Pra Cipta Buana Wahyu Mustika ^{1,4} Edward Chandra Suryanaga ¹ Indra Perdana ¹ Sutijan ^{1,2} Widi Astuti ³ Himawan Tri Bayu Murti Petrus ^{1,2} Agus Prasetya ^{1,2,*}

- ¹ Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika No.2, Kampus UGM, Yogyakarta, 55281
- ² Unconventional Geo-resources Research Center, Faculty of Engineering, UGM, Jl. Grafika No.2, Kampus UGM, Yogyakarta, 55281
- ³ Research Center for Mining Technology, National Research and Innovation Agency (BRIN), Jl. Ir. Sutami Km. 15, Tanjung Bintang, Lampung Selatan, Lampung, 35361, Indonesia
- ⁴ Chemical Engineering Department, Faculty of Engineering, Universitas Surabaya, Jl. Raya Kalirungkut, Surabaya, 60293
- *e-mail: aguspras@ugm.ac.id

Submitted 14 March 2023 Revised 27 July 2023

Accepted 4 August 2023

Abstract. Recycling lithium batteries (LIB) has emerged as an attractive solution in the global pursuit of environmentally friendly practices. The aim of achieving zero-waste hydrometallurgical technology is within reach. This research focuses on utilizing the low-pressure nanofiltration process to address this challenge by separating lithium ions from other ions and achieving a desirable permeate flux. The NCA battery leachate concentrate was obtained through a hydrometallurgical process involving sulfuric acid-peroxide. To ensure the prevention of potential nanofiltration membrane (TS80) fouling, the concentrate is initially filtered using an ultrafiltration membrane (UH004) to remove any particles. The research investigates the impact of pressure (4, 6, and 7 bar), solution concentration (concentrate, 10x, and 50x dilution), and the concentration of the complexing agent (EDTA) on the desired separation performance. The investigation reveals that pressure variations exhibit consistent rejection rates, remaining stable above 80%. A similar trend is observed with the addition of EDTA, which consistently yields rejection rates above 80%. However, when examining different feed concentrations, the rejection of lithium falls below 80% for leachate concentrates. In summary, satisfactory results are obtained by employing nanofiltration with a TS80 membrane at a pressure of 7 bar, a dilution factor of 10x, and using a 0.02M EDTA complexing agent. Meanwhile, it was found that the separation factors ($Li^+/Ni^{2+} = -8.6$, $Li^+/Co^{2+} =$ ~7.3, $\text{Li}^{+}/\text{Al}^{3+} = ~4.9$) and permeate flux ±46.58 L m⁻² h⁻¹. The findings demonstrate good selectivity along with relatively high flux.

Keywords: Battery Leachate, EDTA, Lithium Ion Battery (LIB), Lithium Separation, Nanofiltration, NCA Battery

INTRODUCTION

The key to transforming environmentally friendly electric vehicle (EVs) technology lies in producing its constituent components. The most prominent role is still determined by battery technology as power storage. Storage efficiency, battery life, and various other factors are important considerations. Among the various types of batteries that have been developed, lithium-ion batteries (LIB) have various advantages, especially in high voltage, longer life-span, compact, and environmentally friendly (Jin et al., 2022). However, the problem with LIB as power storage is more complex, especially the problems that arise after the end of the battery life. The leading solution to this problem is reuse or recycling. Recycling used batteries is receiving special attention from several circles, especially environmentalists and the battery industry. Recycling these batteries is beneficial for the environment and from an economic point of view (Kim et al., 2021; J. Kumar et al., 2022). On the other hand, if these batteries are not recycled or reused, it is certain that millions of tons of waste will be generated and become an environmental issue (Chen et al., 2019; Jin et al., 2022; Tian et al., 2022).

The recycling process hopes to divide the components of the device into chemically pure, distinct phases. Knowledge of the nature and types of components needs to be possessed to facilitate the separation process. Related properties include size, density, solubility, oxidation-reduction, charge, appearance, and others (Thompson *et al.*, 2020). Information related to the components of LIB is also important, including the anode, cathode, current collector, and separator containing lithium salt-organic solvent. The anode contains active components such as

graphite and a bonding polymer, while the cathode contains a carbon conductive agent and a bonding polymer (Jo *et al.*, 2018).

The anode and cathode active materials are coated on Cu and Al, which act as current collectors. Apart from Cu and Al, battery cases made of Fe can also be recycled. Among all existing metals, Co is the most sought-after, the main target for recycling because of its high price value (Ku et al., 2016). Besides Co, another metal that is interesting for recycling is Li from the battery. The facts prove that extracting Li from nature requires high energy and costs and the depletion of existing natural resources. Recycling techniques can be classified into pyrometallurgy, hydrometallurgy, and direct recycling (Harper et al., 2019). Recycling uses a pyrometallurgical process utilizing high temperatures, to reduce metal oxides to alloys.

In contrast to the pyrometallurgical process, the hydrometallurgical process takes place at a lower temperature than the pyrometallurgical process, which is sufficient for separation or purification. The critical aspect of the hydrometallurgical process is the dissolving process of metals in the leachate. The metals are recovered through various processes, including precipitation, solvent extraction, electrical deposition, and others (Aryani et al., 2021; Purnomo et al., 2017; Yao et al., 2018). Each process has advantages disadvantages and that determine whether the process is feasible for an industrial scale. The results of recycled LIBs usually contain low lithium and high impurities. To extract lithium, various methods have been developed but also have many obstacles. Therefore, developing more environmentally friendly technologies must be considered and continue to be developed, in which a process based on membrane separation is possible to meet these criteria.

