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## A GREEN APPROACH TO RECOVERING LITHIUM AND COBALT FROM SPENT LITHIUM-ION BATTERIES USING DILUTE HCI SOLUTION MIXED WITH *H. SABDARIFFA* FLOWER EXTRACT AS A LEACHING AGENT

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#### Abstract

Studies on the recovery of lithium and cobalt from spent lithium-ion batteries have attracted a lot of attention in recent years. For a sustainable battery industry, processes for the recycling of valuable metals from spent batteries have been continuously improved and developed via a "green" approach. In this work, an effective process for the recycling of lithium and cobalt from spent cell phone lithium batteries was investigated using HCl solution at low concentrations in combination with H. sabdariffa flower extract. The influence of parameters such as the concentration of the extract and HCl, pulp density, reaction temperature, and time on the percentage of leached metals was investigated. In these leaching systems, the extract, which contains organic compounds, acts as a complexing and reductive agent for dissolved metals. The optimum conditions for the leaching of these metals were 90% (v/v) of extract, 0.5 mol/L HCl, 10 g/L pulp density, 90°C, and 2.0 hours. 100% Li(1) and 91.3% Co(II) were leached under the optimum leaching conditions. Li(1) and Co(II) from the leachate were completely separated by the use of AG®50W-X4 resins and the presence of the extract in the leach solution had little effect on the recovery capacity for these metals. The metal loading capacity of the resin was determined to be 37.4 mg/g Co(II) and 1.2 mg/g Li(1). Thus, the use of plant extracts such as the flower of H. sabdariffa can be considered as a promising agent for the recovery of valuable metals from spent batteries.

Keywords: H. sabdariffa flower extract; Leaching; Ion exchange; Spent lithium-ion batteries; Cobalt; Lithium

#### 1. Introduction

Lithium-ion batteries (LIBs) are an important device for energy storage in electronics such as mobile phones, personal care, portable devices, and others because of their high energy density, high voltage, long lifespan, low self-discharge, and no memory effect [1, 2]. The growing demand for LIBs in recent years, especially electric vehicles (EVs), has remarkably increased this battery production [3, 4]. As a result, the price of materials, especially strategic metals like cobalt and lithium, has been pushed up due to the depletion of high-grade sulfide ores [5]. Along with the increasing LIBs production, large numbers of LIBs have been generated after reaching the end of their life, which causes potential environmental issues because of their toxic composition (e.g. organic matter and heavy metals) [6]. The number of spent

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LIBs was estimated to be 10,700 tons in 2012 and reached up to 250,000 tons in 2020, while only 2 to 5% of their proportion was collected and recycled [7]. Hence, spent LIBs recycling is considered an important strategy to reduce environmental damage, save valuable metals, bring economic value, and lead toward sustainable manufacturing in the future [8, 9].

Many efforts have been made for the spent LIBs recycling [6, 10, 11]. A hydrometallurgical method is mostly used in the recovery of metals because of its advantages such as low consumed energy, simple operation process, and metals being recovered with high purity [12-14]. The spent LIBs were first discharged to avoid short circuits and self-igniting and then ground and calcined to remove outer cases and organic matters (e.g. plastic or electrolyte). These steps facilitate the recovery of the metals in further steps such as increasing the metal leaching efficiency



and reducing the acid consumption and impurities [15-17]. Subsequently, these metals in the cathode and anode materials obtained from the above treatment processes were leached and purified to recover pure metals or their compounds. Although inorganic acids including HCl, H2SO4, and HNO3 are effective leaching agents in the dissolution of metals, these acids could cause harmful impacts on the natural environment and be corrosive to equipment at high concentrations [18, 19]. Generally, the metal leaching effectiveness of lixiviants from spent LIBs notably depends on the characteristics of leaching agents such as acidic and reductive properties, and the stability of dissolved metals by complexing with anions. Therefore, using low-acidic solutions with chelating agents could improve the leaching rate of metals and decrease acid consumption. Reported literature indicated that the use of organic acids showed the effective leaching for metals from the spent LIBs due to their acidic and complexing properties [18, 20, 21]. However, the application of organic acids (e.g. acetic, oxalic, maleic acids) in the recovery of metals is still limited on industrial scales owing to their high-cost operation [22].

