minerals

MDPI

Article

Separation of Valuable Metals in the Recycling of Lithium Batteries via Solvent Extraction

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

Department of Resources Engineering, National Cheng Kung University, Tainan 70101, Taiwan
* Correspondence: stella1728627@gmail.com; Tel.: +886-979368585

Abstract: With the development trend and technological progress of lithium batteries, the battery market is booming, which means that the consumption demand for lithium batteries has increased significantly, and, therefore, a large number of discarded lithium batteries will be generated accordingly. Solvent extraction is a promising approach because it is simple. Solvent extraction is low in time consumption and is easy to industrialize. This paper is focused on the selective recovery of cobalt (Co), nickel (Ni), and manganese (Mn) contained in leachate obtained by digesting a cathodic material from spent lithium batteries with hydrochloric acid. After leaching the cathodic material, Mn was selectively extracted from leachate by using solvent extraction with D2EHPA diluted in kerosene in an optimized condition. Afterward, Co was extracted from the Mn-depleted aqueous phase using Cyanex272 diluted in kerosene. Finally, the raffinate obtained via a stripping reaction with H_2SO_4 was used in the Ni extraction experiments. Cyanex272 extractant was employed to separate Ni and Li. The process can recover more than 93% of Mn, 90% of Co, and 90% of Ni. The crucial material recovered in the form of sulfuric acid solutions can be purified and returned to the manufacturer for use. This process proposes a complete recycling method by effectively recovering Mn, Co, and Ni with solvent extraction, to contribute to the supply of raw materials and to reduce tensions related to mineral resources for the production of lithium batteries.

Keywords: recycling; circular economy; hydrometallurgy; lithium batteries; solvent extraction

check for updates

Citation: 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. https://doi.org/10.3390/min13020285

Academic Editor: Rajesh Kumar Jyothi

Received: 11 January 2023
Revised: 4 February 2023
Accepted: 15 February 2023
Published: 17 February 2023

Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Lithium batteries show great promise for electrical transportation applications owing to their high energy efficiency, high power density, long service life and environmental friendliness [1]. The cathode materials in commercial power lithium batteries are generally lithium cobalt (LCO), lithium iron phosphate (LFP), lithium nickel cobalt manganite (NCM), etc. In recent years, NCM has become the mainstream cathode material for new energy vehicles due to its good overall performance, especially in the passenger car sector [2]. It is evident that the demand for lithium batteries (LIBs) is significantly increasing as the demand for electric vehicles expands. According to the International Energy Agency (IEA), roughly 15 to 25 million electric vehicles will be sold annually by 2025, and 25 to 40 million by 2030. With regard to the resources issue, the soar in EV production brought an explosive increase in demand for critical functional battery elements, including Li, Co, Ni, and Mn [3].

At present, the recycling of waste lithium batteries is mainly based on hydrometallurgical and pyrometallurgical processes [4]. Among them, hydrometallurgy technology is suitable for recycling metals from spent LIBs due to lower energy consumption, higher product purity, and fewer exhaust gas emissions [5]. According to earlier reports, spent LIBs were often leached in an inorganic acid (hydrochloric acid, sulfuric acid, and nitric acid) [6–11], followed by ion exchange, solvent extraction [12–16], chemical precipitation [17,18], or electrodeposition [19] for valuable metal separation. There are many kinds of metals in the leachate of waste ternary lithium batteries, which are challenging to separate and recycle one by one from the complex solutions in an efficient and environmentally friendly

manner. Solvent extraction is the most preferred technique for the separation and recovery of metals from complex matrices. It has several advantages over the other techniques used in the separation or removal of metals [20]. The technique is less time consuming, with a cost-efficient and simpler chemical process in high-purity products [21]. Metallic ions are separated due to the different solubilities of their corresponding compounds in different liquid phases that are immiscible with each other [22]. The common agents for extracting valuable metals from the leaching liquor of spent cathode materials include D2EHPA, PC88A, Cyanex272, Versatic10, and LIX 84-IC [20,23–25]. Combinations of them are necessary for efficient separation due to the complexity of the cathode leachate [26,27].

One important strategy for circulating the critical battery materials in the supply chain is proposing the most efficient approach for refining the valuable materials from waste LIBs. However, few articles with an efficient and complete solvent extraction method have been published in the research domain of recycling critical materials by using the separation process. The technical route of solvent extraction was optimized by adjusting the pH value first to decrease the addition of extractants and the loss of metal ions. Through this process, extractants could be recycled and reused to reduce the cost. If the valuable metals can be recycled and reused properly directly with solvent extraction, the shortage of mineral resources can be reduced. Finally, the sulfuric acid solution was used as the stripping agent. Mn, Co, and Ni were recovered in the form of sulfuric acid solutions, which can be purified and returned to the manufacturer for use.

2. Materials and Methods

2.1. Materials

The materials used in this study were the cathode materials of spent lithium batteries. For the sake of safety, the spent lithium batteries (NCM111) were fully discharged in saturated NaCl solution for 24 h, and were then disassembled and separated manually to extract the ternary cathode material. In order to separate the cathode material and aluminum, we used a crusher to crush the cathode material into 0.5 mm pieces. Further, we used an 80-mesh sieve to separate cathode powder and aluminum. Table 1 lists the main metal contents of the cathode material of spent lithium batteries. Since the contents of aluminum and iron were quite low, the influence on the separation procedure was ignored.

Table 1. Main metal contents in cathode material of spent lithium batteries.

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

Table 2 lists the contents of the leachate obtained by leaching the cathode material of spent lithium batteries with 1N hydrochloric acid (adding 1 vol.% H_2O_2 initially) at 343 K, 20 g/L pump density, and 200 rpm speed for 12 min (140 g cathode material of spent lithium batteries was mixed with 1N HCl (7 L) in a beaker with water jacket). The compositions of Li, Co, Ni, and Mn in the cathode material were 1459, 3333, 3878, and 2956 ppm, respectively, as measured by Atomic Absorption Spectroscopy (AAS, PinAAcle 900F AA Spectrometer, PerkinElmer Inc., Waltham, MA, USA) after leaching.

Table 2. The metal composition of leachate.

Element	Li	Co	Ni	Mn
Concentration (ppm)	1459	3333	3878	2965

Chemicals of analytical grade were obtained from Echo Chemical Co., Ltd, Miaoli, Taiwan. All aqueous solutions were prepared in deionized water.