Meanwhile, the idea of using membranebased technology for Li separation from battery leachate was previously initiated by Li et al, whose research used ion-imprinted membranes (Li et al., 2021). The ion selectivity achieved was high: Li/Mn, Li/Co, Li/Ni were 6.71, 5.84, and 3.03. However, remember that this process relies on molecular diffusion, which tends to be slow and takes a long time to process. As a reminder, their research only relies on the driving force of different concentrations for the separation process. Thus, it is necessary to think about other technologies that might be developed as the this membrane-based successor to idea. this separation In research, nanofiltration is expected to meet these expectations. As is well known, nanofiltration relies on a driving force from hydraulic pressure, which is easily controlled and engineered.

Nanofiltration (NF) as an alternative to direct lithium separation is often applied to extracting lithium from water sources (ex: continental salt lakes, seawater, geothermal brine, etc.). The technology has matured to full-scale (Li et al., 2019). Previously, Kumar et al. (2022) made notable strides in applying nanofiltration to FLP battery recycling. Their pioneering work revealed a significant enhancement in product purity of up to 90% and an impressive yield of 88.2%. Based on these encouraging outcomes, it becomes increasingly plausible to extrapolate the concept of utilizing nanofiltration techniques for NCA batteries (Kumar et al., 2022). Measurement of the effectiveness of this nanofiltration (NF) technology is usually indicated by parameters, especially flux and implications rejection. The rejection themselves describe the separation phenomenon of ions, which subsequently

becomes known as the separation factor or selectivity. This research selected а nanofiltration membrane (TFC-PA), specifically TS80, due to its notable selectivity for both monovalent and multivalent species. this Furthermore, membrane has demonstrated robust performance in acidic conditions, particularly in hydrometallurgical applications such as acid mine drainage (AMD) (López et al., 2020). Moreover, an investigation regarding the isoelectric point has also been carried out by López et al. (2020) and found at 2.54. The obtained data revealed a low IEP value, indicating the prevalence of dissociable acid carboxylic groups over dissociable basic amine groups (Wadekar and Vidic, 2017a). Information was obtained that the TS80 membrane could be used at extreme pH (2-11). However, the selectivity of a membrane cannot be separated from various factors such as pore size, surface charge, and so on. Research on measuring the pore size of the TS80 membrane has been carried out by Micari et al, which obtained a stokes radius of 0.488 nm (Micari et al., 2020). To comprehensively address these factors, the investigation of the dilution factor, operating pressure, and addition of complexing agent is conducted during the operation, aiming to provide a comprehensive understanding of their influences.

MATERIALS AND METHOD

Materials

End-of-life NCA 18650 batteries are laboratory-assembled batteries based on a series of battery developments by several researchers from Indonesia (Purwanto *et al.*, 2020; Yudha *et al.*, 2019). Commercially, the NCA battery is produced by The Smart UNS

Manufacturing, which has a capacity of 2700 mAh with a voltage of 3.7 volts. Meanwhile, chemical reagents, including: sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), sodium chloride (NaCl), and sodium hydroxide (NaOH) were purchased from Merck® with analytical standards, so no further purification was required. Sodium Hydroxide was purchased from Sigma Aldrich, an analytical standard so no purification is required before use. The tap water was subjected to demineralization through a reverse osmosis process, resulting in the production of deionized water. This deionized water exhibited a maximum total conductivity of 15 µS, indicating its high purity level. Membranes applied for lithium separation must be acid-base resistant because often the leachate pH is highly dependent on the leachate agent used. This research used two types of membranes for mechanical and ionic separation. First, a hydrophilic polyether sulfone (PESH) membrane was selected for mechanical separation, for which this membrane was supplied from Microdyn[™] (UH004, 4kDa). Second, a polyamide-based thin-layer composite membrane (TFC-PA) [Fully Aromatic] supplied by TriSep[™] (TS80, ~150Da) was used for ion separation as the second membrane (Wadekar and Vidic, 2017b; Żyłła *et al.*, 2022).

Method

Lithium Extraction Procedure

Lithium (Li) extracted from end-of-life NCA batteries can be obtained through certain procedures. The procedures briefly include: discharging, dismantling, acid leaching, and membrane separation. In more detail, the procedure can be observed in Figure 1.



Fig.1: Schematic diagram of lithium extraction from an NCA battery.