In recent years, using "green lixiviants" for recovering metals from secondary resources has attracted much interest [23, 24]. Among green lixiviates, plant extracts could be considered a possible candidate for recovering metals due to their metal complexing and acidic components such as organic acids, polyphenols, flavonoids, tannins, etc., [25]. H. sabdariffa, known as roselle has been widely planted in tropical and subtropical countries (e.g., India, Vietnam, China, Malaysia, Indonesia, Sudan, Egypt, Nigeria, and Mexico) and is majorly used to produce jute and allied fiber and other industries like food and medicine [26, 27]. H. sabdariffa flower contains various organic acids, anthocyanins, and polyphenols (see in Fig.1) [25]. With its chemical constituents, H. sabdariffa extract could be used in the



Figure 1. Some chemical constituents of H. sabdariffa flower extract [25]



dissolution of the metal ions from secondary resources like spent LIBs because of their acidic, reductive, and metal complexing properties and could contribute to an increase in the economic value of this plant.

Therefore, in this work, H. sabdariffa flower extract derived from plants was employed as a leaching agent to dissolve metals from spent LIBs of mobile phones [25, 28]. The effect of factors such as concentration of the extract and acid, reaction time, and temperature on the leaching of metals was studied. Our previous works showed that Co(II) adsorption capacity from simulated HCl leaching solutions was confirmed by AG®50W-X4 resin [29]. So, this resin was also employed to separate Co(II) and Li(I) from the leachate. After the adsorption process, elution experiments of these metals from the loading resin were studied. The obtained results could open the application capacity of plant extracts as potential leaching agents in the recovery of Co(II) and Li(I) from spent LIBs.

# Experimental Chemicals and Materials

Acidic aqueous solutions were prepared by diluting from concentrated hydrochloric acid (HCl, Sigma-Aldrich, 37%) to desirable concentrations in doubly distilled water. AG $^{\odot}$ 50W-X4 resin was supplied from Bio-Rad Laboratories, Inc., US. The AG $^{\odot}$ 50W-X4 resin exhibits strong cation exchange in the hydrogen form, 4% crosslink, 100-200 dry mesh, and 106-250 µm wet bead size.

**Preparation of material powders:** Spent LIBs were gathered at mobile phone stores in Can Tho City, Vietnam. After dismantling, the black powder of cathodes and anodes from the batteries was collected and then calcined at 500 °C for 1.0 h for the removal of organic matter. To determine the weight percentage of metals in the calcined materials, a certain amount of the materials was completely dissolved into aqua regia. Metal content in the resulting solution was determined by Inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany) measurement. Since Co and Li are the two main metals in these batteries, this study mostly focused on the recovery ability of these two metals.

*The preparation of H. sabdariffa flower extract: H. sabdariffa* flowers were bought from a local market in Can Tho city and then washed several times with distilled water to remove dirt. The cleaned flowers were dried in an oven at 50 °C for 48 h and ground to a fine powder. Due to the dissoluble properties of organic compounds, an aqueous extract from *H. sabdariffa* flower was prepared in this work. 15 g/L of the fine powder was extracted with doubly distilled water for 30 min at room temperature  $(25\pm1^{\circ}C)$  and then an aqueous extract was separated from the residue by filtration. The pH of the aqueous extract was measured to be 2.1. The obtained extract of *H. sabdariffa* flower was kept at 4 °C for leaching experiments.

#### 2.2. Leaching procedure

Leaching experiments were carried out by mixing 1.0 g of the calcined materials with 100 mL of dilute HCl mixed with *H. sabdariffa flower* extract at known concentrations, which corresponded to 10 g/L pulp density. Reaction mixtures were stirred on a heating mantle to handle temperature and stirring speed. After the required period, the residues after the reactions were filtered out with filtration paper. The concentration of metal ions in the filtrate was determined by ICP-OES. The leaching percentage of a metal was calculated as follows:

Leaching percentage(%) = 
$$\frac{m_i}{m_o} \cdot 100\%$$
 (1)

where  $m_0$  and  $m_i$  are the mass of metal in the initial calcined powder and the aqueous solution after the leaching, respectively.

#### 2.3. Ion exchange procedure

Bach experiments were performed by adding a specific amount of AG<sup>®</sup>50W-X4 resins into 10 mL of the leachate of spent LIBs. Reactions were done in a shaking incubator (HB-201SF, Hanbaek Scientific Co., Korea) for 2.0 h at room temperature. After the reaction, the resins were filtered out of the solution by filtration. The loading percentage of metal on the resins was calculated based on mass balance.

Leaching percentage(%) = 
$$\frac{m_a}{m_b} \cdot 100\%$$
 (2)

where  $m_b$  and  $m_a$  are the mass of a metal in the aqueous solution before and after the ion exchange experiment, respectively.

To determine the loading capacity of the resin for Co(II)/Li(I), 30 mL of a solution containing metals was added to 0.6 g of resin in plastic bottles and then the mixture was shaken for 2 h. The experiment was repeated six times for the same amount of resin to obtain six corresponding stages. The metal loading capacity of the resin was calculated by the following equation:

Loading capacity = 
$$\sum_{i=1}^{6} \frac{m_i}{0.6}$$
 (3.1)



where  $m_i$  is the mass of metal loaded into resin at stage i (i=1-6).