2.2. Analysis

The concentration of metal ions in the solutions obtained after the extraction experiments were determined by using Atomic Absorption Spectroscopy (AAS, PinAAcle 900F AA Spectrometer, PerkinElmer Inc., Waltham, MA, USA). The pH of the solution was monitored by a pH meter (PL-700PVS, Dogger Science, Taipei, Taiwan).

2.3. Solvent Extraction Procedure

D2EHPA (extractant) and Cyanex272 (extractant) were miscible with kerosene diluents. The recovery of Li, Co, Ni, and Mn from the leachate using solvent extraction was carried out via glass vial operation. Solvent extraction experiments were conducted by contacting 5 mL of the aqueous phase with 5 mL of the organic phase (except for the O/A ratio tests) in closed 25 mL glass vials. We used a vibrator (the vibrating speed was 3500 rpm) so that the liquid was fully mixed. After 15 min, we drained the aqueous solution from the glass vials to separate the oil from the water.

In this study, D2EHPA was used as an extractant to separate Mn and other metals (Li, Co, and Ni) from the solution in the solvent extraction process. Cyanex272 was used as an extractant to separate Co and Ni from the raffinate in the solvent extraction process. The main parameters investigated included pH value, extractant concentration, oil–water ratio, and reaction time. We adjusted the pH by adding the amount of NaOH and simultaneously converted the extractant into the corresponding sodium salt. In the solvent extraction process, the separation of metal ions was based on the difference in solute distribution between two immiscible solution phases, extracting the target metal ions from the aqueous phase to the organic phase, and then calculating the extraction efficiency with the extraction rate formula. The higher the extraction rate, the easier it is to extract the substance completely, expressed as E_M, as shown in Equation (1) [25,26]. When the extraction equilibrium is reached, the ratio of the metal solute concentration in the extract phase and the raffinate phase is called the distribution ratio, denoted by D_M, as shown in Equation (2) [23,26]. A flowchart is shown in Figure 1.

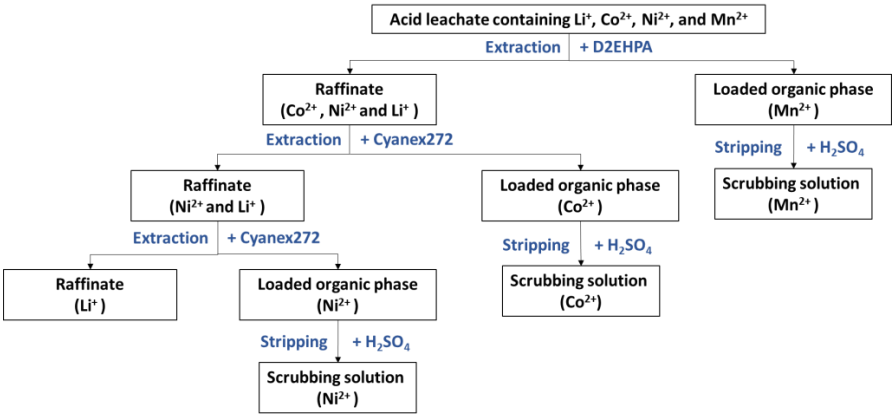


Figure 1. Proposed flowchart for recovering Li, Co, Ni, and Mn from the leachate via solvent extraction.

Extraction formula:

$$E_M = \frac{[M]_o - [M]}{[M]} \times 100\% \quad (1)$$

where $[M]_o$ is the initial concentration in the aqueous phase and [M] is the metal ion concentration in the aqueous phase after the reaction equilibrium.

Distribution ratio formula:

$$D_M = \frac{C_o - C}{C} \times \frac{[V]}{[\overline{V}]} = \frac{[\overline{M}]}{[M]} \quad (2)$$

where $\overline{[M]}$ is the total concentration of metal solute in the extract phase, $[M]$ is the total concentration of metal solute in the raffinate phase, C_o is the initial metal concentration in the aqueous solution, C is the residual concentration in the extracted aqueous solution, and $[V]$ and $\overline{[V]}$ are the volumes of the raffinate phase and the extract phase, respectively. The volume in the formula is the volume after adding sodium hydroxide.

2.4. Stripping Procedure

In this study, sulfuric acid was used as the stripping agent because the aqueous solution can be concentrated under reduced pressure to obtain sulfuric acid compounds and returned to the battery supplier. Stripping experiments were conducted by contacting 5 mL of the aqueous phase with 5 mL of the organic phase (except for the O/A ratio tests) in closed 25 mL glass vials. We used a vibrator (the vibrating speed was 3500 rpm) so that the liquid was fully mixed. After 15 min, we drained the aqueous solution from the glass vials to separate the oil from the water.

3. Results and Discussion

3.1. Extraction of Manganese

Extraction of Mn and other ions using the acidic form of the extractants: First, we adjusted the pH by adding the amount of NaOH and simultaneously converted the extractant into the corresponding sodium salt. Extractions were carried out with 1M sodium salts of D2EHPA; the equilibrium pH of the solution was in a range of 2.5–4.0. The extraction behavior of Mn is shown in Figure 2. In Figure 2a, the extraction of Mn is lower when the acidity of the equilibrium pH is low. At equilibrium pH from 2.5 to 3.0, the extraction behavior of Mn increased with NaOH addition, and the extraction behavior of Li, Co, and Ni was not significantly affected. Apparently, at a pH below 3.0, sodium salts of D2HPA had a high affinity to Mn, whereas at a pH above 3.0, sodium salts of D2EHPA had a high affinity for both Mn and Co. According to Table 3, a maximum distribution ratio value can be obtained at an equilibrium pH of 3.