NCA Battery Leaching Protocol

The NCA battery is discharged with the expectation of promoting the transfer of lithium ions from the anode to the cathode. Apart from that, complete discharging is done to avoid short circuits or self-ignition. Next, the battery begins to be disassembled to separate every part of the battery, especially the case and the battery internal compounds. Each part other than the cathode is separated and further managed in other research. Preceding the milling process, an initial step of alkaline leaching was conducted using a 1.5-2M sodium hydroxide (NaOH) solution to effectively eliminate any residual aluminum present on the cathode sheet fragments. Subsequently, thorough rinsing with deionized water and subsequent filtration was performed to isolate the cathode powder. Subsequent drying was accomplished by subjecting the material to a temperature of 65°C for 24 hours under vacuum conditions. Further purification steps were undertaken by subjecting the material to calcination at 610°C for 4 hours, followed by gradual cooling to reach ambient temperature, to remove any remaining impurities. The cathode sheet fragments containing precious metal and lithium were then ground using a ball mill to a size of 200 mesh (fine powder). The leaching process of the cathode powder was conducted in a three-neck flask, employing a mixture of dilute sulfuric acid (2M) and hydrogen peroxide (1.5%). The leaching procedure was executed at a temperature of 70°C for 1 hour, maintaining atmospheric pressure while ensuring a constant stirring speed of 300 revolutions per minute (rpm). The leachate acquired from the process was subsequently separated from the cathode powder employing an ultrafiltration technique utilizing a polyethersulfone hydrophilic

composite membrane (UH004, PESH, 4kDa) supplied by Microdyn[™]. This specialized membrane demonstrates excellent pH tolerance, functioning efficiently within the range of 0 to 14. The resulting refined leachate will commonly be referred to as the "mother liquor" for future utilization.

Lithium Extraction from Leachate

Lithium (Li) as a precious metal is extracted from battery leachate through the previously mentioned nanofiltration (NF) scheme. Therefore, nanofiltration with a dead-end stirred system, which has a hold-up volume of 100 mL and an active area of 15.9 cm² was chosen for this research. Nitrogen gas (N₂) is used as the driving force of the process, and the stirring rate is set constant in the 500 RPM process. This research chooses the operating pressure as the driving force is chosen with the following variations: 4, 5, and 7 bar were selected. In addition to variations in pressure, there are variations in the dilution factor and the addition of complexing agents. This research determined two specific dilution factors (which will be elaborated upon later in the discussion). Furthermore, the addition of EDTA as a complexing agent was examined at two levels: 0.02 and 0.05 M. Permeate flux data was acquired every 5 minutes. At the same time, the concentration measurements were carried out on the leachate before the filtration process and the resulting permeate. Analysis of sample concentration using ICP-OES (Optima 8300, Parkin Elmer). Based on the DSPM-DE theory, separation in nanofiltration (NF) is modeled as a porous membrane with a uniform parallel cylindrical structure. Thus, the Hagen-Poiseuille model (1) can be applied to calculate the permeate flux (I_{V}) as shown in Equation (1).

$$J_V = \frac{r_p^2(\Delta P - \Delta \pi)}{8\eta L_e} \tag{1}$$

348 Optimization of Lithium Separation from NCA Leachate Solution: Investigating the Impact of Feed Concentration, Pressure, and Complexing Agent Concentration

where J_V is flux permeate (L.m⁻².h⁻¹), r_p is the average membrane pore (m), ΔP is hydraulic pressure difference across the membrane (atm), $\Delta \pi$ is osmotic pressure difference across the membrane (atm), η is water dynamic viscosity (kg. m⁻¹.h⁻¹), and L_e is the effective membrane thickness (m⁻¹). At the same time, a simple calculation of osmotic pressure can be approximated by the Van't Hoff equation as follows:

$$\Delta \pi = RT \sum_{i=1}^{N} (C_{i,f} - C_{i,p})$$
(2)

Where R is the ideal gas constant $(L.atm.mol^{-1}.K^{-1}),$ Т is the solution temperature (K), $C_{i,f}$ and $C_{i,p}$ (mol. L⁻¹) are concentration of ion *i* at the membranesolution interface of both feed and permeate sides, respectively. The experimental permeate flux was calculated by Equation (3), while the rejection used Equation (4). The permeate flux (J_V) is calculated through the following equation,

$$J_V = \frac{\Delta V}{S \cdot \Delta t} \tag{3}$$

where ΔV is a volume permeate (L), S is active membrane area (m²), and Δt is time (h). Rejection (%R) is calculated through the following equation,

$$\% R = \left(1 - \frac{(C_{M+})_p}{(C_{M+})_i}\right) x \ 100 \tag{4}$$

where $(C_{M+})_p$ and $(C_{M+})_i$ are the concentrations of metals the permeate and initial solutions, respectively. The membrane separation factor (SF) (5) is calculated through the following equation,

$$SF_{Li/Mg} = \frac{(C_{Li+}/C_{M+})_p}{(C_{Li+}/C_{M+})_i}$$
(5)

where $(C_{Li+})_p$ and $(C_{Li+})_i$ are the lithium permeate and initial solution concentrations, respectively. The schematic diagram of the dead-end process is presented in Figure 2.



Fig. 2: Schematic diagram of the nanofiltration process with dead-end module

RESULTS AND DISCUSSION

Lithium Separation from Battery Leachate

Performance indicators for separating lithium and other metals in battery leachate using the TS80 membrane rely on ion separation and rejection. In the mother liquor, the concentrations of lithium, aluminum, nickel, and cobalt were 3003.41, 790.69, 5061.24, and 538.65 ppm, respectively. Meanwhile, the measured pH of the mother liquor was 1.4. From the mother liquor preparation, several derivative solutions were prepared by diluting 10x (DF 10x) and 50x (DF 50x). As for the dilution results, the feed DF

10x and DF 50x pH were: 2.2 and 3.2 respectively. In more detail, the properties of the mother liquor, 10x and 50x dilutions are presented in Table 1, as follows:

Table	1. Detailed properties of mother
	liquor, DF 10x and DF 50x.