Each experiment in this work was duplicated with errors within  $\pm 5\%$ .

#### 3. Results and discussion

3.1. Leaching of metals from the material powders using HCl mixed H. sabdariffa flower extract

3.1.1. Effect of HCl concentration

In our previous study, although cobalt and lithium from the spent LIBs were completely leached by HCl solution at higher concentrations than 4.0 mol/L, the use of high acid can cause some drawbacks in the real operation such as erosion of equipment, treatment of acidic wastewater, and chemical consumption [30]. Therefore, to overcome these disadvantages, a dilute HCl solution mixed with sabdariffa flower extract was employed for the leaching of metals from spent LIBs in the present study.

To consider the effect of HCl concentration on the dissolution of cobalt and lithium, HCl concentration in the leaching solution was varied from 0.0 to 0.5 mol/L and the concentration of *H. sabdariffa* flower extract was kept at 90% (v/v). Leaching reactions were done at 50 °C for 2.0 h. As was presented in Fig. 2, the leaching percentage of cobalt and lithium by a single *H. sabdariffa* flower extract was 17.2 and 61.3 %, respectively. The leaching capability of the *H. sabdariffa* flower extract for Co(II) and Li(I) could be attributed to the acidic, reductive, and chelating properties of compounds in the aqueous extract,

which includes major acids such as citric acid, hydroxycitric acid, hibiscus acid, and malic and tartaric acids and some organic compounds like delphinidin-3-sambubioside (hibiscin), delphinidin-3-glucoside, cyanidin-3-glucoside, etc. [28]. Moreover, antioxidant compounds like ascorbic acid presented in the exact can reduce Co(III) ions to a more stable state like Co(II) ions, increasing the dissolution efficiency of Co(II) [31]. The stability of metal ions in the extract could be due to the interaction of dissolved metal ions with functional groups (e.g., hydroxyl (-OH), and carboxyl (-COOH)) presented on organic compounds to form stable complexes. However, the complete leaching of the metals by only H. sabdariffa flower extract was difficult because of the low concentration of the organic acids in the extract. Hence, the addition of HCl into the leaching solution is necessary to enhance the leaching effectiveness of metals. This was confirmed that the leaching percentage of the metals significantly increased from 17.2 to 74.5% for Co(II) and from 61.3 to 98.6% for Li(I) as rising HCl concentration in the leaching solution from 0.03 to 0.50 mol/L. Since the chemical components of the extract are complicated, the leaching reactions of cobalt and lithium from the spent LIBs could be proposed as:

$$LiCoO_{2(s)} + 4H^{+}_{(a)} + nA^{-}_{(a)} + 1e = Li^{+}_{(a)} + [CoA_{n}]^{(2-n)}_{(a)} + 2H_{2}O_{(l)}$$
(3.2)

where A<sup>-</sup> is an anion of organic acid.

From the obtained results, 0.5 mol/L HCl was selected for further leaching studies.



Figure 2. Effect of HCl concentration on the leaching percentage of Co(II) and Li(I) from the spent LIBs by HCl solution mixed with H. sabdariffa flower extract. Leaching conditions: [HCl] = 0 - 0.5 mol/L; [H. sabdariffa flowerextract] = 90% (v/v); time = 2 h; temperature = 50°C; pulp density= 10 g/L



*3.1.2. Effect of the concentration of H. sabdariffa flower extract* 

To investigate the effect of the H. sabdariffa flower extract on the leaching effectiveness of the metals, the concentration of the extract in the leaching solution was varied from 0 to 90% (v/v) with fixing 0.5 mol/L HCl. All leaching experiments were done at 50 °C for 2.0 h with 10 g/L of pulp density. Fig. 3 indicates that most lithium was leached at any extract concentration, whereas the leaching percentage of cobalt significantly rose from 51.3 to 74.5% as the concentration of the extract increased. This result can be ascribed to an increase in the presence of organic compounds, which enhance the acidic, reductive, and complex of the leaching solution and increase the leaching effectiveness of cobalt [20]. From the studied data, the optimum concentration of H. sabdariffa flower extract was 90% (v/v).

#### 3.1.3. Effect of reaction time

To consider the effect of reaction time on the leaching percentage of lithium and cobalt, leaching time was prolonged from 1.0 to 5.0 h while keeping at 0.5 mol/L HCl, 90% (v/v) *H. sabdariffa* flower extract, 10 g/L of pulp density, and 50 °C of reaction temperature. In **Fig.4**, the leaching percentage of metals increased with expanding the reaction time, in which that of lithium and cobalt was approximately 100% and 78.2% for 2.0 h, and there was a trivial increase as prolonging reaction time. These results agreed well with the reported literature about the

leaching efficiency of metals at an initial period [32, 33]. Thus, 2.0 h of reaction time was selected for further studies.

