the worst leaching efficiency due to its high solid-to-liquid ratio and the lowest acid concentration, so it was excluded in the first stage selection. It takes TWD 16.03 and TWD 24.10 to leach 10 g of lithium battery powder with sulfuric acid and nitric acid, respectively. The final sulfuric acid was the acid solution with the highest leaching efficiency and relatively low cost among inorganic acids.

Keywords: lithium batteries; hydrometallurgy; MFCA; environmental and economic impact assessment

1. Introduction

Lithium batteries, due to their long storage life and superior energy density [1], are often used in computers, mobile phones, cameras, and car batteries [2,3]. PHEVs, HEVs, and EVs can effectively reduce exhaust emissions compared to gasoline vehicles, thus helping to reduce air pollution and the greenhouse effect [4,5]. Each year, it is estimated that 17,000, 19,000, 65,000, and 22,000 tons of Li, Co, Ni, and Mn are consumed for the production of lithium batteries for vehicles [5]. By 2030, the growing demand for lithium batteries for vehicles is expected to increase the consumption of these valuable metals to 185,000, 180,000, 925,000, and 177,000 tons per year, respectively [5]. According to the US Geological Survey report for 2023 [6], the main raw materials for lithium batteries are concentrated in a few countries. Approximately 70% of lithium production is concentrated in Australia and Chile, approximately 70% of cobalt production is concentrated in the Democratic Republic of the Congo and Indonesia [7], and approximately 70% of manganese production is concentrated in South Africa. Due to limited natural resources and geographically concentrated ore deposits, the valuable metals from discarded lithium batteries are considered valuable recyclable waste streams [8,9]. Compared to the primary production of metal resources (ore mining), secondary resources (recovering metal resources from discarded lithium batteries) are less dependent on geographical factors and can also reduce supply chain and raw

material cost instability [7]. Therefore, it is extremely important to recover these valuable metals from discarded lithium batteries in scrapped cars [10].

State-of-the-art industrial processes for recycling spent lithium batteries mainly use pyrometallurgy or hydrometallurgy approaches. Pyrometallurgy involves melting spent lithium batteries at extremely high temperatures (>1000 °C) to recover the metal resources from the remaining slag. In contrast, hydrometallurgy is an energy-efficient method that uses concentrated corrosive acids to dissolve and extract metals at room temperature (25 °C) with a higher recovery efficiency than pyrometallurgy [11]. Inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid [12–16] have been commonly used to leach spent lithium batteries, and various systematic approaches have been developed [17]. However, most of the existing approaches for spent lithium battery recovery do not consider the high experimental counts required for factorial designs. The statistical approach of "Design of Experiments" allows for the variation of multiple factors simultaneously to screen the "reaction space" for a particular process, enabling the evaluation of a large number of reaction parameters with relatively few experiments [18]. Taguchi's design is a more efficient and systematic alternative to Trial-and-Error, One-Factor-at-a-Time (OFAT), and Full-Factor Design (FFD). This method can address the problem of having a huge number of experimental counts [18–21] in a variable setting from the chosen levels for experimentation [22,23].

Material Flow Cost Accounting (MFCA), a tool of Environmental Management Accounting (EMA), provides an opportunity for us to accurately capture waste cost information [24]. By analyzing the flow of materials and energy in a production process, MFCA offers detailed and in-depth waste cost information [25]. The MFCA system will integrate well into a lab-scale recycling process that collects considerable detailed waste data for the leaching process [26]. According to Strobel and Redmann [27], MFCA considers four types of costs: material, system, energy, and waste management costs. These costs are attributed to specific activities associated with the generation of products and waste streams [28,29]. Most of the developed spent lithium batteries recovery approaches do not account for the hidden costs incurred from various processing steps. This research aims to determine which leaching process (sulfuric acid, hydrochloric acid, and nitric acid environment) can offer the highest leaching rate by examining five key parameters (temperature, solid-to-liquid ratio, time, acid concentration, and the amount of H_2O_2 added) and the relatively low leaching cost using the Material Flow Cost Accounting method.
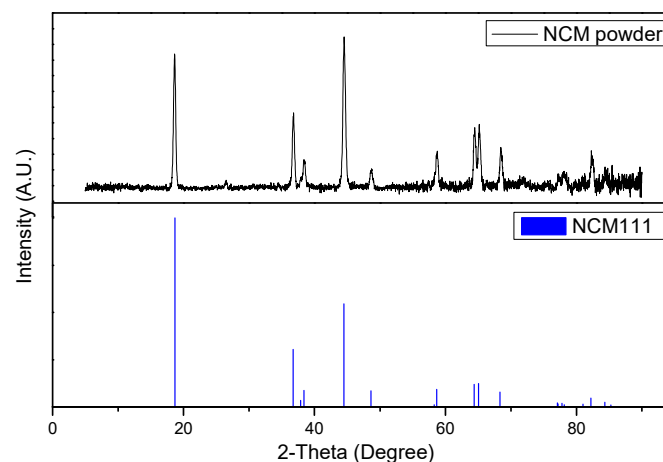
2. Materials and Methods

2.1. Materials

The cathode materials of spent lithium batteries were used in this study. To ensure safety, the spent lithium batteries (NCM111) were fully discharged in a saturated NaCl solution for 24 h. After that, they were manually disassembled and separated to extract the ternary cathode material. Using a crusher and sieving (80-mesh) can reduce the contents of aluminum, which is an impurity in cathode materials during the leaching process, because it avoids chunks of aluminum foil being incorporated easily. Table 1 lists the main metal contents of the cathode materials of spent lithium batteries. Given that the contents of aluminum and iron were quite low, the influence on the leaching procedure was deemed negligible. Figure 1 illustrates the results of the XRD analysis, showing that the major peaks of NCM powder at 18.683°, 36.723°, and 44.463° confirm the presence of crystalline NCM111 ($LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$) as the dominating phase. Analytical grade chemicals were obtained from Echo Chemical Co., Ltd., Miaoli, Taiwan, and all aqueous solutions were prepared using deionized water.

Table 1. The main metal contents in cathode materials of spent lithium batteries.

Element	Li	Co	Ni	Mn	Fe	Al
wt%	8.04	21.46	22.27	15.09	0.127	0.122

Figure 1. The results of the XRD analysis and the major peaks of NCM powder.

2.2. Equipment

To control the temperature during the experiment, a thermostatic bath with magnetic stirring (Shin-Kwang Precision Industry Ltd., Gwangju, Korea) was employed. The concentration of metal ions in the solutions obtained after the leaching experiments was determined using Atomic Absorption Spectroscopy (AAS, PerkinElmer AA900, Waltham, MA, USA).