Species	Mother Liquor	DF 10x	DF 50x
Li⁺	3003.41	298.83	55.85
Ni ²⁺	5061.24	502.64	96.53
Co ²⁺	538.65	52.92	5.34
Al ³⁺	790.69	75.82	15.7
рН	1.4	2.2	3.2



Fig.3: Separation Factor (a), Rejection (b), Flux Permeate (c): As a function of dilution factor.

The separation factor, rejection, flux permeate of the three solutions can be observed in Figure 3. In Figure 3a, it can be observed that the lithium-ion separation from other ions is significantly enhanced at DF 10x compared to both the mother liquor and DF 50x. The increased separation efficiency for aluminum ions, reaching up to approximately 9. Subsequently, the mother liquor exhibits a relatively high separation factor of around 4.5 for all ions. As a result, a higher number of lithium ions escape from DF10x compared to other concentrations. This observation is supported by the relatively low rejection value shown in Figure 3b. However, it should be noted that in the mother liquor, lithium's rejection was lower than that of DF10x. Furthermore, it is important to mention that the values of the separation and rejection factors have yet to fully establish themselves as a definitive process reference, which will be discussed in more detail in the following section.

In Figure 3b it can be observed that lithium rejection is lower than the other metals. This is reasonable, considering that the hydrated radius of the lithium-ion tends to be smaller than the other ions in the mother liquor (see Table 2). The consistency of this rejection is for all dilution factors (DF 10x and DF 50x).

Theoretically, this is related to steric hindrance, in which monovalent ions penetrate more easily than multivalent ions (Wen et al., 2006). In addition, consistency related to the rejection of multivalent ions in solutions with low pH was also found in several previous studies (> 90%) (Gasparini et al., 2019; Ricci et al., 2015). Observation in Figure 3b also found that the dilution has quite an effect on lithium separation, and conversely, other metals have almost no effect. However, the trend between the dilution factor and the rejection value cannot be fully explained. This can be seen in Figure 3b, where lithium rejection at DF 50x is higher than that at DF 10x and concentrate. This phenomenon is probably due to the density of ions in the solution system, which pushes certain ions to pass through the pores, especially ions with small sizes. Naturally, the interaction between ions in a solution with a high ion density will be directly proportional to the competition for penetration of ions on the membrane. It is plausible that the augmentation in the hydraulic pressure across the membrane (ΔP) can be attributed to the dilution process, wherein the osmotic pressure of the solution pressure across the membrane ($\Delta \pi$) is contingent upon its con-

Table 2. Comparison of diffusivity coefficient (D_s), ionic radius (r_s), hydration radius (r_h), and hydration free energy (Dimaculangan *et al.*, 2022; Gao *et al.*, 2020b, 2020a; Lobo and Quaresma, 1990; Ribeiro *et al.*, 2007; Tansel *et al.*, 2006).

Species	Diffusion coefficient	Ionic radius Hydrated ionic		Hydration free energy
	(D _s) [10 ⁻⁹ .m ² .s ⁻¹]*	(r _s) [nm] *	radius (r _h) [nm] *	(ΔG) [kJ.mol ⁻¹] [*]
Li⁺	1.030	0.076 - 0.090	0.24 – 3.82	-515
Ni ²⁺	1.010	0.069 – 0.070	4.04	-2042 ± 44**
Co ²⁺	1.085 ± 0.003**	0.072	4.23	-1975 ± 46**
Al ³⁺	1.140 ± 0.032**	0.057	4.44 - 4.75	-4550 ± 81**

Notes: (*) Data on pressure: 1 atm, and temperature: 25°C, (**) Data mean and standard deviation.

centration (*C*). Specifically, the order of osmotic pressure is mother liquor > DF 50x > DF 10x.

Apart from the driving force, the possibility of anion-cation interactions also influences the separation that occurs in nanofiltration. This has been confirmed by the results of molecular dynamic research conducted by (Zhai et al., 2022), which stated that co-ions' electrostatic repulsive force also limits ion's permeability across the membrane. Therefore, the presence of anions in leachate cannot be ignored. Of note, this leachate is rich in sulfate ions (SO₄²⁻) and hostile to the surface-active membrane TS80 (polyamide), which is rich in hydrolyzable carboxyl and amino groups (Laurio et al., 2022). As a result, electronegative repulsion between the sulfate ions (SO42-) and the surface is unavoidable, and a highly valent sulfate ion is formed. As another effect, the penetration of lithium ions (Li⁺) continues to maintain a neutral charge (Gao et al., 2020a). It is possible that other factors have an effect, such as the relative distance of the lithium ions to the membrane. As an emphasis, in this research carried out batch in dead-end cells, in which the agitation speed controls the hydrodynamic. This also underlies the relative distance between the ions and the membrane. Different hydrodynamic phenomena can occur in membranes with a crossflow configuration. Previous research conducted by Imbrogno & Schäfer stated that dead-end cells have a similar tendency (Imbrogno and Schäfer, 2019). Therefore, this study has limitations related to hydrodynamic studies, which will be carried out in future research.