#### 3.1.4. Effect of reaction temperature

Leaching experiments were done in the range of 30 to 90 °C. Leaching parameters were kept constant including 0.5 mol/L HCl, and 90 % (v/v) *H. sabdariffa* flower extract, pulp density of 10 g/L, and 2.0 h reaction time. **Fig.5** displays that the leaching efficiency of cobalt and lithium increased from 33.8 and 51.2% to 91.3 and 100 %, respectively. It can explain that high temperature accelerates the reaction velocity, leading to the high leaching efficiency of metals [34]. Therefore, 90 °C reaction temperature was chosen to be the best condition for the leaching of the metals.

From the above-studied results, optimal leaching conditions for the metals from the spent LIBs of mobile phones were found to be 0.5 mol/L HCl, 90% (v/v) *H. sabdariffa* flower extract, 10 g/L pulp density, 2.0 h reaction time, and 90°C reaction temperature. The complete leaching of the metals can be attained by a decrease in the pulp density or an increase in the number of leaching stages. Under the optimum leaching conditions, the concentration of metals in the leachate was 635 mg/L Co(II) and 366 mg/L Li(I). Thus, ion exchange experiments were performed to separate these two metal ions from the leachate containing the extract in further experiments. These results could consider the effect of the extract on the recovery performance of the metals from the leachate.



*Figure 3.* Effect of H. sabdariffa flower extract concentration on the leaching percentage of Co(II) and Li(I) from the spent LIBs by HCl solution mixed with H. sabdariffa flower extract. Leaching conditions: [HCl] = 0.5 mol/L; [H. sabdariffa flower extract] = 0-90 % (v/v); time = 2.0 h; temperature =50°C; pulp density= 10 g/L



# 3.2. Purification of Co(II) and Li(I) from the leachate by ion-exchange resin

3.2.1. Effect of AG<sup>®</sup>W50-X4 resin concentration

In our previous study, the adsorption behavior of AG<sup>®</sup>W50-X4 resin for Co(II) from simulated HCl solution at low concentrations was investigated and the optimum conditions for the adsorption of Co(II) were determined to be 0.2 mol/L HCl for 2.0 h [29]. Therefore, in the present work, the AG<sup>®</sup>W50-X4 resin was employed to separate Co(II) over Li(I) from the leachate containing the *H. sabdariffa* flower extract.

To decrease the HCl concentration, the dilution of the leachate at 2.5 times was done by doubly distilled water, and the leachate after the dilution contained 254.0 mg/L Co(II), 146.4 mg/L Li(I), and 0.2 mol/L HCl.

To consider the effect of resin dosage on the selective adsorption of metals from the leachate, the concentration of  $AG^{\circledast}W50$ -X4 resin was surveyed from 10 to 80 g/L with a shaking time of 2.0 h. **Fig.6** shows that the loading percentage of Co(II) increased from 40.9 to 95.8%, whereas that of Li(I) was lower



*Figure 4.* Effect of reaction time on the leaching percentage of Co(II) and Li(I) from the spent LIBs by HCl solution mixed with H. sabdariffa flower extract. Leaching conditions: [HCl] = 0.5 mol/L; [H. sabdariffa flower extract] = 90 % (v/v); time = 1-5 h; temperature = 50°C; pulp density= 10 g/L.



**Figure 5.** Effect of reaction temperature on the leaching percentage of Co(II) and Li(I) from the spent LIBs by HCl solution mixed with H. sabdariffa flower extract. Leaching conditions: [HCl] = 0.5 mol/L; [H. sabdariffa flower extract] = 90% (v/v); time = 2.0 h; temperature = 30-90°C; pulp density= 10 g/L



than 20 % in the range of studied resin concentration. These results were attributed to an increase in the ion exchange of Co(II) cationic species with hydrogen ions of the resin. The presence of *H. sabdariffa* flower extract in the HCl solution trivially affected the Co(II) loading efficiency of the resin as compared to the previous study [29]. The stable characteristics of Li(I) ions in aqueous solutions can explain their low adsorption by the resin [35]. The ion exchange reaction between Co(II) ions and AG<sup>®</sup>W50-X4 resin can be written as follows:

$$2RH_{(s)} + Co^{2+}_{(a)} = R_2 Co_{(s)} + H^+_{(a)}$$
(4)

where RH is AG®W50-X4 resin.

The obtained results proved that AG<sup>®</sup>W50-X4 resin can be employed to selectively recover Co(II) over Li(I) from the leachate of spent LIBs using HCl solution mixed with *H. sabdariffa* flower extract.