2.3. Inorganic Acid Leaching

The leaching experiments were conducted in a 250 mL Erlenmeyer flask by charging a known amount of cathode scrap powder in 100 mL of leaching reagents containing hydrochloric acid, sulfuric acid, nitric acid, and ultrapure water. The leaching efficiency was mainly influenced by five key factors, namely temperature, solid-to-liquid ratio (S/L ratio), time, acid concentration, and the amount of H_2O_2 added. To perform the leaching experiment, a L_{16} (4^5) orthogonal array based on Taguchi's design was employed. This orthogonal array comprised 5 control factors, each with 4 levels, leading to a total of 16 experiments. The control factors included temperature (°C), solid-to-liquid ratio (g L^{-1}), time (min), acid concentration (mol L^{-1}), and the amount of H_2O_2 added (vol%). The range of the temperature was 60–90 °C, the range of the solid-to-liquid ratio was 5–40 g L^{-1}, the range of the time was 10–80 min, the range of the acid concentration was 0.5–4.0 mol L^{-1}, and the range of the amount of H_2O_2 added was 0–4.0 vol%. Firstly, the leaching efficiency was defined using Formula (1) and orthogonal table experiments were completed. Secondly, by analyzing the leaching efficiency, the impact of the control factors on the leaching efficiency was determined. Finally, a confirmation experiment was carried out to identify the optimal leaching parameters. In addition, when the optimal parameters for the leaching of all acids were identified, the total leaching efficiency was used in this study to find the optimal leached acids. The total leaching efficiency was defined using Formula (2):

$$L(\%) = \frac{V_1(L) \times C_1\left(gL^{-1}\right)}{M_1(g) \times W_1} \times 100\% \tag{1}$$

where L was the leaching efficiency, M_1 was the mass of the alloy sample, W_1 was the metal content of the alloy sample, V_1 was the volume of the leach solution, and C_1 was the mass concentration of the metal in the leach solution.

$$X_a = (X_{Li} \times X_{Co} \times X_{Ni} \times X_{Mn}) \times 100\% \tag{2}$$

where X_a was the total leaching efficiency, X_{Li} was the leaching efficiency of Li, X_{Co} was the leaching efficiency of Co, X_{Ni} was the leaching efficiency of Ni, and X_{Mn} was the leaching efficiency of Mn.

2.4. Material Flow Cost Accounting

The costs associated with the leaching process were divided into four categories under the MFCA calculations, namely material cost, energy cost, system cost, and waste management cost [27]. Depreciation was the primary item considered in the system cost category, while the waste management cost focused on solid waste. In this study, each leaching unit was considered as a quantity center (QC), and all inputs and outputs were determined. The cost of leaching 10 g of spent lithium batteries using various inorganic acids was analyzed, and both physical and monetary units were included in the material flow balance equation for the calculation system. Waste is considered a by-product of MFCA. The information required for material flow cost accounting comprised the material flow system and a defined database, which was used as the basis for calculating the quantities, values, and costs related to the flow model (Table 2). Table 2 illustrates the amount of money spent on 4 materials (H_2SO_4, HCl, HNO_3, and H_2O_2), 2 types of energy (water and electricity), 2 depreciation items (thermostatic bath with magnetic stirring and vacuum pump), and 1 waste type (solid waste) in the leaching process at lab scale. The units were measured in New Taiwan Dollars (TWD). The prices for hydrogen peroxide, sulfuric acid, hydrochloric acid, and nitric acid were obtained by Sin-Sin Chemical Co., Ltd. (Tainan, Taiwan). The water fee was determined based on the price charged by Taiwan's water supply company, which was TWD 12.08 per 1000 L. The electricity bill was calculated based on the electricity price table provided by the Taiwan Power Company, which was TWD 3.79 per kWh. The waste was analyzed at around TWD 0.056 per gram of solid waste treatment by the National Cheng Kung University Environmental Resources Center.

Table 2. The expenditure of materials, energy types, depreciation items, and waste type in the leaching process at lab scale.

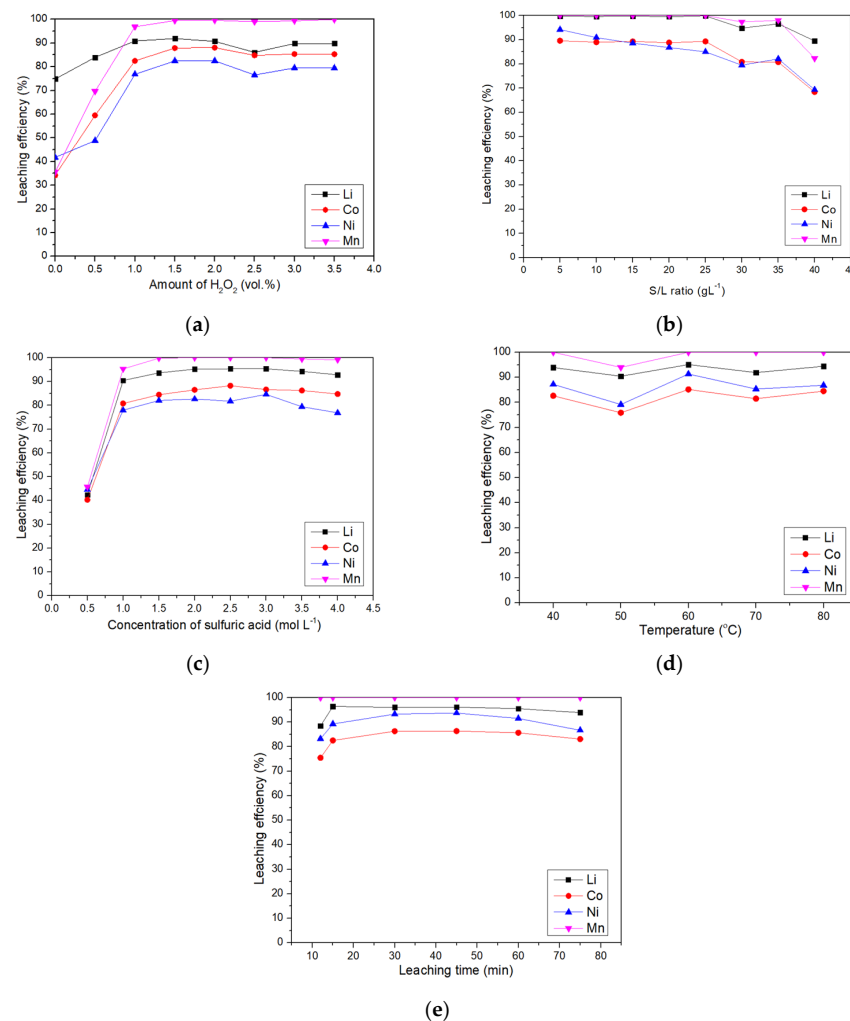| Materials	Price	Unit	Price	Unit
H_2SO_4	0.043	TWD/mL	116	USD/gal
HCl	0.043	TWD/mL	5.3	USD/gal
HNO_3	0.043	TWD/mL	5.3	USD/gal
H_2O_2	1.4	TWD/mL	174.1	USD/gal
Energytypes	**Price**	**Unit**	**Price**	**Unit**
Water	0.000012	TWD/mL	1.4	USD/m^3
Electricity	3.79	TWD/kWh	432,000	USD/J
Depreciation items	**Price**	**Unit**	**Price**	**Unit**
Thermostatic bath with magnetic stirring	79,000	TWD/set	2604.2	USD/set
Vacuum pump	27,920	TWD/set	920.4	USD/set
Waste type	**Price**	**Unit**	**Price**	**Unit**
Solid waste	0.056	TWD/g	1.85	USD/kg