Overall, the optimum dilution factor from the separation review cannot be determined. Simultaneously, flux as a performance parameter is considered. In Figure 3c, the highest permeate flux is achieved when the dilution factor is 50x, followed by 10x, and finally for concentrate. The permeate flux for the 50x and 10x dilution factors did not differ much. This is possible because of the flux limitations imposed by the resistance of the membrane itself, and the competition for water molecules to move through the membrane is not significant. But mostly, the phenomenon of separation using NF membranes is influenced by the interaction between ions and the membrane from a complex combination effect (Steric, Donnan, Dielectric). Kumar et al. conducted research affirming that the Donnan effect influences the mechanistic separation of bivalent ions, such as Ni²⁺, Co²⁺, and Mn²⁺. However, the Donnan effect does not significantly contribute to the overall separation process. Conversely, the steric effect assumes a more crucial role (Kumar et al., 2022). These findings align with the work of Wadekar et al., who investigated different bivalent ions and concluded that the steric effect outweighs the Donnan effect when employing membranes with fully aromatic (FA) characteristics, as opposed to semi-aromatic (SF) membranes (Wadekar and Vidic, 2017a).

As previously mentioned, the membrane surface charge is also considered a permeate flux factor close enough between the two dilution factors (10x and 50x). Thus, the dilution factor implies that the optimum concentration of a separation process also needs to be considered. Technically, excessive dilution factors are avoided. This is based on the energy that would later be required for the concentration and precipitation of lithium itself. On the other hand, investigations concerning the impact of operational pressure were conducted, adhering to the specified variations outlined in the methodology. Simultaneously, under varying

352 Optimization of Lithium Separation from NCA Leachate Solution: Investigating the Impact of Feed Concentration, Pressure, and Complexing Agent Concentration

pressure conditions, a dilution factor of 10x was employed, strategically intended to enhance the one-sided permeation of a specific concentration.

Several pressure variations have been carried out in this research, showing that pressure has a significant effect on the separation of lithium (see Figure 4b). On the other hand, the rejection performance of other ions is not outstanding and is almost the same for every applied pressure. On the other hand, the rejection performance of other ions is not outstanding and is almost the same for every applied pressure. As an explanation, the hydration energy of multivalent ions tends to be higher than monovalent (see Table 1). Breaking of hydration bonds requires external energy, which in this case is supplied by hydrostatic pressure. In figure 4a, the selectivity pattern cannot be determined properly. However, lithium's tendency to separate from nickel

and cobalt metals at low pressure (4 bar) can be observed. In the case of the effect of pressure on ion separation in NF systems, the membrane's steric hindrance is most prominent compared to the Donna and dielectric effects. The permeate flux at various pressures is shown in Figure 4c. Obviously, it is observed that the increase in pressure is proportional to the flux produced. However, at high pressure, a gentle decrease in flux is found. This is possible due fouling originating from the remaining particulate leaching of the battery that escapes through the ultrafiltration process. Instead, the concentration of the feed also increases osmotic pressure that needs to be resisted. In this research, efforts to improve both performance parameters were carried out by adding complex compounds. In particular, EDTA was chosen as a complexing agent, which is expected to be selective only for multivalent ions.



Fig.4: Separation Factor (a), Rejection (b), Flux Permeate (c): As a function of operating pressure.



Fig. 5: Selectivity (a), Rejection (b), Permeate Flux (c): As a function of complexing agent concentration.

As already explained, adding EDTA complexing agents is expected to have a significant effect. This is in line with the expected results. Figure 5 shows that the selectivity of Li/Ni and Li/Co increases with the presence of EDTA. However, the selectivity for Li/Al decreased due to EDTA. This phenomenon may be related to the influence of the valence of aluminum ions (Al³⁺), which bind strongly to EDTA. This results in the diffusion of the aluminum complex. It should be remembered that this fully aromatic membrane is composed of functional groups with an affinity with EDTA. The presence of the EDTA complex affected the decrease in the diffusivity coefficient of cobalt ions (Co²⁺). Thus, the selectivity of the cobalt ion will also

decrease. However, the concentration of EDTA must be controlled, otherwise, the expectation of selectivity may not be achieved. In this case, using 0.02 M of EDTA is more advisable than 0.05 M or not using EDTA. Moreover, considerations related to rejection also support the superiority of using 0.02M EDTA compared to 0.05M. In addition, permeate flux shows that using EDTA has certain limitations in increasing performance. This is evidenced by the flux values that tend to be the same between 0.02M and 0.05M. As a reminder, the presence of aluminum ions tends to be minor than nickel and cobalt ions.

Comparison of Selected Studies on Lithium Extraction from Battery Leachate

The presence of various metal ions in battery leachate has been discussed previously, and the selection of appropriate techniques is necessary to deal with them. Table 3 summarizes the comparison of lithium separation methods using membranes.