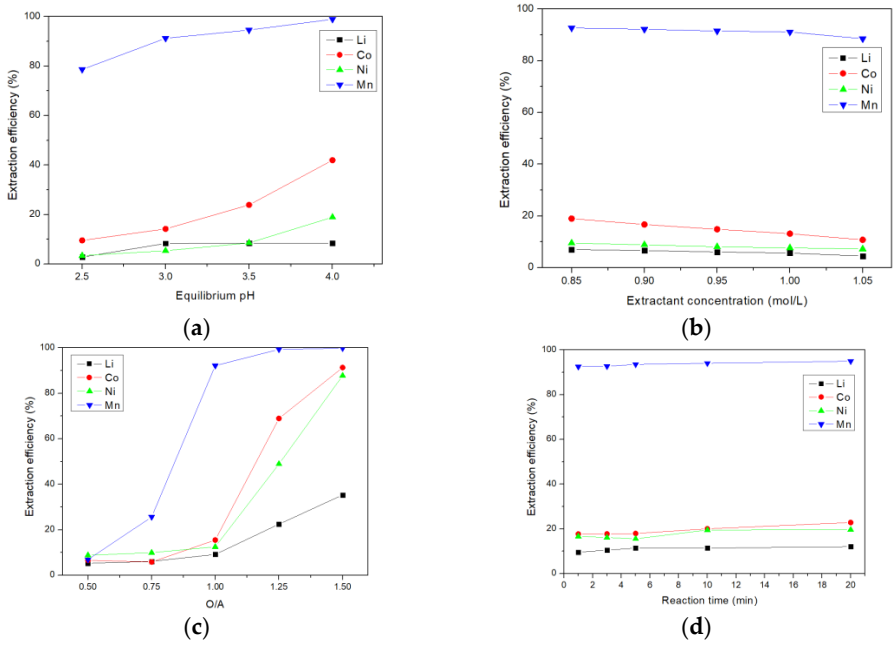


Figure 2. Effects of (**a**) pH ([D2EHPA] = 1.0 M, O/A = 1, t = 15 min), (**b**) extractant concentration (pH = 3.0, O/A = 1, t = 15 min), (**c**) oil–water ratio (pH = 3.0, [D2EHPA] = 1.0 M, t = 15 min), and (**d**) reaction time (pH = 3.0, [D2EHPA] = 1.0 M, O/A = 1) on manganese extraction.

Table 3. The relationship between the equilibrium pH and separation coefficient.

Equilibrium pH	2.5	3.0	3.5	4.0
D_{Mn}	2132	1184	1491	3.6
D_{Co}	1.1	0.4	5.0	0.9
$\beta_{Mn/Co}$	1878	2716	297	4.0

The cationic acidic extractant D2EHPA released protons as the extraction proceeded. Therefore, it was expected that the pH of the aqueous solution would decrease during extraction. One effective way to maintain the equilibrium pH value is the conversion of D2EHPA to the corresponding sodium salt in the aforementioned process. The equilibrium pH was approximately 3 for all the extractions. In Figure 2b, the extraction of Mn remained at approximately 90%, with the extractant concentration increasing from 0.85 to 1.05 M, whereas co-extraction of Co was apparently detected with the extractant concentration below 1.0 M. It can be seen from Table 4 that the maximum distribution ratio can be obtained when the extractant concentration is 1.0 M, achieving the most effective Mn extraction with the lowest co-extraction of other metals. As shown in Figure 2c, the O/A ratios were 0.5, 0.75, 1.0, 1.25, and 1.5 with 1 M sodium salts of D2EHPA, shaking time of 15 min, pH of 3, and at room temperature. The limited cation loading capacity of D2EHPA leads to a higher O/A ratio. Therefore, at an O/A ratio of 0.5 to 1.0, the manganese extraction is from 6.89% to 92.17%. As shown in Figure 2d, the reaction times were 1, 3, 5, 10, and 20 min with 1 M sodium salts of D2EHPA, a pH of 3.0, and at room temperature. The reaction time did not significantly affect extraction efficiency. Considering the entire process time consumption, a reaction time of 1 min was chosen and the Mn extraction reached 92.48%.

Table 4. The relationship between the equilibrium pH and separation coefficient.

Extractant Concentration	0.85	0.90	0.95	1.00	1.05
D_{Mn}	12.70	11.82	10.79	10.29	7.73
D_{Co}	0.23	0.20	0.18	0.15	0.21
$\beta_{Mn/Co}$	54.24	59.00	61.84	67.88	64.08

The Mn extraction mechanism is shown in Formula (3) [28]. Hydrogen ions will be released during the extraction process and the Mn extraction efficiency has a significant relationship with the pH value [29,30]. Therefore, this study initially explored the effect of equilibrium pH on Mn extraction.

In terms of extraction time, Hossain et al. [31] also observed that the kinetics of the Mn extraction using D2EHPA were fast, and the equilibrium was achieved in 5 min. Thus, low contact times are required for the extraction of Mn.

Compared with previous studies [30,32–34], this study can effectively extract Mn under a lower oil–water ratio and one-stage extraction.

$$Mn^{2+} + \overline{2(HA)_2} \leftrightarrow \overline{MnA_4H_2} + 2H^+ \quad (3)$$

3.2. Stripping of Manganese

Mn was back extracted from the loaded 1 M sodium salts of D2EHPA using H_2SO_4 as the stripping agent. The loaded organic was stripped with different H_2SO_4 concentrations in a range of 0.05–0.5 M at an equal phase ratio in order to bring the metal values back to the aqueous solution. It can be seen from Figure 3a that a stripping percentage of 99% is obtained with 0.2 M of sulfuric acid. The next variable investigated was the oil–water ratio from the stripping process. It can be seen from Figure 3b that the decreasing stripping efficiency occurred with different oil–water ratios in a range of 1.0–3.0. The decrease in the stripping efficiency was due to the oil–water ratio above 1.5, as the stripping agent

did not have the full ability to load Mn. As shown in Figure 3b, after extraction and stripping, the concentration of Mn in the solution was enriched 1.5-times compared to the original solution. Figure 3c shows that the stripping is fast and is completed in 1 min. After stripping experiments, the extractant can be reused because all metals are stripped to the aqueous phase.

