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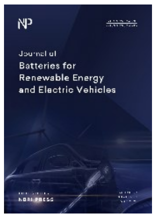

Advanced Recycling and Recovery of Spent Lithium-Ion Batteries with Bioleaching Processes using A. *ferroxidans* to Achieve Cleaner Battery Production

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A B S T R A C T

Nowadays, large amounts of Lithium-Ion Battery Waste (WLIB) are a serious problem. WLIB waste is hazardous and toxic waste. If special handling is not carried out, it will give a serious hazard to the environment and human health. The project aims to extract WLIB in the form of Li_2CO_3 electrodes, which will then be recovered using a bioleaching process using A. *ferrooxidans* as biological agent to achieve improved Life Cycle Assessment of battery production. By cultivating the bacteria at a low pH, maximized through the use of strong acids, metal catalyst, the metal waste can be dissolved into ions. These ions can then be chemically consolidated and transformed into new battery electrodes. Subsequently, the material was subjected to chemical and electrochemical testing using cyclic voltammetry (CV) at a scan rate of 0.1 mV/s and charge-discharge (CD) measurements at a scan rate of 0.1 C. Effect of catalysis at bioleaching process using A.*ferooxidans* is dissolve 99.9% cobalt and gives 94% efficiency at S/L ratio of 6. The purity of Li_2CO_3 produced by bioleaching is higher than commercial Li_2CO_3. Electrochemical tests show that recycled Li2CO3 has initial capacity respectively of 102 mAh/g and capacity retention of 79% after 50 cycles at 1C while commercial percussors lower. WLIB recycling using bioleaching processes could produce weak organic acid waste, more environmentally friendly than the cathode synthesis process from metal precursors (commercial Li_2CO_3). This innovation is interesting to develop because it will produce batteries that are cleaner and more efficient than commercial battery products.

INTRODUCTION

Lithium Battery is a battery with lithium as an electrolyte and primary cathode element. Lithium-Battery developed rapidly used for our gadget life. Lithium batteries are mainly classified into two main categories, lithium metal (LMBs) and lithium-ion (LIBs). With increasing supply and demand for portable electronics and vehicles, the production of LIBs is increasing rapidly [1].

Large amounts of Lithium-Ion Battery Waste (WLIB) or Spent LIBs are a serious problem. Around 10,700 tons in 2012, LIBs increase to 464,000 tons in 2025 and approximate reach 11 million tons by 2030 worldwide [2]. Materials inside LIBs are lithium, nickel, cobalt, manganese and other chemical compounds that may damage organisms if exposed. In Indonesia, Lithium-Ion Battery categorized as B3 waste (*Bahan Berbahaya dan Beracun*). According to Government Regulation No. 22 of 2021, batteries including Li-Ion battery are classified as B3 waste because it contains heavy metals.

Ministry of Environment and Forestry Republic of Indonesia has issued regulations related to B3 waste management. Attachment XIII of the regulation explains about utilization of B3 waste, but not specifically into battery waste. This fact leads to looking for the best way to recover Battery Waste, especially LIBs, in order to reduce the number of LIBs in 5-7 years.

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LIBs still contain high raw materials or elements for the new production of batteries although the battery can't be used anymore. With cradle-to-cradle approach of Life Cycle Assessment of LIBs, LIBs recycling is very significant and important, because it represents a triple challenge: (i) environmental, allows energy savings compared to mining so it can achieve cleaner battery production; (ii) economic, the development of recycling infrastructure and processes will create waste tax savings, and (iii) strategic, it is a future plan for cleaner battery production and as an implementation of SDGs. Refer to these data, a pilot-scale advance process is needed to support the implementation of cleaner production in the battery industry.

Processing of LIBs usually uses hydrometallurgical and pyrometallurgical processes. Metallurgical processes have drawbacks, namely the presence of harmful gas emissions, high Co-LiBs requirements, and high capital costs. The hydrometallurgical process has drawbacks, namely the recovery process will produce wastewater that has a high COD, incomplete electrolyte recycling, and complex procedures [4]. Therefore, as an alternative to the disadvantages above, the LIBs recovery process using the bioleaching process will be used, a process in mining and biohydrometallurgy (natural processes of interactions between microbes and minerals) that extracts valuable metals from a low-grade ore with the help of microorganisms such as bacteria or archaea [5]. Bioleaching answers the disadvantages of hydrometallurgy and pyrometallurgy processes.