3. Results and Discussion

3.1. Taguchi Design

The Taguchi design is a promising approach that can be used to address a plethora of experimental count problems in a variable setting, given the reduced number of experiments required. As a result, the careful selection of the variable setting and levels chosen is crucial. It is argued by many that improving the leaching efficiency and accelerating the leaching reaction were the most significant ways to impact the leaching process. For instance, based on the shrinking core from the chemical, diffusion, and mixed control

perspectives, the effect of the reaction temperature on the leaching can be attributed to an increase in the reaction temperature, improving the rate of external diffusion [30]. Additionally, various leaching studies [31,32] have shown that increasing the acid concentration is advantageous for leaching lithium, cobalt, nickel, and manganese. The leaching efficiencies for metals (Li, Ni, Co, and Mn) were significantly increased due to the higher concentration of acidic solution, which more easily destroyed the bonding of M-O (M: Li, Ni, Co, and Mn) in lithium batteries [33]. The solid-to-liquid ratio (S/L ratio) in the current research was determined by the ratio of the weight of the cathode scrap powder to the volume of the leaching solution (g L^{-1}). Industrially, a high S/L ratio was desirable to improve the processing throughput; however, an increase in the S/L ratio always results in a lower leaching efficiency. This indicated that a lower S/L ratio can enlarge the contact areas of solids (the cathode scrap powder) and liquids (acidic solution) to accelerate the leaching reactions [34]. In most leaching cases, it is essential to add H$_2$O$_2$ (reductant) as compounds containing metal ions with a valence higher than +2 are insoluble. The metal valence must be reduced to +2 to dissolve the compounds easily in the form of complexes with inorganic acids. Reducing the metal valence may weaken the chemical bond in the insoluble compounds, making dissolution easier [35,36]. It is frequently believed that for solid/liquid reactions, increasing the contact time between reagents favors the dissolution reaction [36]. Based on the leaching kinetics model, it can be more clearly explained that the leaching efficiency of lithium, cobalt, nickel, and manganese increases with the increase in the leaching time [37]. Therefore, the setup of the orthogonal experiment is based on the five variable settings. In our previous study [32], the priority order of the leaching process from lithium batteries by a sulfuric acid-based system was as follows: amount of H$_2$O$_2$ > solid-to-liquid ratio > sulfuric acid concentration > temperature > time. The priority order of the leaching process from lithium batteries by a hydrochloric acid-based system was as follows: hydrochloric acid concentration > amount of H$_2$O$_2$ > solid-to-liquid ratio > temperature > time. The priority order of the leaching process from lithium batteries by a nitric acid-based system was as follows: amount of H$_2$O$_2$ > nitric acid concentration > solid-to-liquid ratio > time > temperature.

3.2. Sulfuric Acid Leaching

The degree of the influence and sequence of each parameter on the leaching process were determined using a previous orthogonal experiment. Regarding the sequence of the influencing factors, the experiment should be carried out in the order of their effect. As shown in Figure 2a, the leaching efficiency of Li, Co, Ni, and Mn increased with the amount of hydrogen peroxide added. The optimal leaching efficiencies for Li, Co, Ni, and Mn were achieved at 1.5 vol.% of hydrogen peroxide, which were 91.91, 87.89, 82.51, and 99.47%, respectively. The effect of the solid-to-liquid ratio on the leaching efficiency was presented in Figure 2b. In this part, the parameter with the highest solid-to-liquid ratio and no significant decrease in the leaching efficiency was selected as the optimal parameter, which was 25 g L^{-1}. The effect of the acid concentration on the leaching efficiency was shown in Figure 2c, where it was found that the acid concentration strongly affected the leaching efficiency. A leaching efficiency of less than 50% was observed for the four metals at an acid concentration of 0.5 mol L^{-1}. No significant improvement in the leaching efficiency was observed until the acid concentration of 2 mol L^{-1}, which was chosen as the optimal parameter. Temperature and time had little effect on the leaching efficiency, as seen in Figure 2d,e. The leaching rate was very fast and could be effectively achieved within 15 min, as shown in Figure 2e. Based on the above results, the optimal conditions for achieving high leaching efficiencies for Li, Co, Ni, and Mn were determined to be: 1.5 vol.% of hydrogen peroxide, 25 g L^{-1} of the solid-to-liquid ratio, 2 mol L^{-1} of the acid concentration, temperature of 60 °C, and 15 min of leaching time. The leaching efficiencies achieved under these conditions were 96.41%, 82.53%, 89.25%, and 99.99%, respectively.

(a)

(b)

(c)

(d)

(e)

Figure 2. Effect of (**a**) amount of H_2O_2 added, (**b**) S/L ratio, (**c**) acid concentration, (**d**) temperature, and (**e**) time on leaching efficiency of sulfuric acid.