Techniques	Membrane Information	Feed Solution	Efficiency	Summary	Reference
Bipolar Electrodialysis	 Cation & Anion Membrane (Selemion) Bipolar (Neosepta BP- 1E) 	Synthetic Solution (Li ⁺ , Co ²⁺ , EDTA [NO₃ ⁻ and Na ⁺])	*Li*/Co ²⁺ selectivity reaches 99%.	Bipolar electrodialysis is effective for Li ⁺ /Co ²⁺ separation, especially with the addition of a chelating agent (EDTA). Recovery rate is affected by the pH of the solution. The semi-batch process can be an alternative for a better performance improvement.	(lizuka <i>et al.,</i> 2013)
Shock Electrodialysis	- Nafion N115 (Ion Power)	Synthetic Solution (Li⁺, Co²⁺, dan Cs⁺)	*High ion removal (Li ⁺ = 82%, Co ²⁺ = 91%, and Cs ⁺ = 85%)	Shock Electrodialysis was successful in separating metals from contaminants in the system. Economically it is economical enough to support further development.	(Alkhadra et al., 2019)
Hydrometallurgy– Electrodialysis	- Neosepta CMX (Astom)	Synthetic Solution (Li ⁺ and Co ²⁺)	*High metal extract (Co ²⁺ = 25.53% ± 0.89% and Li ⁺ = 56.36% ± 0.96%)	The combination of techniques provides relatively high metal purity, but needs further development.	(Cerrillo- Gonzalez <i>et</i> <i>al.</i> , 2020)
Electrodialysis	 Neosepta CMX, AMX, CMS (Astom) PCA PC 400D 	Synthetic Solution (Li*, Ni ²⁺ , Mn ²⁺ and Co ²⁺)	*High metal extract (Ni ²⁺ = 99.3%, Co ²⁺ = 87.3%, Li ⁺ = 99%)	The step-by-step metal extraction technique using electrodialysis assisted by complexing agent EDTA is capable of providing high metal purity.	(Chan <i>et al.,</i> 2022)

Table 3. Comparison of research related to metal extraction using membrane processes.

Techniques	Mombrano	Food Solution	Efficiency	Summary	Reference
rechniques	Information	reeu solution	Enciency	Summary	Reference
Supported Ionic Liquid	- Modified PVDF-UF membrane by Ionic Liquid	Synthetic Solution (Li ⁺ , Ni ²⁺ , and Co ²⁺)	*Extraction efficiency up to 80%	The extraction option using this technique is quite interesting to develop, even though its wide application is still not possible.	(Zante <i>et al.,</i> 2019)
Polymer Inclusion Electrodialysis Membrane	 PVDF-HFP based modified membrane CJMA-3 (AEM) & CJMC-5 (CEM) obtain from Hefei Chemjoy Polymer Material AGU (AEM) & MVAM obtain from ASTOM 	Synthetic Solution (Li ⁺ , and Co ²⁺)	*Separation of Co ²⁺ to Li ⁺ reaches 100%.	Electrodialysis systems equipped with inclusion polymer membranes provide options for developing more effective techniques in lithium separation.	(Wang <i>et al.,</i> 2022)
lon-Imprinted Membrane	- SP – IIM (Modified PVDF)	Synthetic Solution (Li ⁺ , Ni ²⁺ , Mn ²⁺ and Co ²⁺)	*High Separation Factors $(Li^{+}/Mn^{2^{+}} =$ 6.71, Li^{+}/Co^{2^{+}} = 5.84, Li^{+}/Ni^{2^{+}} = 3.03)	The technique is quite good in lithium separation and the adsorption capacity is quite high.	(Li <i>et al.</i> , 2021)
Nanofiltration	- VNF1 & VNF2 (Vontron Membrane Technology Ltd)	FLP Battery leachate (Li, Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Fe ³⁺ , Al ³⁺ , and PO_4^{3-}	*High rejection bivalent ion (Ni ²⁺ ~92.5%, Co ²⁺ ~94.6%, Mn ²⁺ ~95.8%) *Permeate Flux ~7.5 L.m ⁻² .h ⁻¹	The operation shows that the separation process is going well, but the permeate flux is still quite low.	(Kumar <i>et al</i> ., 2022)

{VNF2@10 bar}

Techniques	Membrane Information	Feed Solution	Efficiency	Summary	Reference
Nanofiltration	- TFC-PA (Commercial Membrane TS80)	NCA Battery leachate (Li ⁺ , Ni ²⁺ , Al ³⁺ and Co ²⁺)	*Separation Factors $(Li^{+}/Ni^{2+} =$ ~8.6, Li ⁺ / Co ²⁺ = ~7.3, $Li^{+}/Al^{3+} =$ ~4.9) *Permeate Flux ±46.58 $L.m^{-2}.h^{-1}$	The research results are quite satisfactory, it is necessary to carry out further research related to the influence of other complexing agents and evaluate the feasibility of the process in total.	This work

CONCLUSIONS

A lithium separation experiment from battery leachate using a TS80 membrane has been carried out. Technically, the separation of lithium from it is necessary to consider related influences such as concentration, pressure, and addition of other compounds. Proof of the effect of concentration has been carried out in the form of a dilution factor in concentrates, DF 10x, and DF 50x, in which DF 10x was selected as the reference concentration. Effect of operating pressure at 4, 6, and 7 for the reference concentration showing the relevant 7 bar pressure for selection. On the other hand, using EDTA as a complexing agent suggests that the concentration of EDTA needs to be considered carefully. In conclusion, lithium separation can be an interesting consideration to develop, especially in continuous crossflow systems.

ACKNOWLEDGEMENTS

We are grateful for the support from Gadjah Mada University (UGM) and the National Research and Innovation Agency (BRIN) for their support in fulfilling the necessary research needs. We also thank Dr. (Cand). Doni Riski Aprilianto for his help in analysis using ICP-OES.