#### 3.2.2. Loading capacity of the resin for metals

To determine the loading capacity of the resin for Co(II) and Li(I) from real leachate of spent LIBs by using HCl mixed with *H. sabdariffa* flower extract, loading experiments were performed. As presented in **Fig.7**, the cumulative loading of Co(II) and Li(I) rose with an increase in the number of stages and five stages were enough to obtain a maximum loading capacity of the resin for the metals. The loading capacity of metals per g of the resin was 37.4 mg for Co(II) and 1.2 mg for Li(I). According to the reported literature, the Langmuir adsorption

isotherm model was described well for the loading of Co(II) by the resin [29]. It was noticeable that the loading capacity of Co(II) from the real leachate by the resin in the present work was higher than that of Co(II) in the previous report (29.8 mg/L). The presence of *H. sabdariffa* flower extract in the leachate could facilitate the loading behavior of metals into the resin. However, the adsorption mechanism has not been elucidated, which needs further study.

#### 3.2.3. Eluting the Co(II) loading resin

The elution of Co(II) from the loading AG®50W-X4 resin was experimented with by varying HCl concentration from 0.2 to 2.0 mol/L. Experiments were shaken for 2.0 h and the resin concentration was kept at 10 g/L. In **Fig.8**, Co(II) ions from the resins were fully eluted as the HCl concentration reached 2.0 mol/L. These results were attributed to the tendency to form Co(II) anionic complexes when the HCl concentration rose [29, 36]. So, the desorption reaction for the Co(II) elution from the loading resin was written as follows:

$$R_2 Co_{(s)} + nHCl_{(a)} = 2RH_{(s)} + (n-2)H^+_{(a)} + [CoCl_n]^{2-n}_{(a)}(5)$$

where n = 3 or 4.

Thus, the presence of *H. sabdariffa* flower extract in dilute HCl solution enhanced the efficient leaching rate of cobalt and lithium from the spent LIBs of mobile phones. The separation of these two metal ions from the diluted leachate was achieved by ion



*Figure 6.* Effect of AG<sup>®</sup>W50-X4 resin concentration on the loading percentage of Co(II) and Li(I) from the leachate of spent LIBs containing the H. sabdariffa flower extract. Experimental conditions: Resin concentration= 10-80 g/L; Shaking time= 2.0 h; Aqueous solution: 254.0 mg/L Co(II) and 146.4 mg/L Li(I)





*Figure 7.* Loading capacity of AG<sup>®</sup>W50-X4 resin for Co(II) and Li(I) from the leachate of spent LIBs containing H. sabdariffa flower extract. Loading conditions: Resin concentration = 40 g/L; Shaking time = 2.0 h; Aqueous solution: 254.0 mg/L Co(II) and 145.4 mg/L Li(I)



Figure 8. Effect of HCl concentration on the elution percentage of Co(II) from loading  $AG^{\$}50W$ -X4 resin. Loading resin of Co(II) = 37.4 mg per g of resin; eluent = 0.2-2.0 mol/L HCl; resin concentration = 10 g/L, Shaking time = 2.0 h

exchange resin, in which Co(II) ions were selectively adsorbed over Li(I) and then eluted by 2.0 mol/L HCl. Li(I) from the aqueous phase after the removal of Co(II) can be recovered by using the precipitation method [37]. The appearance of *H. sabdariffa* flower extract in the HCl leaching solution supported the Co(II) adsorption into the resin. The recovery of Li(I) from filtrate. From the studied data, *H. sabdariffa* flower can be used in the recovery of cobalt and lithium from the spent LIBs.

#### 4. Conclusions

The recycling of cobalt and lithium from the spent LIBs of mobile phones using *H. sabdariffa* flower extract mixed with HCl solution as a lixiviant and AG®50W-X4 resin to purify these two metals was investigated. The leaching parameters including HCl concentration, *H. sabdariffa* flower extract concentration, reaction temperature and time, affecting the leaching efficiency of the two metals by



the leaching agents were investigated. The results indicated that a single H. sabdariffa flower extract can be used as a lixiviant for the dissolution of cobalt and lithium, with organic compounds in the extract playing an important roles as acidifying agents, reducing agents, and complexing agents in the dissolution of the metals. Since the complete leaching of the metals by a single H. sabdariffa flower extract was difficult due to the low concentration of acidic agents, the addition of an HCl solution was required to increase the leaching efficiency. From the studied results, the optimum conditions for the leaching of these metals by the mixture of HCl and H. sabdariffa flower extract were 0.5 mol/L HCl and 90% (v/v) of the extract at 90°C for 2.0 h. Co(II) and Li(I) from the diluted true leachate were completely separated using AG®50W-X4 resin. The total Co(II) ions were selectively adsorbed by the resin, while the Li(I) ions remained in the aqueous solution. The loading capacity of the resin for Co(II) and Li(I) was determined to be 37.4 mg/g and 1.2 mg/g, respectively. The desorption of Co(II) from the loading resin was completely achieved by 2.0 mol/L HCl. With the obtained results, the H. sabdariffa flower extract is a promising agent for the recycling of valuable metals from spent LIBs.