The optimization results of the sulfuric acid leaching parameters were compared with those of other studies [38,39], as presented in Table 3. This study was able to dissolve similar metal contents at lower temperatures and shorter leaching time conditions. This was the result of optimizing the leaching efficiency using the Taguchi method in this study.
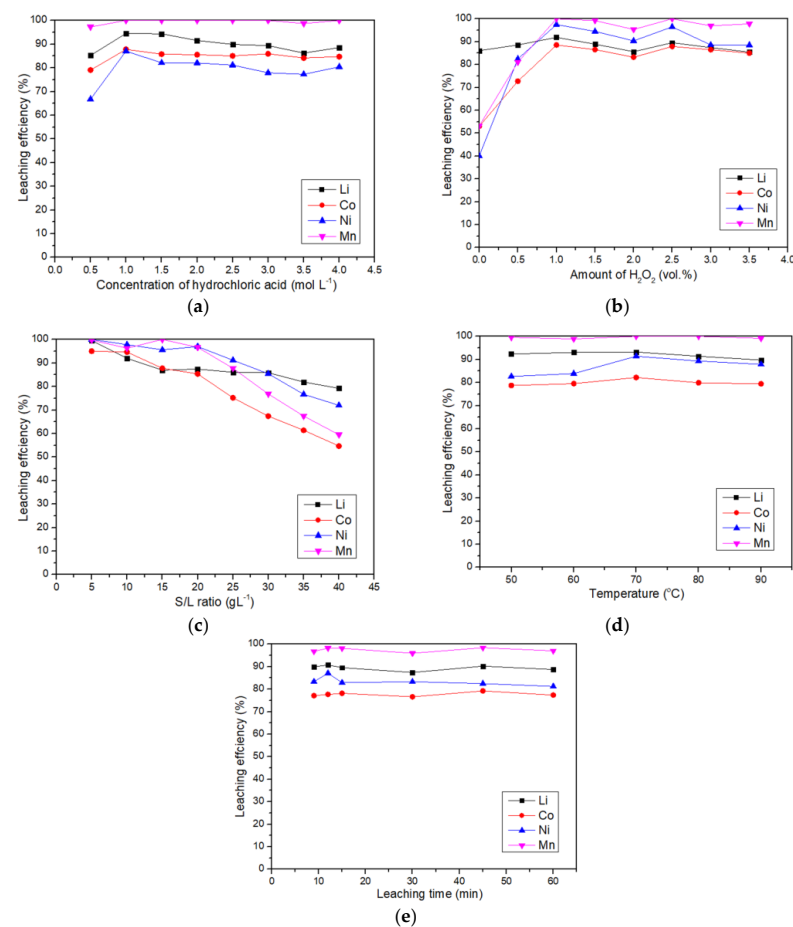
3.3. Hydrochloric Acid Leaching

In this investigation, hydrochloric acid was used to leach Li, Co, Ni, and Mn. The influence and sequence of each leaching parameter on the process was determined by an orthogonal experiment from the previous study. The priority order for the leaching process from lithium batteries by a hydrochloric acid-based system was as follows: hydrochloric acid concentration > amount of H_2O_2 > solid-to-liquid ratio > temperature > time. Figure 3 follows this above priority order for further in-depth exploration of each factor. The hydrochloric acid concentration played a significant role in the leaching process. As the hydrochloric acid concentration increased from 0.5 mol L^{-1} to 1.0 mol L^{-1}, the leaching efficiency of Li, Co, Ni, and Mn increased from 85.25% to 94.52%, 79.03% to 87.78%, 66.75% to 87.07%, and 97.27% to 99.99%, respectively. In the absence of H_2O_2 in the leaching solutions, the leaching efficiencies were only 86.08% for Li, 53.04% for Co, 40.04% for Ni, and 53.18% for Mn. When the H_2O_2 concentration was increased to 1.0 vol%, the leaching efficiencies increased to 91.88% for Li, 88.52% for Co, 97.47% for Ni, and 99.99% for Mn. The leaching efficiency decreased as the solid-to-liquid ratio increased. The results indicated that the leaching efficiencies for Li, Co, Ni, and Mn were nearly constant in the solid-to-

liquid ratio of 15–20 g L^{-1}. However, when the solid-to-liquid ratio was increased to more than 20 g L^{-1}, the leaching efficiencies for all of the metals decreased dramatically. The leaching efficiencies for Li, Co, Ni, and Mn increased as the temperature increased. When the temperature was increased to 70 °C, the leaching efficiencies reached 93.20% for Li, 82.19% for Co, 91.37% for Ni, and 99.99% for Mn. The maximum leaching efficiency could be obtained when the reaction time was 12 min. Based on the results, the optimal theoretical conditions can be determined as a hydrochloric acid concentration of 1.0 mol L^{-1}, amount of H$_2$O$_2$ of 1.0 vol%, solid-to-liquid ratio of 20 g L^{-1}, temperature of 70 °C, and reaction time of 12 min.

Table 3. Comparison of sulfuric acid leaching results.

No	This Study	Zhang et al. [38]	Asadi et al. [39]
Temperature	60 °C	95 °C	60 °C
Acid concentration	2 mol L^{-1}	2 mol L^{-1}	2 mol L^{-1}
Solid-to-liquid ratio	25 g L^{-1}	100 g L^{-1}	30 g L^{-1}
Time	15 min	240 min	80 min
Addition of hydrogen peroxide	1.5 vol.%	0 vol.%	4 vol.%
Li leaching rate	96.41%	100%	98.40%
Co leaching rate	82.53%	98.13%	99.0%
Ni leaching rate	89.25%	97.27%	96.78%
Mn leaching rate	99.99%	97.37%	97.53%

Figure 3. Effect of (**a**) acid concentration, (**b**) amount of H$_2$O$_2$ added, (**c**) S/L ratio, (**d**) temperature, and (**e**) time on leaching efficiency of hydrochloric acid.

The optimization results for the hydrochloric acid leaching parameters were compared with other studies [40,41], as shown in Table 4. This study was able to dissolve similar metal contents at lower acid concentrations and in less time. This is the result of optimizing the leaching efficiency using the Taguchi method in this study.