REFERENCES

- Alkhadra, M.A., Conforti, K.M., Gao, T., Tian, H., and Bazant, M.Z., 2019. "Continuous Separation of Radionuclides from Contaminated Water by Shock Electrodialysis." *Environ. Sci. Technol. 54 (1),* 527–536.
- Aryani, W., Anggraini, A.G., Bahfie, F., Herlina, U., Al Muttaqii, M., and Prasetyo, E., 2021. "A Kinetic study of manganese leaching from low-grade psilomelane ore by acetic-tannic acid lixiviant." ASEAN Journal of Chemical Engineering 21, 188–200.
- Cerrillo-Gonzalez, M.M., Villen-Guzman, M., Vereda-Alonso, C., Gomez-Lahoz, C., Rodriguez-Maroto, J.M., and Paz-Garcia, J.M., 2020. "Recovery of Li and Co from LiCoO 2 via hydrometallurgical – electrodialytic treatment." *Applied Sciences 4*, 2367.
- Chan, K.H., Malik, M., and Azimi, G., 2022. "Separation of lithium, nickel, manganese, and cobalt from waste lithium-ion batteries using electrodialysis." *Resour. Conserv. Recycl. 178*, 106076.

- Chen, M., Ma, X., Chen, B., Arsenault, R., Karlson, P., Simon, N., and Wang, Y., 2019. "Recycling end-of-life electric vehicle lithium-ion batteries." *Joule 3*, 2622–2646.
- Dimaculangan, D.A.A., Bungay, V.C., and Soriano, A.N., 2022. "Determination of diffusion coefficients of heavy metal ions electrolytic conductivity measurements." *ASEAN Journal of Chemical Engineering*, *22*, 58–71.
- Gao, L., Wang, H., Zhang, Y., and Wang, M., 2020a. "Nanofiltration membrane characterization and application: Extracting lithium in lepidolite leaching solution." *Membranes 10*, 1– 18.
- Gao, L., Wang, H., Zhao, Y., and Wang, M., 2020b. "The Application of nanofiltration for separating aluminium and lithium from lepidolite leaching solution." *Chemistry Select.* 5, 4979–4987.
- Gasparini, B., Lívia, A., Araújo, B., Vieira, C.C., Cristina, M., Amaral, S., and Conceição, H., 2019. "Assessing potential of nanofiltration for sulfuric acid plant effluent reclamation: Operational and economic aspects." *Sep. Purif. Technol.* 222, 369–380.
- Harper, G., Sommerville, R., Kendrick, E., Driscoll, L., Slater, P., Stolkin, R., Walton, A., Christensen, P., Heidrich, O., Lambert, S., Abbott, A., Ryder, K., Gaines, L., and Anderson, P., 2019. "Recycling lithium-ion batteries from electric vehicles." *Nature 575*, 75–86.
- lizuka, A., Yamashita, Y., Nagasawa, H.,
 Yamasaki, A., and Yanagisawa, Y., 2013.
 "Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electrodialysis coupled

with chelation." *Sep. Purif. Technol. 113*, 33–41.

- Imbrogno, A., and Schäfer, A.I., 2019. "Comparative study of nanofiltration membrane characterization devices of different dimension and configuration (cross flow and dead end)." *J. Memb. Sci. 585*, 67–80.
- Jin, S., Mu, D., Lu, Z., Li, R., Liu, Z., Wang, Y., Tian, S., and Dai, C., 2022. "A comprehensive review on the recycling of spent lithium-ion batteries: Urgent status and technology advances." *J. Clean. Prod. 340*, 130535.
- Jo, M., Ku, H., Park, S., Song, J., and Kwon, K., 2018. "Effects of residual lithium in the precursors of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ on their lithium-ion battery performance." *Journal of Physics and Chemistry of Solids 118*, 47–52.
- Kim, S., Bang, J., Yoo, J., Shin, Y., Bae, J., Jeong, J., Kim, K., Dong, P., and Kwon, K., 2021. "A comprehensive review on the pretreatment process in lithiumion battery recycling." J. Clean. Prod. 294, 126329.
- Ku, H., Jung, Y., Jo, M., Park, S., Kim, S., Yang,
 D., Rhee, K., An, E.M., Sohn, J., and
 Kwon, K., 2016. "Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching." *J. Hazard. Mater. 313*, 138–146.
- Kumar, J., Neiber, R.R., Park, J., Ali Soomro, R., Greene, G.W., Ali Mazari, S., Young Seo, H., Hong Lee, J., Shon, M., Wook Chang, D., and Yong Cho, K., 2022. "Recent progress in sustainable recycling of LiFePO₄-type lithium-ion batteries: Strategies for highly selective lithium recovery." *Chemical Engineering Journal 431*, 133993.
- Kumar, R., Liu, C., Ha, G.S., Park, Y.K., Ali Khan, M., Jang, M., Kim, S.H., Amin,

M.A., Gacem, A., and Jeon, B.H., 2022. "Downstream recovery of Li and valueadded metals (Ni, Co, and Mn) from leach liquor of spent lithium-ion batteries using a membraneintegrated hybrid system." *Chemical Engineering Journal 447*, 137507.