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#### **Author Contributions**

Methodology and editing: Thi Hong Nguyen; writing-review and editing: Man Seung Lee and Phuc Dam Nguyen; writing-original draft preparation: Thanh Tuan Tran. All authors have read and agreed to the published version of the manuscript.

#### Data availability

The data of this work could be obtained by contacting the corresponding author by e-mail.

#### **Declarations of competing interest**

The authors declare no conflict of interest.

#### References

- E. Gratz, Q. Sa, D. Apelian, Y. Wang, A closed loop process for recycling spent lithium-ion batteries, Journal of Power Sources, 262 (2014) 255– 262. https://doi.org/10.1016/j.jpowsour.2014.03.126
- [2] W. Zhang, C. Xu, W. He, G. Li, J. Huang, A review on

management of spent lithium ion batteries and strategy for resource recycling of all components from them, Waste Management and Research, 36 (2) (2017) 99-112. https://doi.org/ 10.1177/0734242X17744655

- [3] L. Li, J. Ge, F. Wu, R. Chen, S. Chen, B. Wu, Recovery of cobalt and lithium from spent lithium-ion batteries using organic citric acid as leachant, Journal of Hazardous Materials, 176 (2010) 288-93. https://doi.org/10.1016/j.jhazmat.2009.11.026
- [4] H. Ali, H.A. Khan, M. Pecht, Preprocessing of spent lithium-ion batteries for recycling: Need, methods, and trends, Renewable and Sustainable Energy Reviews, 168 (2022) 112809. https://doi.org/10.1016/j.rser.2022.112809
- [5] R. Sattar, S. Ilyas, H.N. Bhatti, A. Ghaffar, Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries, Separation and Purification Technology, 209 (2019) 725-33. https://doi.org/ 10.1016/j.seppur.2018.09.019
- [6] E.A. Dalini, G. Karimi, S. Zandevakili, M.A. Goodarzi, A review on environmental, economic, and hydrometallurgical processes of recycling spent lithium-ion batteries, Mineral Processing and Extractive Metallurgy Review, 42 (7) (2021) 451-472. https://doi.org/10.1080/08827508.2020.178162
- [7] Z. Dobó, T. Dinh, T. Kulcsár. A review on recycling of spent lithium-ion batteries, Energy Reports, 9 (2023) 6362-6395. https://doi.org/ 10.1016/j.egyr.2023.05.264
- [8] S.H. Joo, D.J. Shin, C.H. Oh, J.P. Wang, G. Senanayake, S.M. Shin, Selective extraction and separation of nickel from cobalt, manganese and lithium in pre-treated leach liquors of ternary cathode material of spent lithium-ion batteries using synergism caused by Versatic 10 acid and LIX 84-I, Hydrometallurgy, 159 (2016) 65-74. https://doi.org/10.1016/j.hydromet.2015.10.012
- [9] M. Bigum, A. Damgaard, C. Scheutz, T.H. Christensen, Environmental impacts and resource losses of incinerating misplaced household special wastes (WEEE, batteries, ink cartridges and cables), Resources, Conservation and Recycling, 122 (2017) 251-60.

https://doi.org/10.1016/j.resconrec.2017.02.013

- [10] T.T. Tran, M.S. Lee, Use of ferric salt solutions as leaching agents of Co, Ni, Cu, Fe, and Mn from metallic alloys of spent lithium-ion batteries and separation of iron from the leaching solution, Journal of Mining and Metallurgy, Section B: Metallurgy, 58 (3) (2022) 405-415. https://doi.org/10.2298/JMMB220311023T
- [11] K. Yan, Q. Chen, Z. Xiong, J. Wu, Z. Zhang, R. Wang, J. Li, S. Zhong, A novel method for the recovery of Li from spent lithium-ion batteries using reduction roasting-countercurrent leaching, JOM, 74 (2022) 3821-3832. https://doi.org/ 10.1007/s11837-022-05432-8
- [12] M. Joulie, E. Billy, R. Laucournet, D. Meyer, Current collectors as reducing agent to dissolve active materials of positive electrodes from Li-ion battery wastes, Hydrometallurgy, 169 (2017) 426–32. https://doi.org/10.1016/j.hydromet.2017.02.010
- [13] W. Gao, C. Liu, H. Cao, X. Zheng, X. Lin, H. Wang, Z. Zhang, Z. Sun, Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries, Waste Management, 75 (2018) 477-485. https://doi.org/ 10.1016/j.wasman.2018.02.023