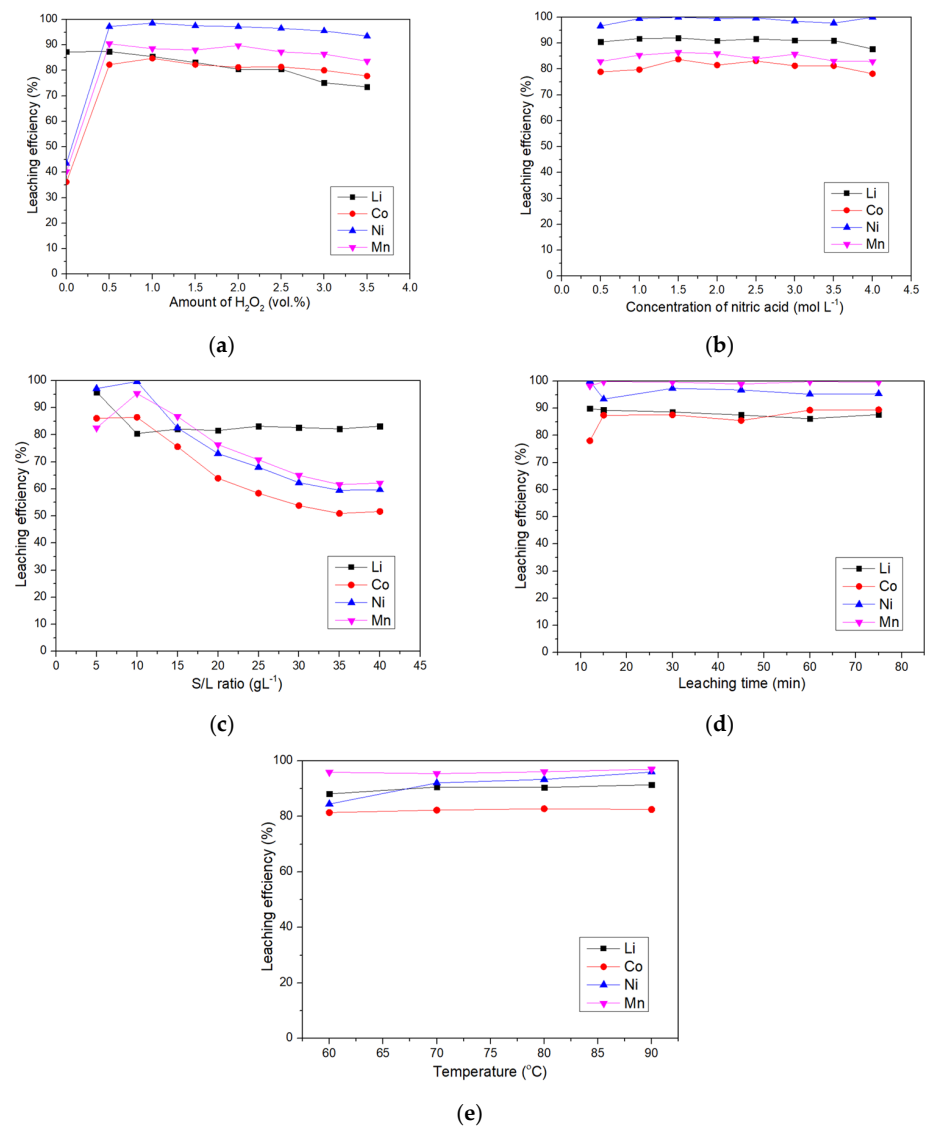**Table 4.** Comparison of hydrochloric acid leaching results.

No	This Study	Barik et al. [40]	Wang et al. [41]
Temperature	70 °C	50 °C	80 °C
Acid concentration	1 mol L^{-1}	1.75 mol L^{-1}	4 mol L^{-1}
Solid-to-liquid ratio	20 g L^{-1}	20 g L^{-1}	20 g L^{-1}
Time	12 min	120 min	60 min
Addition of hydrogen peroxide	1.0 vol.%	0 vol.%	0 vol.%
Li leaching rate	90.72%	>99%	>99%
Co leaching rate	77.66%	>99%	>99%
Ni leaching rate	87.07%	-	>99%
Mn leaching rate	98.24%	>99%	>99%

3.4. Nitric Acid Leaching

In this investigation, nitric acid was used to leach Li, Co, Ni, and Mn. The degree of influence and sequence of each parameter in the leaching process were determined through orthogonal experiments in a previous study. The priority order of the leaching process from lithium batteries using a nitric acid-based system was as follows: amount of H_2O_2 > nitric acid concentration > solid-to-liquid ratio > time > temperature. Figure 4 follows the above priority order for further in-depth exploration of each factor. When the amount of H_2O_2 added was increased to 0.5 vol%, the leaching efficiencies significantly increased to 87.41% for Li, 82.26% for Co, 97.25% for Ni, and 90.48% for Mn. With an increase in the nitric acid concentration from 0.5 mol L^{-1} to 1.5 mol L^{-1}, the leaching efficiencies increased from 90.48% to 92.01% for Li, from 78.91% to 83.74% for Co, from 96.63% to 99.99% for Ni, and from 82.89% to 86.42% for Mn. However, a further increase in the nitric acid concentration to 2.0 mol L^{-1} did not cause a significant change in the leaching efficiencies. A higher solid-to-liquid ratio always resulted in a lower leaching efficiency. Figure 4c illustrates that the leaching efficiency decreased rapidly when the solid-to-liquid ratio reached 15 g L^{-1}. The leaching efficiencies remained stable with a reaction time of 15 min. The leaching efficiencies for Li, Co, Ni, and Mn increased as the temperature increased. When the temperature reached 70 °C, the most significant change in the Ni leaching efficiency was an increase from 84.13% to 92.08%. Based on the results, the optimal theoretical conditions could be determined as follow: amount of H_2O_2 of 0.5 vol%, nitric acid concentration of 1.5 mol L^{-1}, solid-to-liquid ratio of 10 g L^{-1}, reaction time of 15 min, and temperature of 70 °C.

The optimization results for the nitric acid leaching parameters were compared with another study [42], as shown in Table 5. This study was able to dissolve similar metal contents at lower temperature and time conditions. This is the result of optimizing the leaching efficiency using the Taguchi method in this study. In addition, according to studies [43] on leaching in lithium batteries, after the leaching process, all metal ions would be present in the solution in the form of Li^+, Ni^{2+}, Co^{2+}, and Mn^{2+}.

(a)

(b)

(c)

(d)

(e)

Figure 4. Effect of (**a**) amount of H_2O_2 added, (**b**) acid concentration, (**c**) S/L ratio, (**d**) time, and (**e**) temperature on leaching efficiency of nitric acid.

Table 5. Comparison of nitric acid leaching results.

No	This Study	Lee et al. [42]
Material	$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$	$LiCoO_2$
Temperature	70 °C	75 °C
Acid concentration	1.5 mol L^{-1}	1.0 mol L^{-1}
Solid-to-liquid ratio	10 g L^{-1}	20 g L^{-1}
Time	15 min	60 min
Addition of hydrogen peroxide	0.5 vol.%	1.7 vol.%
Li leaching rate	90.60%	>95%
Co leaching rate	82.26%	>95%
Ni leaching rate	92.08%	-
Mn leaching rate	95.42%	-

3.5. Overall Leaching Efficiency

This section compiled the findings from Sections 3.1–3.3. Table 6 presents the leaching efficiency of each acid under optimal leaching conditions. Sulfuric acid demonstrated the highest leaching rate owing to its higher acid concentration. Nitric acid had the second-highest total leaching efficiency. Hydrochloric acid displayed the lowest leaching efficiency due to its high solid-to-liquid ratio and the lowest acid concentration.

Table 6. The leaching rate of each metal under the optimal parameters.