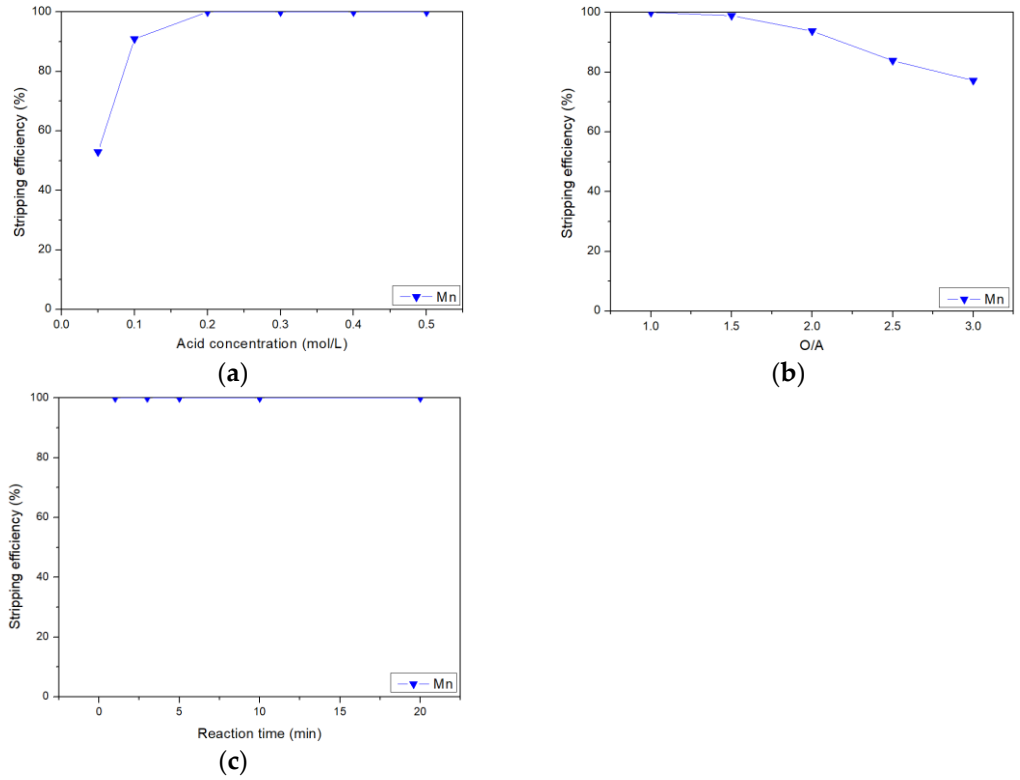


Figure 3. Effects of (**a**) acid concentration (O/A = 1, t = 15 min), (**b**) oil–water ratio ([H_2SO_4] = 0.2 M, t = 15 min), and (**c**) reaction time ([H_2SO_4] = 0.2 M, O/A = 1.5) on manganese stripping.

Compared with previous studies [30,31], this study can complete Mn stripping under the condition of a higher oil–water ratio, so as to achieve the goal of reducing wastewater.

3.3. Extraction of Cobalt

The raffinate containing Li, Co, and Ni by stripping with 0.2M H_2SO_4 from the oil phase was used in the solvent extraction experiments. Cyanex272 is a cationic acidic extractant and releases protons as the extraction proceeds. It is important to control the pH so that the extraction of cobalt can take place. First, adjust the pH by adding the amount of NaOH and simultaneously convert the extractant into the corresponding sodium salt. Extractions were carried out with 0.4 M sodium salts of Cyanex272; the equilibrium pH of the solution was in a range of 5–6.5. The extraction behavior of Co is shown in Figure 4. In Figure 4a, the extraction of Co is lower when the acidity of the equilibrium pH. At equilibrium pH from 6.0 to 6.5, the extraction behavior of Ni increased significantly with NaOH addition. At a pH of 6.0, sodium salts of Cyanex272 had a high affinity to Co, whereas at a pH above 6.0, sodium salts of Cyanex272 had a high affinity for both Ni and Co. The equilibrium pH was approximately 6.0 for all the extractions. The extraction of Co remained at approximately 90%, with the extractant concentration increasing from 0.25 to 0.45 M. It can be seen from Table 5 and Figure 4b that the maximum distribution ratio can be obtained when the extractant concentration is 0.4 M, achieving the most effective coextraction with the lowest co-extraction of other metals. As shown in Figure 4c, the O/A ratios were 0.5, 0.75, 1.0, 1.25, and 1.5 with 0.4 M sodium salts of Cyanex272, shaking time of 15 min, pH of 6.0, and at room temperature. The higher organic-to-aqueous ratio of

Cyanex272 leads to a severely high co-extraction of Ni. At an O/A ratio of 1.0, the Ni extraction could be controlled under 10%, whereas the high extraction efficiency of Co could be obtained at the same time. As shown in Figure 4d, the reaction times were 1, 3, 5, 10, and 20 min with 0.4 M sodium salts of Cyanex272, a pH of 6.0, and at room temperature. The reaction time did not significantly affect extraction efficiency. At a reaction time of 1 min, the Co extraction reaction was completed.

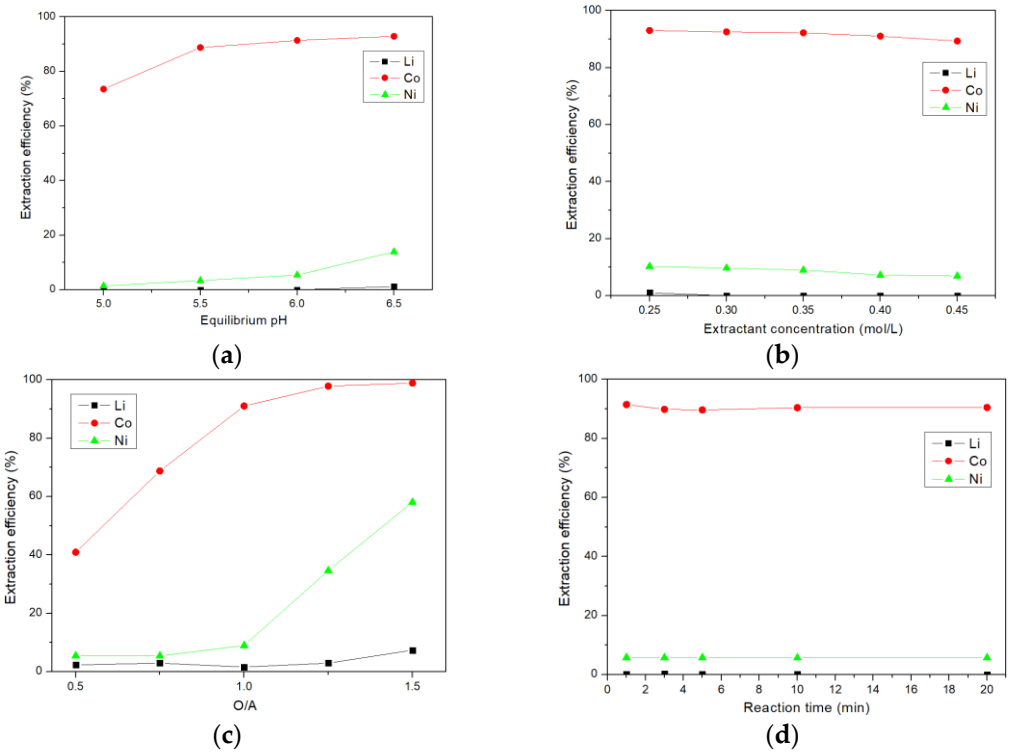


Figure 4. Effects of (**a**) pH ([Cyanex272] = 0.4 M, O/A = 1, t = 15 min), (**b**) extractant concentration (pH =6.0 , O/A = 1, t = 15 min), (**c**) oil–water ratio (pH = 6.0 , [Cyanex272] = 0.4 M, t = 15 min), and (**d**) reaction time on cobalt extraction (pH = 6.0 , [Cyanex272] = 0.4 M, O/A = 1).