- [14] N. Vieceli, C.A. Nogueira, C. Guimaraes, M.F.C. Pereira, F.O. Durao, F. Margarido, Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite, Waste Management, 71 (2018) 350-61. https://doi.org/ 10.1016/j.wasman.2017.09.032
- [15] L. Li, J. Lu, Y. Ren, X.X. Zhang, R.J. Chen, F. Wu, K. Amine, Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries, Journal of Power Sources, 218 (2012) 21-27. https://doi.org/10.1016/j.jpowsour.2012.06.068
- [16] P. Meshram, B.D. Pandey, T.R. Mankhand, Recovery of valuable metals from cathodic active material of spent lithium-ion batteries: Leaching and kinetic aspects, Waste Management, 45 (2015) 306-313. https://doi.org/ 10.1016/j.wasman.2015.05.027
- [17] J. Diekmann, C. Hanisch, L. Frobose, G. Schalicke, T. Loellhoeffel, A.S. Folster, A. Kwade, Ecological recycling of lithium-ion batteries from electric vehicles with focus on mechanical processes, Journal of the Electrochemical Society, 164(1) (2017) A6184–A6191. https://doi.org/10.1097/00043426-200404000-00001
- [18] T.H. Nguyen, M.S. Lee, A review on the separation of lithium ion from leach liquors of primary and secondary resources by solvent extraction with commercial extractants, Processes, 6(5) (2018) 55. https://doi.org/10.3390/pr6050055
- [19] W. Urbańska, Recovery of Co, Li, and Ni from spent Li-ion batteries by the inorganic and/or organic reducer assisted leaching method, Minerals, 10(6) (2020) 555. https://doi.org/10.3390/mim10060555
- [20] R. Golmohammadzadeh, F. Rashchi, E. Vahidi, Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects, Waste Management, 64 (2017) 244-54. https://doi.org/ 10.1016/j.wasman.2017.03.037
- [21] G. Gao, X. He, X. Lou, Z. Jiao, Y. Guo, S. Chen, X. Luo, S. Sun, J. Guan, H. Yuan, A citric acid/Na2S2O3 system for the efficient leaching of valuable metals from spent lithium-ion batteries, JOM, 71 (2019) 3673-3681. https://doi.org/ 10.1007/s11837-019-03629-y
- [22] L. Li, L. Zhai, X. Zhang, J. Lu, R. Chen, F. Wu, K. Amine, Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process, Journal of Power Sources, 262 (2014) 380-385. https://doi.org/ 10.1016/j.jpowsour.2014.04.013
- [23] K. Binnemans, P.T. Jones. Solvometallurgy, An emerging branch of extractive metallurgy, Journal of Sustainable Metallurgy, 3 (2017) 570–600. https://doi.org/10.1007/s40831-017-0128-2
- [24] J.A. Whitehead, G.A. Lawrance, A. McCluskey, 'Green' leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid, Green Chemistry, 6 (2004) 313-315. https://doi.org/10.1039/B406148A
- [25] A.O. Owoade, A. Adetutu, O.S. Olorunnisola, A review of chemical constituents and pharmacological properties of *Hibiscus sabdariffa L*, International Journal of Current Research in Biosciences and Plant Biology, 6 (4) (2019) 42-51. https://doi.org/ 10.20546/ijcrbp.2019.604.006
- [26] S. Ranjan, Medicinal Plants in India: Importance and Cultivation, Jaya Publishing House, New Delhi, 2019, p.215-227
- [27] R. D. Lokhande, D. P. Pacharne, D.V. Deshmukh, P. S. Belhekar, Production potential, economics and

sustainability of high yielding genotypes of roselle (Hibiscus Sabdariffa L.), International Journal of Scientific Research in Science and Technology, 11 (2024) 236-242.