No.	Temp.	Acid	S/L	Time	H_2O_2	Li	Co	Ni	Mn	Total Leaching Efficiency
Unit	°C	mol L^{-1}	g L^{-1}	min	vol.	%	%	%	%	%
H_2SO_4	60	2.0	25	15	1.5	96.41	82.53	89.25	99.99	71.01
HCl	70	1.0	20	12	1.0	90.72	77.66	87.07	98.24	60.26
HNO$_3$	70	1.5	10	15	0.5	90.60	82.26	92.08	95.42	65.48

3.6. Material Flow Cost Accounting

In this case study, it was assumed that the cathode materials from spent lithium batteries had zero cost because the process wastes were collected from electric vehicle manufacturing; thus, it is practically impossible to allocate a cost to wastes. Moreover, the cost of the cathode materials from spent lithium batteries had no effect on the MFCA calculations, as the purpose was to calculate the total cost of the leaching process and the cost associated with each treatment unit. To perform complete MFCA calculations, it was necessary to determine the material, energy, system, and depreciation costs for each QC. The expenditure of the materials, energy types, depreciation items, and waste types in the leaching process at the lab scale were prorated for all QCs. The depreciation items were assumed to be ignored in the calculation of the total cost, which had no effect on comparing which leaching system provided the lowest cost in this project, as the same equipment was used during the leaching process. The cost accounting of the leaching process, using 10 g of spent lithium batteries cathode scraps under sulfuric acid, hydrochloric acid, and nitric acid environment, based on reconciled data, is shown in Tables 7–9, respectively. As can be seen from the Table, the main expenditures on materials were the acid solution and hydrogen peroxide in each QC. In the materials, considerably more than 50% of the money spent was on hydrogen peroxide compared to the acid solution in each leaching process. Since nitric acid is a powerful oxidizing agent, the amount of H_2O_2 added was slightly less than in the other systems. However, the amount of acid used was twice that of the other two, resulting in a higher material cost. In terms of energy consumption, more than 90% of the money spent was on electricity in each leaching system. Consequently, the reaction time would have a considerable impact on the energy expenditure of the procedure. The money spent on solid waste was slightly lower than that spent on sulfuric and nitric systems compared to a hydrochloric system. Hydrochloric acid leaching systems will be the most competitive in the future as landfill disposal becomes more and more expensive. Overall, the total expenditures of the sulfuric system and hydrochloric system were approximately two-thirds of those in a nitric environment. The expense of the energy consumption and the amount of acid added of the nitric system were much higher than those of the other systems. The amount of money spent on the 2 energy types (electricity and water) and materials in a nitric environment was TWD 12.14 and TWD 11.46, respectively.

Table 7. Sulfuric acid leaching cost.

Materials	Cost	Unit	Amount	Unit	Total Cost	Unit
H_2SO_4	0.043	TWD/mL	44.44	mL	1.92	TWD
H_2O_2	1.47	TWD/mL	6	mL	8.82	TWD
Energytypes	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Electricity	3.79	TWD/kWh	1.28	kWh	4.8512	TWD
Water	0.000012	TWD/mL	355.56	mL	0.0043	TWD
Depreciation items	**Purchase cost**	**TWD/set**	**Durable number of years**	**Years of use**	**Depreciation**	**Unit**
Thermostatic bath	79,000	TWD/set	7	7	7090	TWD
Vacuum pump	27,920	TWD/set	7	7	2506	TWD
Waste type	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Solid waste	0.056	TWD/g	7.75	g	0.43	TWD
Total price (Does not include the depreciation)					16.03	TWD
Total price in USD (TWD 1 = USD 0.033)					0.53	TWD

Table 8. Hydrochloric acid leaching cost.

Materials	Cost	Unit	Amount	Unit	Total Cost	Unit
HCl	0.043	TWD/mL	42.6	mL	1.84	TWD
H_2O_2	1.47	TWD/mL	5	mL	7.35	TWD
Energytypes	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Electricity	3.79	TWD/kWh	1.28	kWh	4.8512	TWD
Water	0.000012	TWD/mL	457.4	mL	0.0055	TWD
Depreciation items	**Purchase cost**	**TWD/set**	**Durable number of years**	**Years of use**	**Depreciation**	**Unit**
Thermostatic bath	79,000	TWD/set	7	7	7090	TWD
Vacuum pump	27,920	TWD/set	7	7	2506	TWD
Wastetype	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Solid waste	0.056	TWD/g	7.14	g	0.40	TWD
Total price (Does not include the depreciation)					14.45	TWD
Total price in USD (TWD 1 = USD 0.033)					0.48	USD

Table 9. Nitric acid leaching cost.

Materials	Cost	Unit	Amount	Unit	Total Cost	Unit
HNO_3	0.043	TWD/mL	95.1	mL	4.11	TWD
H_2O_2	1.47	TWD/mL	5	mL	7.35	TWD
Energytypes	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Electricity	3.79	TWD/kWh	3.2	kWh	12.128	TWD
Water	0.000012	TWD/mL	904.9	mL	0.0109	TWD
Depreciation items	**Purchase cost**	**TWD/set**	**Durable number of years**	**Years of use**	**Depreciation**	**Unit**
Thermostatic bath	79,000	TWD/set	7	7	7090	TWD
Vacuum pump	27,920	TWD/set	7	7	2506	TWD
Wastetype	**Cost**	**Unit**	**Amount**	**Unit**	**Total cost**	**Unit**
Solid waste	0.056	TWD/g	8.91	g	0.50	TWD
Total price (Does not include the depreciation)					24.10	TWD
Total price in USD (TWD 1 = USD 0.033)					0.79	USD

3.7. Selection of Leachate

The process of selecting the optimal leachate is shown in Figure 5. In the first stage, hydrochloric acid was eliminated because it had the lowest total leaching efficiency. Subsequently, nitric acid was excluded based on cost analysis as it requires a considerable amount of leaching solution, leading to high expenses. Finally, sulfuric acid was deemed the most

suitable leaching acid, as it exhibited the highest leaching efficiency and a relatively low cost.

Leachate	H_2SO_4	HNO_3	HC1
Total Leaching Efficiency (%)	**71.01**	**65.48**	60.26

Leachate	H_2SO_4	HNO_3
Cost (NT\$)	**16.03**	24.10

$$H_2SO_4$$

Figure 5. Optimal leachate selection.