Table 5. The relationship between the equilibrium pH and separation coefficient.

Extractant Concentration	0.25	0.30	0.35	0.40	0.45
D_{Co}	13.32	12.40	11.83	10.14	8.35
D_{Ni}	0.11	0.10	0.09	0.07	0.07
$\beta_{Co/Ni}$	116.18	116.01	120.12	130.60	113.07

The Co extraction reaction mechanism is shown in Formula (4) [35,36], and hydrogen ions are released during the Co extraction process, resulting in a decrease in the equilibrium pH value. Therefore, in order to effectively extract Co, this study first explored the effect of equilibrium pH on extraction efficiency. Similar results were obtained in this study when compared with other studies [35–37].

$$Co^{2+} + \overline{2(HA)_2} \leftrightarrow \overline{CoA_4H_2} + 2H^+ \quad (4)$$

3.4. Stripping of Cobalt

Co was back extracted from the loaded 0.4 M sodium salts of Cyanex272 using H_2SO_4 as the stripping agent. The loaded organic was stripped with different H_2SO_4 concentrations in a range of 0.05–0.5 M at an equal phase ratio to bring the metal values back to

the aqueous solution. As demonstrated in Figure 5a, an almost full stripping of Co can be completely achieved with 0.1 M of sulfuric acid. The next variable investigated was the oil–water ratio from the stripping process. As shown in Figure 5b, the decreasing stripping efficiency occurred with different oil–water ratios in a range of 1.0–3.0. The decrease in the stripping efficiency was due to an oil–water ratio above 1.5, as the stripping agent did not have the full ability to load Co. Figure 5b shows the Co value in the solution was enriched 1.5-times compared to the original solution. It can be seen from Figure 5c that the reaction time did not considerably affect stripping efficiency and was completed in 1 min. After stripping experiments, the extractant can be reused because all metals are stripped to the aqueous phase.

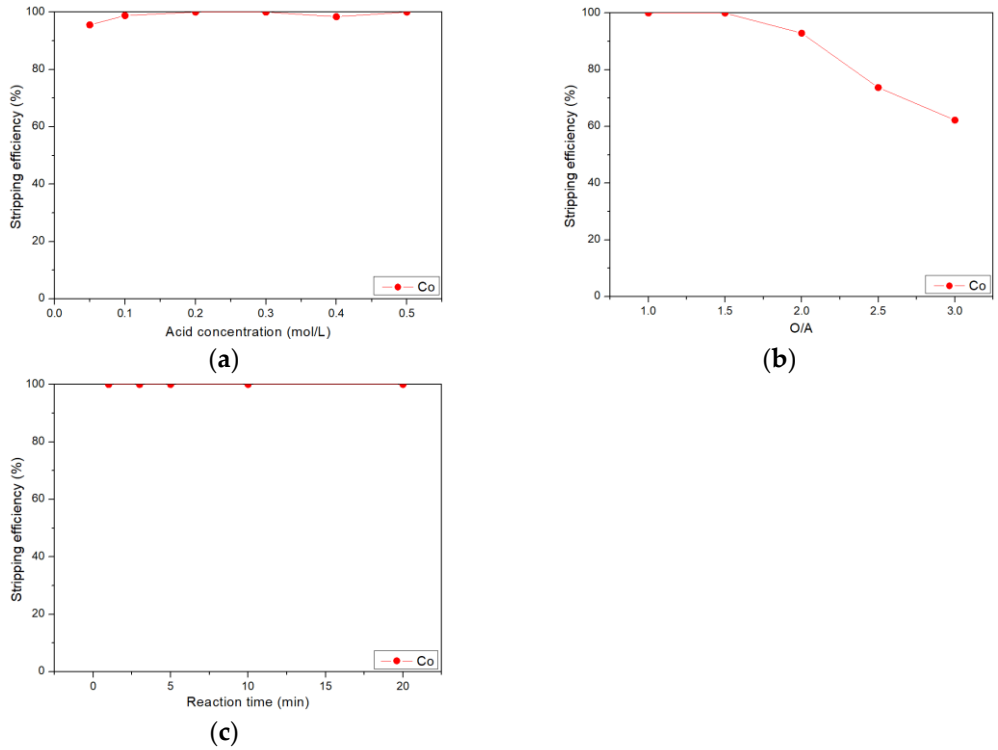


Figure 5. Effects of (**a**) acid concentration (O/A = 1, t = 15 min), (**b**) oil–water ratio ([H_2SO_4] = 0.1 M, t = 15 min), and (**c**) reaction time ([H_2SO_4] = 0.1 M, O/A = 1.5) on cobalt stripping.

Compared with other studies [35,36], stripping Co under the condition of a higher oil–water ratio to achieve the goal of wastewater reduction.

3.5. Extraction of Nickel

The raffinate obtained via stripping reaction with 0.1M H_2SO_4 was used in the Ni extraction experiments. First, the pH was adjusted by adding the amount of NaOH and simultaneously converting the extractant into the corresponding sodium salt. Extractions were carried out with 0.4 M sodium salts of Cyanex272; the equilibrium pH of the solution was in a range of 6.5–8.0. The extraction behavior of Ni is shown in Figure 6a. At the equilibrium pH from 7.0 to 8.0, the extraction efficiency behavior of Ni stably reached above 97%. The equilibrium pH was approximately 7.0 for all the extractions. The extraction of Ni remained at approximately 97%, with the extractant concentration increasing from 0.30 to 0.50 M. Almost no Li extraction occurs because Li ions do not form extractable anionic species in acidic media. It can be seen from Table 6 and Figure 6b that the maximum distribution ratio can be obtained when the extractant concentration is 0.4 M, achieving the most effective Ni extraction with the lowest co-extraction of other metals. As shown in Figure 6c, the O/A ratios were 0.5, 0.75, 1.0, 1.25, and 1.5 with 0.4 M sodium salts of Cyanex272, shaking time of 15 min, pH of 7.0, and at room temperature. Apparently, at

an O/A ratio of 1.0, the nickel extraction reached 97.88%, with no co-extraction of lithium at the same time. As shown in Figure 6d, the reaction times were 1, 3, 5, 10, and 20 min with 0.4 M sodium salts of Cyanex272, a pH of 7.0, and at room temperature. At a reaction time of 1 min, the Ni extraction reaction was certainly completed and achieved the most effective Ni extraction with the lowest co-extraction of other metals.