https://doi.org/10.32628/IJSRST24114842

- [28] I. Da-Costa-Rocha, B. Bonnlaender, H. Sievers, I. Pischel, M. Heinrich, *Hibiscus sabdariffa* L.- a phytochemical and pharmacological review, Food Chemistry, 165 (2014) 424-43. https://doi.org/ 10.1016/j.foodchem.2014.05.002
- [29] T.H. Nguyen, M.S. Lee, T.T. Tuan, Q.C.T. Nguyen, Adsorption of Co(II) from simulated low acid leaching solution of spent lithium-ion batteries by AG®50W-X4 resin, International Journal of Environmental Analytical Chemistry, 2022 (Publish online). https://doi.org/ 10.1080/03067319.2022.2130062
- [30] T.H. Nguyen, T.H.N. Duong, Separation and recovery of Co(II) and Li(I) from spent lithium-ion mobile phone batteries, Can Tho University Journal of Science, 12 (2) (2020) 60-67. https://doi.org/ 0.22144/ctu.jen.2020.017
- [31] J. Kang, G. Senanayake, J. Sohn, S.M. Shin, Recovery of cobalt sulfate from spent lithium-ion batteries by reductive leaching and solvent extraction with Cyanex 272, Hydrometallurgy, 100 (3-4) (2010) 168-171. https://doi.org/ 10.1016/j.hydromet.2009.10.010
- [32] R. Banda, T.H. Nguyen, S.H. Sohn, M.S. Lee, Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction, Hydrometallurgy, 133 (2013) 161-167. https://doi.org/ 10.1016/j.hydromet.2013.01.006
- [33] F. Wang, R. Sun, J. Xu, Z. Chen, M. Kang, Recovery of cobalt from spent lithium-ion batteries using sulphuric acid leaching followed by solid–liquid separation and solvent extraction, RSC Advances, 6 (2016) 85303-85311. https://doi.org/ 10.1039/C6RA16801A
- [34] Y. Guo, F. Li, H. Zhu, G. Li, J. Huang, W. He, Leaching lithium from the anode electrode materials of spent lithium-ion batteries by hydrochloric acid (HCl), Waste Management, 51 (2016) 227-233. https://doi.org/ 10.1016/j.wasman.2015.11.036
- [35] J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, J. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, J.C. Neuefein, Y. Ren, K. Amine, L.W. Wang, K. Xu, F. Pan, Understanding thermodynamic and kinetic contributions in expanding the stability sindow of aqueous electrolytes, Chem 4 (12) (2018) 2872-2882. https://doi.org/ 10.1016/j.chempr.2018.09.004
- [36] M.S. Lee, Y.J. Oh, Chemical equilibria in a mixed solution of nickel and cobalt chloride, Materials Transaction, 46 (1) (2005), 59-63. https://doi.org/ 10.2320/matertrans.46.59
- [37] T.T. Tran, S.H. Son, M.S. Lee, Recovery of high-purity lithium compounds from the dust of the smelting reduction process for spent lithium-ion batteries, Korean Journal of Metals and Materials, 60 (4) (2023) 291-300.

https://doi.org/ 10.3365/KJMM.2022.60.4.291



### ZELENI PRISTUP EKSTRAKCIJI LITIJUMA I KOBALTA IZ ISTROŠENIH LITIJUM-JONSKIH BATERIJA KORIŠĆENJEM RAZBLAŽENOG HCL RASTVORA POMEŠANOG SA EKSTRAKTOM CVETA *H. SABDARIFFA* KAO AGENSA ZA LUŽENJE

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#### Apstrakt

Studije o ekstrakciji litijuma i kobalta iz istrošenih litijum-jonskih baterija privukle su veliku pažnju poslednjih godina. Za održivu industriju baterija, procesi za reciklažu dragocenih metala iz istrošenih baterija kontinuirano se unapređuju i razvijaju kroz "zeleni" pristup. U ovom radu je istražen efikasan proces reciklaže litijuma i kobalta iz istrošenih litijumskih baterija mobilnih telefona korišćenjem HCl rastvora niske koncentracije u kombinaciji sa ekstraktom cveta H. sabdariffa. Ispitivan je uticaj parametara kao što su koncentracija ekstrakta i HCl, gustina pulpe, temperatura reakcije i vreme na procenat luženih metala. U ovim sistemima luženja, ekstrakt, koji sadrži organske spojeve, deluje kao kompleksirajući i reduktivni agens za rastvorene metale. Optimalni uslovi za luženje ovih metala bili su 90% (v/v) ekstrakta, 0,5 mol/L HCl, gustina pulpe od 10 g/L, temperatura od 90°C i vreme od 2 sata. Pod optimalnim uslovima luženja, 100% Li(I) i 91,3% Co(II) je dobijeno. Li(I) i Co(II) iz luženog rastvora su potpuno odvojeni korišćenjem AG®50W-X4 smola, a prisustvo ekstrakta u rastvoru za luženje imalo je mali uticaj na kapacitet ekstrakcije ovih metala. Kapacitet smole za vezivanje metala iznosio je 37,4 mg/g za Co(II) i 1,2 mg/g za Li(I). Stoga se upotreba biljnih ekstrakata, kao što je cvet H. sabdariffa, može smatrati obećavajućim agensom za ekstrakciju dragocenih metala iz istrošenih baterija.

Ključne reči: Ekstrakt cveta H. sabdariffa; Luženje; Jonska izmena; Istrošene litijum-jonske baterije; Kobalt; Litijum