4. Conclusions

This study examined the optimal leaching parameters of three different acids: sulfuric acid, hydrochloric acid, and nitric acid. The study revealed that sulfuric acid had the highest total leaching efficiency of 71.01% at a temperature of 60 °C, an acid concentration of 2.0 mol L^{-1}, a solid-to-liquid ratio of 25 g L^{-1}, a time of 15 min, and hydrogen peroxide addition of 1.5 vol.%. Meanwhile, hydrochloric acid had a total leaching efficiency of 60.26% under the conditions of a temperature of 70 °C, an acid concentration of 1.0 mol L^{-1}, a solid-to-liquid ratio of 20 g L^{-1}, a time of 12 min, and hydrogen peroxide addition of 1.0 vol.%. Furthermore, nitric acid had a total leaching efficiency of 65.48% at a temperature of 70 °C, an acid concentration of 1.5 mol L^{-1}, a solid-to-liquid ratio of 10 g L^{-1}, a time of 15 min, and hydrogen peroxide addition of 0.5 vol.%. Hydrochloric acid was excluded from further consideration due to its low total leaching efficiency.

Furthermore, this study assessed the leaching costs of using sulfuric acid and nitric acid to leach 10 g of lithium battery powder. The cost of leaching 10 g of powder with sulfuric acid was TWD 16.03, whereas the cost of leaching the same amount of powder with nitric acid was TWD 24.10. This difference in cost can be attributed to the higher amount of nitric acid required to leach the same amount of powder as sulfuric acid due to the lower leaching solid-to-liquid ratio. As a result, this study selected sulfuric acid as the optimal leaching acid due to its high leaching efficiency and relatively low cost.

In conclusion, this study determined that sulfuric acid was the most effective and cost-efficient acid for leaching among the inorganic acids examined, based on the results obtained using the Taguchi method and the MFCA method.

References

1. Ordoñez, J.; Gago, E.J.; Girard, A. Processes and technologies for the recycling and recovery of spent lithium-ion batteries. *Renew. Sustain. Energy Rev.* **2016**, *60*, 195–205. [CrossRef]
2. Castillo, S.; Ansart, F.; Rpbert, C.L.; Portal, J. Advances in the recovering of spent lithium battery compounds. *J. Power Sources* **2002**, *112*, 247–254. [CrossRef]
3. Torkaman, R.; Asadollahzadeh, M.; Mostaedi, M.T.; Maragheh, M.G. Recovery of cobalt from spent lithium ion batteries by using acidic and basic extractants in solvent extraction process. *Sep. Purif. Technol.* **2017**, *186*, 318–325. [CrossRef]
4. Hannan, M.A.; Hoque, M.M.; Mohamed, A.; Ayob, A. Review of energy storage systems for electric vehicle applications: Issues and challenges. *Renew. Sustain. Energy Rev.* **2017**, *69*, 771–789. [CrossRef]
5. Jung, J.C.Y.; Sui, P.C.; Zhang, J. A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments. *J. Energy Storage* **2021**, *35*, 102217. [CrossRef]
6. Mineral Commodity Summaries. 2023. Available online: https://www.kriittisetmateriaalit.fi/wp-content/uploads/2023/02/Mineral-Commodity-Summaries-2023-USGS-Jan-2023.pdf (accessed on 12 March 2023).
7. Wu, X.; Ma, J.; Wang, J.; Zhang, X.; Zhou, G.; Liang, Z. Progress, Key Issues, and Future Prospects for Li-Ion Battery Recycling. *Glob. Chall.* **2022**, *6*, 2200067. [CrossRef] [PubMed]
8. Du, K.; Ang, E.H.; Wu, X.; Liu, Y. Progresses in Sustainable Recycling Technology of Spent Lithium-Ion Batteries. *Energy Environ. Mater.* **2022**, *5*, 1012–1036. [CrossRef]
9. Fan, M.; Chang, X.; Meng, Q.; Wan, L.J.; Guo, Y.G. Progress in the sustainable recycling of spent lithium-ion batteries. *SusMat* **2021**, *1*, 241–254. [CrossRef]
10. Tang, Y.C.; Wang, J.Z.; Shen, Y.H. Separation of Valuable Metals in The Recycling of Lithium Batteries via Solvent Extraction. *Minerals* **2023**, *13*, 285. [CrossRef]
11. Roy, J.J.; Rarotra, S.; Krikstolaityte, V.; Zhuoran, K.W.; Cindy, Y.D.L.; Tan, X.Y.; Carboni, M.; Meyer, D.; Yan, Q.; Srinivasan, M. Green Recycling Methods to Treat Lithium-Ion Batteries E-Waste: A Circular Approach to Sustainability. *Adv. Mater.* **2022**, *34*, 2103346. [CrossRef]
12. Meshram, P.; Abhilash; Pandey, B.D.; Mankhand, T.R.; Deveci, H. Acid baking of spent lithium ion batteries for selective recovery of major metals: A two-step process. *J. Ind. Eng. Chem.* **2016**, *43*, 117–126. [CrossRef]
13. Bertuol, D.A.; Machado, C.M.; Silva, M.L.; Calgaro, C.O.; Dotto, G.L.; Tanabe, E.H. Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction. *Waste Manag.* **2016**, *51*, 245–251. [CrossRef] [PubMed]
14. Jha, M.K.; Kumari, A.; Jha, A.K.; Kumar, V.; Hait, J.; Pandey, B.D. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manag.* **2013**, *33*, 1890–1897. [CrossRef]
15. Swain, B.; Jeong, J.; Lee, J.C.; Lee, G.H.; Sohn, J.S. Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries. *J. Power Sources* **2007**, *167*, 536–544. [CrossRef]
16. Shin, S.M.; Kim, N.H.; Sohn, J.S.; Yang, D.H.; Kim, Y.H. Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy* **2005**, *79*, 172–181. [CrossRef]
17. Werner, D.; Peuker, U.A.; Mütze, T. Recycling Chain for Spent Lithium-Ion Batteries. *Metals* **2020**, *10*, 316. [CrossRef]
18. Murray, P.M.; Ballany, F.; Benhamou, L.; Bucar, D.K.; Tabor, A.B.; Sheppard, T.D. The application of design of experiments (DoE) reaction optimisation and solvent selection in the development of new synthetic chemistry. *Org. Biomol. Chem.* **2016**, *14*, 2373–2384. [CrossRef]
19. Chen, Y.C.; Tsai, P.J.; Mou, J.L. Determining Optimal Operation Parameters for Reducing PCDD/F Emissions (I-TEQ values) from the Iron Ore Sintering Process by Using the Taguchi Experimental Design. *Environ. Sci. Technol.* **2008**, *42*, 5298–5303. [CrossRef]
20. Li, L.; Zhang, X.; Ning, Z.; Mayne, J.; Moore, J.I.; Butcher, J.; Chiang, C.K.; Mack, D.; Stintzi, A.; Figeys, D. Evaluating in Vitro Culture Medium of Gut Microbiome with Orthogonal Experimental Design and a Metaproteomics Approach. *J. Proteome Res.* **2018**, *17*, 154–163. [CrossRef]
21. Gilman, J.; Walls, L.; Bandiera, L.; Menolascina, F. Statistical Design of Experiments for Synthetic Biology. *ACS Synth. Biol.* **2021**, *10*, 1–18. [CrossRef]
22. Lee, B.C.Y.; Mahtab, M.S.; Neo, T.H.; Farooqi, I.H.; Khursheed, A. A comprehensive review of Design of experiment (DOE) for water and wastewater treatment application—Key concepts, methodology and contextualized application. *J. Water Process Eng.* **2022**, *47*, 102673. [CrossRef]
23. Cai, Q.Q.; Wu, M.Y.; Li, R.; Deng, S.H.; Lee, B.C.Y.; Ong, S.L.; Hu, J.Y. Potential of combined advanced oxidation–Biological process for cost-effective organic matters removal in reverse osmosis concentrate produced from industrial wastewater reclamation: Screening of AOP pre-treatment technologies. *Chem. Eng. J.* **2020**, *389*, 123419. [CrossRef]
24. Fakoya, M.B.; Poll, H.M. Integrating ERP and MFCA systems for improved waste-reduction decisions in a brewery in South Africa. *J. Clean. Prod.* **2013**, *40*, 136–140. [CrossRef]
25. Mahmoudi, E.; Jodeiri, N.; Fatehifar, E. Implementation of material flow cost accounting for efficiency improvement in wastewater treatment unit of Tabriz oil refining company. *J. Clean. Prod.* **2017**, *165*, 530–536. [CrossRef]
26. Wan, Y.K.; Ng, R.T.L.; Ng, D.K.S.; Tan, R.R. Material flow cost accounting (MFCA)–based approach for prioritisation of waste recovery. *J. Clean. Prod.* **2015**, *107*, 602–614. [CrossRef]
27. Strobel, M.; Redmann, C. Flow cost accounting, an accounting approach based on the actual flows of materials. *Environ. Manag. Account. Inf. Inst. Dev.* **2002**, *9*, 67–82. [CrossRef]