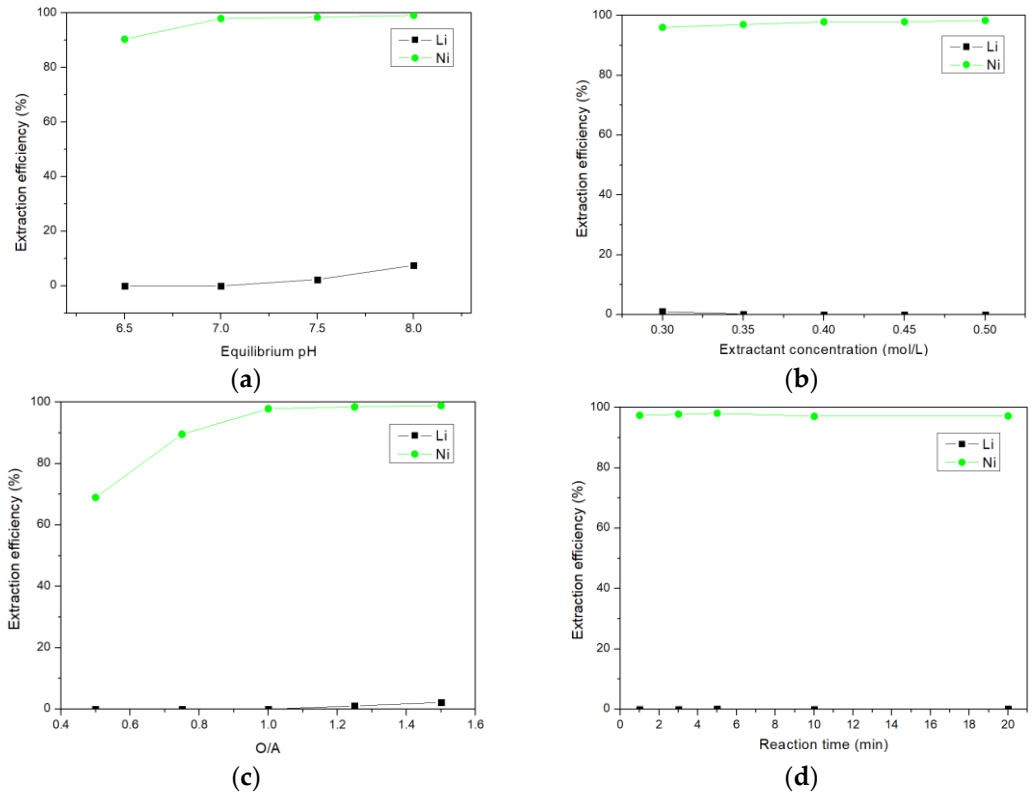


Figure 6. Effects of (**a**) pH ([Cyanex272] = 0.4 M, O/A = 1, t = 15 min), (**b**) extractant concentration (pH = 7.0, O/A = 1, t = 15 min), (**c**) oil–water ratio (pH = 7.0, [Cyanex272] = 0.4 M, t = 15 min), and (**d**) reaction time (pH = 7.0, [Cyanex272] = 0.4 M, O/A = 1) on nickel extraction.

Table 6. The relationship between the equilibrium pH and separation coefficient.

Extractant Concentration	0.3	0.35	0.4	0.45	0.5
D_{Ni}	24.06	32.11	46.17	45.94	45.95
D_{Li}	0.01	0.002	0.0001	0.0001	0.0001
$\beta_{Ni/Li}$	2312	15,259	461,651	459,437	459,437

The Ni extraction reaction mechanism is shown in Formula (5). Most studies [21,38,39] use Cyanex272 for the separation of Co and Ni. In this study, Cyanex272 was used for Ni and Li separation for the first time and excellent results were obtained.

$$Ni^{2+} + \overline{2(HA)_2} \leftrightarrow \overline{NiA_4H_2} + 2H^+ \quad (5)$$

3.6. Stripping of Nickel

Ni was back extracted from the loaded 0.4M sodium salts of Cyanex272 using H_2SO_4 as the stripping agent. The loaded organic was stripped with different H_2SO_4 concentrations in a range of 0.05–0.5 M at an equal phase ratio to bring the metal values back to the aqueous solution. It can be seen from Figure 7a that an almost-full stripping of Ni could be completely achieved with 0.1 M of sulfuric acid. As shown in Figure 7b, the decreasing

stripping efficiency occurred with different oil–water ratios in a range of 1.0–3.0. The decrease in stripping efficiency was due to the oil–water ratio above 1.0, as the stripping agent did not have the full ability to load Ni. The Ni in the solution could not be efficiently enriched from the original solution. It can be seen from Figure 7c that when a loaded H_2SO_4 solution was used, the stripping efficiency did not enhance with increased significant contact time in a range of 1–20 min. This indicated that the stripping reaction was completed in 5 min. After stripping experiments, the extractant can be reused because all metals are stripped to the aqueous phase. However, in the Ni stripping study, the acid concentration was relatively low, resulting in no effective reduction in water usage.