- Laurio, M.V.O., Yenkie, K.M., and Slater, C.S., 2022. "Optimization of vibratory nanofiltration for sustainable coffee extract concentration via response surface methodology." *Separation Science and Technology 57*, 112–130.
- Li, X., Mo, Y., Qing, W., Shao, S., Tang, C.Y., and Li, J., 2019. "Membrane-based technologies for lithium recovery from water lithium resources: A review." J. Memb. Sci. 591, 117317.
- Li, Z., He, G., Zhao, G., Niu, J., Li, L., Bi, J., Mu, H., Zhu, C., Chen, Z., Zhang, L., Zhang, H., Zhang, J., Wang, B., and Wang, Y., 2021. "Preparation of a novel ionimprinted membrane using sodium periodate-oxidized polydopamine as the interface adhesion layer for the direction separation of Li+ from spent lithium-ion battery leaching solution." *Sep. Purif. Technol. 277*, 119519.
- Lobo, V.M.M., and Quaresma, J.L., 1990. "Diffusion coefficients in aqueous solutions of cadmium chloride at 298 K." *Electrochim. Acta. 35*, 1433–1436.
- López, J., Reig, M., Vecino, X., Gibert, O., and Cortina, J.L., 2020. "Comparison of acid-resistant ceramic and polymeric nanofiltration membranes for acid mine waters treatment." *Chemical Engineering Journal 382*, 122786.
- Micari, M., Diamantidou, D., Heijman, B., Moser, M., Haidari, A., Spanjers, H., and Bertsch, V., 2020. "Experimental and theoretical characterization of commercial nanofiltration membranes

for the treatment of ion exchange spent regenerant." *J. Memb. Sci. 606*, 118117.

- Purnomo, C.W., Kesuma, E., Wirawan, S.K., Hinode, Н., 2017. "The and development of lithium ion recovery method by activated carbon and natural zeolite-based adsorbent." ASEAN Journal of Chemical *Engineering 17*, 91–98.
- Purwanto, A., Yudha, C.S., Ikhwan Muhammad, K., Algifari, B.G., Widiyandari, H., and Sutopo, W., 2020. "Synthesis of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode material via flame-assisted spray pyrolysis method." Advanced *Powder Technology* 31, 1674–1681.
- Ribeiro, A.C.F., Valente, A.J.M., Sobral, A.J.F.N., Lobo, V.M.M., Burrows, H.D., and Esteso, M.A., 2007. "Diffusion coefficients of aluminium chloride in aqueous solutions at 298.15, 303.15 and 315.15 K." *Electrochim. Acta. 52*, 6450–6455.
- Ricci, B.C., Ferreira, C.D., Aguiar, A.O., and Amaral, M.C.S., 2015. "Integration of nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent." *Sep. Purif. Technol.* 154, 11–21.
- Tansel, B., Sager, J., Rector, T., Garland, J., Strayer, R.F., Levine, L., Roberts, M., Hummerick, M., and Bauer, J., 2006. "Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes." *Sep. Purif. Technol. 51*, 40–47.
- Thompson, D.L., Hartley, J.M., Lambert, S.M., Shiref, M., Harper, G.D.J., Kendrick, E., Anderson, P., Ryder, K.S., Gaines, L., and Abbott, A.P., 2020. "The importance of design in lithium ion battery recycling-

a critical review." *Green Chemistry 22*, 7585–7603.

- Tian, G., Yuan, G., Aleksandrov, A., Zhang, T., Li, Z., Fathollahi-Fard, A.M., and Ivanov, M., 2022. "Recycling of spent Lithiumion Batteries: A comprehensive review for identification of main challenges and future research trends." Sustainable Energy Technologies and Assessments 53, 102447.
- Wadekar, S.S., and Vidic, R.D., 2017a. "Influence of active layer on separation potentials of nanofiltration membranes for inorganic ions." *Environ. Sci. Technol. 51*, 5658–5665.
- Wang, B., Liu, F., Zhang, F., Tan, M., Jiang, H., Liu, Y., and Zhang, Y., 2022. "Efficient separation and recovery of cobalt(II) and lithium(I) from spent lithium ion batteries (LIBs) by polymer inclusion membrane electrodialysis (PIMED)." *Chemical Engineering Journal 430*, 132924.
- Wen, X., Ma, P., Zhu, C., He, Q., and Deng, X., 2006. "Preliminary study on recovering lithium chloride from lithiumcontaining waters by nanofiltration." *Sep. Purif. Technol.* 49, 230–236.
- Yao, Y., Zhu, M., Zhao, Z., Tong, B., Fan, Y., and Hua, Z., 2018. "Hydrometallurgical processes for recycling spent lithiumion batteries: A critical review." ACS Sustain. Chem. Eng. 6, 13611–13627.
- Yudha, C.S., Muzayanha, S.U., Widiyandari, H., Iskandar, F., Sutopo, W., and Purwanto, A., 2019. "Synthesis of LiNi_{0.85}Co_{0.14}Al_{0.01}O₂ cathode material and its performance in an NCA / graphite full-battery." *Energies, 12*, 1886.
- Zante, G., Boltoeva, M., Masmoudi, A., Barillon, R., and Trébouet, D., 2019. "Lithium extraction from complex

aqueous solutions using supported ionic liquid membranes." *J. Memb. Sci. 580*, 62–76.

- Zhai, X., Wang, Y.L., Dai, R., Li, X., and Wang, Z., 2022. "Roles of anion-cation coupling transport and dehydrationinduced ion-membrane interaction in precise separation of ions by nanofiltration membranes." *Environ. Sci. Technol.* 56, 14069–14079.
- Żyłła, R., Foszpańczyk, M., Kamińska, I., Kudzin, M., Balcerzak, J., and Ledakowicz, S., 2022. "Impact of polymer membrane properties on the removal of pharmaceuticals." *Membranes, 12(2)*, 150