28. Kokubu, K.; Tachikawa, H. Material flow cost accounting: Significance and practical approach. In *Handbook of Sustainable Engineering*; Springer: Dordrecht, The Netherlands, 2013; pp. 351–369. [CrossRef]
29. Christ, K.L.; Burritt, R.L. Material flow cost accounting: A review and agenda for future research. *J. Clean. Prod.* **2015**, *108*, 1378–1389. [CrossRef]
30. Meshram, P.; Pandey, B.D.; Mankhand, T.R. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects. *Waste Manag.* **2015**, *45*, 306–313. [CrossRef]
31. Nayl, A.A.; Elkhashab, R.A.; Badawy, S.M.; Khateeb, M.A.E. Acid leaching of mixed spent Li-ion batteries. *Arab. J. Chem.* **2017**, *10*, S3632–S3639. [CrossRef]
32. Tang, Y.C.; Wang, J.Z.; Shen, Y.H. Recycling Metal from Waste Lithium-ion Batteries for Use as Electrochemical Sensor Material. *Sens. Mater.* **2022**, *34*, 2025–2035. [CrossRef]
33. He, L.P.; Sun, S.Y.; Song, X.F.; Yu, J.G. Leaching process for recovering valuable metals from the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode of lithium-ion batteries. *Waste Manag.* **2017**, *64*, 171–181. [CrossRef] [PubMed]
34. Zheng, X.; Gao, W.; Zhang, X.; He, M.; Lin, X.; Cao, H.; Zhang, Y.; Sun, Z. Spent lithium-ion battery recycling—Reductive ammonia leaching of metals from cathode scrap by sodium sulphite. *Waste Manag.* **2017**, *60*, 680–688. [CrossRef] [PubMed]
35. Refly, S.; Floweri, O.; Mayangsari, T.R.; Sumboja, A.; Santosa, S.P.; Ogi, T.; Iskandar, F. Regeneration of LiNi1/3Co1/3Mn1/3O2 Cathode Active Materials from End-of-Life Lithium-Ion Batteries through Ascorbic Acid Leaching and Oxalic Acid Coprecipitation Processes. *ACS Sustain. Chem. Eng.* **2020**, *8*, 16104–16114. [CrossRef]
36. Pinna, E.G.; Ruiz, M.C.; Ojeda, M.W.; Rodriguez, M.H. Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors. *Hydrometallurgy* **2017**, *167*, 66–71. [CrossRef]
37. Li, L.; Bian, Y.; Zhang, X.; Xue, Q.; Fan, E.; Wu, F.; Chen, R. Economical recycling process for spent lithium-ion batteries and macro- and micro-scale mechanistic study. *J. Power Sources* **2018**, *377*, 70–79. [CrossRef]
38. Zhang, Y.; Yu, M.; Guo, J.; Lui, S.; Song, H.; Wu, W.; Zheng, C.; Gao, X. Recover value metals from spent lithium-ion batteries via a combination of in-situ reduction pretreatment and facile acid leaching. *Waste Manag.* **2023**, *161*, 193–202. [CrossRef]
39. Dalini, E.A.; Karimi, G.; Zandevakili, S. Treatment of valuable metals from leaching solution of spent lithium-ion batteries. *Miner. Eng.* **2021**, *173*, 107226. [CrossRef]
40. Barik, S.P.; Prabaharan, G.; Kumar, L. Leaching and separation of Co and Mn from electrode materials of spent lithium-ion batteries using hydrochloric acid: Laboratory and pilot scale study. *J. Clean. Prod.* **2017**, *147*, 37–43. [CrossRef]
41. Wang, R.C.; Lin, Y.C.; Wu, S.H. A novel recovery process of metal values from the cathode active materials of the lithium-ion secondary batteries. *Hydrometallurgy* **2009**, *99*, 194–201. [CrossRef]
42. Lee, C.K.; Rhee, K.I. Preparation of $LiCoO_2$ from spent lithium-ion batteries. *J. Power Sources* **2002**, *109*, 17–21. [CrossRef]
43. Fan, E.; Yang, J.; Huabg, Y.; Lin, J.; Arshad, F.; Wu, F.; Li, L.; Chen, R. Leaching Mechanisms of Recycling Valuable Metals from Spent Lithium-Ion Batteries by a Malonic Acid-Based Leaching System. *ACS Appl. Energy Mater.* **2020**, *3*, 8532–8542. [CrossRef]