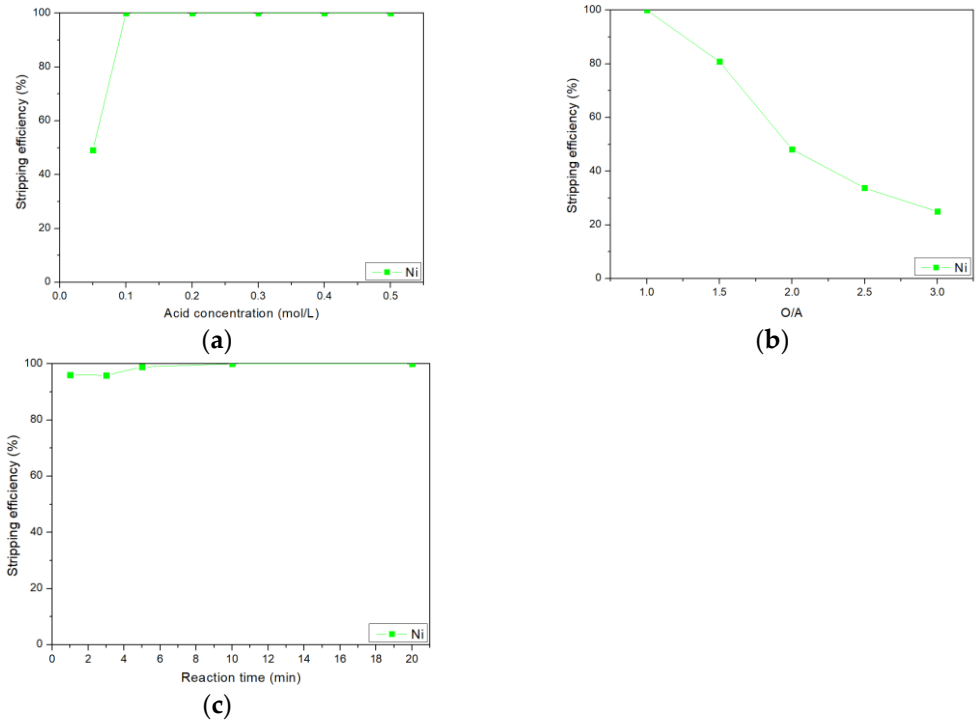


Figure 7. Effects of (**a**) acid concentration (O/A = 1, t = 15 min), (**b**) oil–water ratio ([H_2SO_4] = 0.1 M, t = 15 min), and (**c**) reaction time ([H_2SO_4] = 0.1 M, O/A = 1) on nickel stripping.

4. Conclusions

With the increase in electric vehicles, the disposal of spent lithium batteries will be a crucial issue. Solvent extraction is an efficient recovery method and can be generally applied in the industry. Therefore, this study proposed a complete solvent extraction approach to separate the valuable metals in the leachate. D2EHPA showed a strong affinity for Mn. The extraction efficiency was mainly affected by the pH value, and the extraction efficiency reached about 93% by controlling the extraction environment. In the raffinate, rich in Co, Ni, and Li, Cyanex272 performed an effective extraction and reached more than 90% of Co. Finally, Cyanex272 effectively separated Ni and Li, and Li co-extraction hardly occurred in this step. Li did not form extractable anion species in acidic media. With no Li co-extraction, approximately 90% Ni extraction efficiency could be achieved. Mn, Co, and Ni were separated in sequence with acidic extractants, and sulfuric acid was employed as a stripping agent to recover the metals in the form of sulfuric acid solutions. Subsequently, manganese sulfate, cobalt sulfate, and nickel sulfate could be purified and returned to the manufacturer.

Author Contributions: Conceptualization, J.-Z.W. and Y.-C.T.; methodology, J.-Z.W. and Y.-C.T.; validation, J.-Z.W. and Y.-C.T.; investigation, J.-Z.W. and Y.-C.T.; resources, J.-Z.W. and Y.-C.T.; data curation, J.-Z.W. and Y.-C.T.; writing—original draft preparation, J.-Z.W. and Y.-C.T.; writing—review

and editing, J.-Z.W. and Y.-C.T.; supervision, Y.-H.S.; project administration, Y.-H.S.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to acknowledge the support of National Cheng Kung University's Department of Resources Engineering and the Ministry of Science and Technology, R.O.C.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fan, E.; Li, L.; Wang, Z.; Lin, J.; Huang, Y.; Yao, Y.; Chen, R.; Wu, F. Sustainable Recycling Technology for Li-Ion Batteries and Beyond: Challenges and Future Prospects. *Chem. Rev.* **2020**, *120*, 7020–7063. [CrossRef]
2. Li, C.; Dai, G.; Liu, R.; Wang, C.; Wang, S.; Ju, Y.; Jiang, H.; Jiao, S.; Duan, C. Separation and recovery of nickel cobalt manganese lithium from waste ternary lithium-ion batteries. *Sep. Purif. Technol.* **2023**, *306*, 122559. [CrossRef]
3. Li, Y.; Zeng, L.; Du, J.; Zhang, G.; Cao, Z.; Wu, S. Improving Extraction Performance of D2EHPA for Impurities Removal from Spent Lithium-Ion Batteries Leaching Solution by TPC[4]. *ACS Sustain. Chem. Eng.* **2022**, *10*, 4312–4322. [CrossRef]
4. Bernardes, A.M.; Espinosa, D.C.R.; Tenório, J.A.S. Recycling of batteries: A review of current processes and technologies. *J. Power Sources* **2004**, *130*, 291–298. [CrossRef]
5. Dutta, D.; Kumari, A.; Panda, R.; Jha, S.; Gupta, D.; Goel, S.; Jha, M.K. Close loop separation process for the recovery of Co, Cu, Mn, Fe and Li from spent lithium-ion batteries. *Sep. Purif. Technol.* **2018**, *200*, 327–334. [CrossRef]
6. 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]
7. 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]
8. Bertuol, D.A.; Machado, M.C.; 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]
9. 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]
10. 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]
11. 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]
12. Sarangi, K.; Reddy, B.R.; Das, R.P. Extraction studies of cobalt (II) and nickel (II) from chloride solutions using Na-Cyanex 272.: Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. *Hydrometallurgy* **1999**, *52*, 253–265. [CrossRef]
13. Rodrigues, I.R.; Deferm, C.; Binnemans, K.; Riano, S. Separation of cobalt and nickel via solvent extraction with Cyanex-272: Batch experiments and comparison of mixer-settlers and an agitated column as contactors for continuous counter-current extraction. *Sep. Purif. Technol.* **2022**, *296*, 121326. [CrossRef]
14. Reddy, B.R.; Park, K.H. Process for the Recovery of Cobalt and Nickel from Sulphate Leach Liquors with Saponified Cyanex 272 and D2EHPA. *Sep. Sci. Technol.* **2007**, *42*, 2067–2080. [CrossRef]
15. Lommelen, R.; Binnemans, K. Thermodynamic Modeling of Salting Effects in Solvent Extraction of Cobalt(II) from Chloride Media by the Basic Extractant Methyltrioctylammonium Chloride. *ACS Omega* **2021**, *6*, 11355–11366. [CrossRef]
16. Qi, D. (Ed.) Extractants Used in Solvent Extraction-Separation of Rare Earths: Extraction Mechanism, Properties, and Features. In *Hydrometallurgy of Rare Earths*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 187–389. [CrossRef]
17. Innocenzi, V.; Ippolito, N.M.; Michelis, I.D.; Prisciandaro, M.; Medici, F.; Veglio, F. A review of the processes and lab-scale techniques for the treatment of spent rechargeable NiMH batteries. *J. Power Sources* **2017**, *362*, 202–218. [CrossRef]
18. Gao, R.; Sun, C.; Xu, L.; Zhou, T.; Zhuang, L.; Xie, H. Recycling $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ material from spent lithium-ion batteries by oxalate co-precipitation. *Vacuum* **2020**, *173*, 109181. [CrossRef]
19. Prabaharan, G.; Barik, S.P.; Kumar, N.; Kumar, L. Electrochemical process for electrode material of spent lithium ion batteries. *Waste Manag.* **2017**, *68*, 527–533. [CrossRef]
20. Alvial-Hein, G.; Mahandra, H.; Ghahreman, A. Separation and recovery of cobalt and nickel from end of life products via solvent extraction technique: A review. *J. Clean. Prod.* **2021**, *297*, 126592. [CrossRef]
21. Coll, M.T.; Fortuny, A.; Kedari, C.S.; Sastre, A.M. Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. *Hydrometallurgy* **2012**, *125–126*, 24–28. [CrossRef]
22. Liang, Z.; Cai, C.; Peng, G.; Hu, J.; Hou, H.; Liu, B.; Liang, S.; Xiao, K.; Yuan, S.; Yang, J. Hydrometallurgical Recovery of Spent Lithium Ion Batteries: Environmental Strategies and Sustainability Evaluation. *ACS Sustain. Chem. Eng.* **2021**, *9*, 5750–5767. [CrossRef]

23. Devi, N.B.; Nathsarma, K.C.; Chakravortty, V. Separation of divalent manganese and cobalt ions from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272. *Hydrometallurgy* **2000**, *54*, 117–131. [CrossRef]
24. Zhang, W.; Cheng, C. Manganese metallurgy review. Part II: Manganese separation and recovery from solution. *Hydrometallurgy* **2007**, *89*, 160–177. [CrossRef]
25. Shuya, L.; Yang, C.; Xuefeng, C.; Wei, S.; Yaqing, W.; Yue, Y. Separation of lithium and transition metals from leachate of spent lithium-ion batteries by solvent extraction method with Versatic 10. *Sep. Purif. Technol.* **2020**, *250*, 117258. [CrossRef]
26. Zhang, K.; Liang, H.; Zhong, X.; Cao, H.; Wang, R.; Liu, Z. Recovery of metals from sulfate leach solutions of spent ternary lithium-ion batteries by precipitation with phosphate and solvent extraction with P507. *Hydrometallurgy* **2022**, *210*, 105861. [CrossRef]
27. Yang, Y.; Lei, S.; Song, S.; Sun, W.; Wang, L. Stepwise recycling of valuable metals from Ni-rich cathode material of spent lithium-ion batteries. *Waste Manag.* **2020**, *102*, 131–138. [CrossRef]
28. Vieceli, N.; Reinhardt, N.; Ekberg, C.; Petranikova, M. Optimization of Manganese Recovery from a Solution Based on Lithium-Ion Batteries by Solvent Extraction with D2EHPA. *Metals* **2021**, *11*, 54. [CrossRef]
29. Yang, Y.; Xu, S.; He, Y. Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes. *Waste Manag.* **2017**, *64*, 219–227. [CrossRef]
30. Li, J.; Yang, X.; Yin, Z. Recovery of manganese from sulfuric acid leaching liquor of spent lithium-ion batteries and synthesis of lithium ion-sieve. *J. Environ. Chem. Eng.* **2018**, *6*, 6407–6413. [CrossRef]
31. Hossain, M.R.; Nash, S.; Rose, G.; Alam, S. Cobalt loaded D2EHPA for selective separation of manganese from cobalt electrolyte solution. *Hydrometallurgy* **2011**, *107*, 137–140. [CrossRef]
32. Peng, C.; Chang, C.; Wang, Z.; Wilson, B.P.; Liu, F.; Lundstrom, M. Recovery of High-Purity MnO2 from the Acid Leaching Solution of Spent Li-Ion Batteries. *JOM* **2020**, *72*, 790–799. [CrossRef]
33. Chen, X.; Chen, Y.; Zhou, T.; Liu, D.; Hu, H.; Fan, S. Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. *Waste Manag.* **2015**, *38*, 349–356. [CrossRef]
34. Keller, A.; Hlawitschka, M.W.; Bart, H.J. Application of saponified D2EHPA for the selective extraction of manganese from spend lithium-ion batteries. *Chem. Eng. Process. Process Intensif.* **2022**, *171*, 108552. [CrossRef]
35. Zhao, J.M.; Shen, X.Y.; Deng, F.L.; Wang, F.C.; Wu, Y.; Liu, H.Z. Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. *Sep. Purif. Technol.* **2011**, *78*, 345–351. [CrossRef]
36. Wang, F.; He, F.; Zhao, J.; Sui, N.; Xu, L.; Liu, H. Extraction and separation of cobalt(II), copper(II) and manganese(II) by Cyanex272, PC-88A and their mixtures. *Sep. Purif. Technol.* **2012**, *93*, 8–14. [CrossRef]
37. Wang, K.; Zhang, G.; Luo, M.; Zeng, M. Separation of Co and Mn from acetic acid leaching solution of spent lithium-ion battery by Cyanex272. *J. Environ. Chem. Eng.* **2022**, *10*, 108250. [CrossRef]
38. Zhou, Y.; Chen, Z.; Chen, A.; Zhang, J.; Wu, X.; Xu, J. Comprehensive recovery of NCM cathode materials for spent lithium-ion batteries by microfluidic device. *Sep. Purif. Technol.* **2022**, *294*, 121185. [CrossRef]
39. Xiao, F.; Wang, Y.; Shen, X.; Perera, J.M.; Stevens, G.W. The effect of DTAC on the extraction of Co(II) with Cyanex272 in a neutral micellar phase. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *482*, 109–114. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.