In this study, *A. ferroxidans* strain ATCC 23270 was used. Bioinformatics analysis provides a result that *A.ferroxidans* can used as industrial bioleaching agent. *A. ferroxidans* role in industrial bioleaching is act as primary procuder of LIBs [6]. To support a pilot-scale bioleaching process for alleviating battery waste problems, studies are needed on the physical and chemical characteristics and impact of *A.ferroxidans* as a bioleaching agent on the product and performance of the batteries it produces. The existing data is used to design a pilot project design of the bioleaching process and will be submitted for implementation in Indonesia. This paper aim to analysis impact of lab-scale *A.ferroxidans* bioleaching processes for the Life Cycle Assesment and feasibility study of pilot project design.

METHODOLOGY

Acidithiobacillus ferrooxidans belongs to a type of acidophilic bacteria. These bacteria grow and develop optimally in an environment with a very low pH (pH 1-2). These bacteria play a major role in the bioleaching process in heavy metal industry, such as tin, gold, silver, nickel and zinc mines. The culture of these microorganisms requires adequate nutrients for optimal bacterial growth. The nutrients needed must has rich in K_2HPO_4 – 0.1 g, $(NH_4)_2SO_4$ – 2.0 g, KCl – 0.1 g, $MgSO_4.7H_2O$ – 4.0 g, $FeSO_4.7H_2O$ – 44,2 g, elemental sulfur – 4.0 g/l, and distilled water, 1000 ml at the initial pH = 1.5. Prior to the bioleaching study, the microorganism has to be adapted by mixing the cathode powder for four weeks. after that, the bioleaching process can only be carried out on spent LIB. Microbial activity was monitored by changes in pH and ORP. The bioleaching process is very slow; therefore, a catalyst is needed to speed up the reaction kinetics. Several metal ions are reported to be catalysts in the bioleaching process, such as Cu^{2+}, Ag^{+}, Bi^{3+}, Hg^{2+}, and Co^{2+}. Addition of catalytic ions accelerates electron transfer in the leaching solution [1].

The process starts with disassembling the LIBs. Then, the LIBs material which can be recycle (contain of cathode material), crushed using crushing tools such as hammers, ceramic balls, or knife mills. However, knife mills are the most effective way to get the cathode material from batteries. After crushing, these materials are separated the active cathode materials (LIB powder) from other materials (such as plastic, casing material, LIBs separator, etc.) in order to obtain the maximum of valuable metals. Microorganisms were first cultured into a 250 mL Erlenmeyer which was mixed with 9K medium to produce bio acid (H_2SO_4).

After 24 hours, LIBs powder is added and mixed to initiate bioleaching process. This process was carried out continuously by refilling the bacterial culture into the medium for three cycles. To accelerate the kinetics of reaction, use metal ions such as Cu^{2+} or Ag^{+} as the catalyst [3]. The microorganism will oxidize the reduced metal, then the reactions led to the production of protons (H^{+} ions) which can determine the metals recovery efficiency.

First of all, the results of bioleaching products from spent Li-Ion Battery analyzed with digital multi meter used to measure the pH of the bioleaching extract. The extract scanned use XRD to analyze the metal recovery. After that, chemical compounds analyzed with Fourier Transform Infrared to know the chemical structure of recovery at wavelength 500-4000 cm^{-1}. After characterization of metal recoveries, to determine the Chemical Oxygen Demand levels of bioleaching wastewater processes as environmental indicator, it can be used with ferric ammonium sulfate (FAS). A total of 2,5 mL sample wastewater was put into a test tube, then 1,5 mL of $K_2Cr_2O_7$ and 3,5 mL of H_2SO_4 as a reagent solution. Then the tube closed and shook until the sample was homogeneous. The reaction tube underwent heating at 150°C for a duration of 2 hours, followed by titration using a 0.05 M FAS (Ferrous Ammonium Sulfate) solution.

Three drops of ferroin indicator were added until a distinct color change occurred, transitioning from green to reddish-brown. To determine the battery capacity, electrochemical tests were conducted CD (Charge-discharge) methods with the NEWARE Battery analyser apparatus. In the CD method, the sample was tested using at voltage range if 2,7 – 4,3 V, a current density of 20 mA/g and a constant current variation of 0,1C and 1C over 50 cycles. The voltage was recorded over time. The data for voltage and current magnitude multiplied by time were then presented in a voltage vs. discharge capacity graph [7].

RESULTS AND DISCUSSION

Bioleaching process is an environmentally friendly method. *A. ferroxidans* bacteria can reduce heavy metal ions, such as iron, which can also apply to other metals. *A. ferroxidans* take energy from metal ions for their metabolism which results in the oxidation of metal ions. These bacteria include as aerobic bacteria that require the presence of sufficient oxygen as a terminal electron acceptor of metal ions (electron donors). The reaction of bioleaching process showed in equation below:

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{A.\ ferroxidans} 4Fe^{3+} + 2H_2O \tag{1a}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^+ + H^+ \tag{1b}$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^+ + 2H^+ \tag{1c}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3^+ + 3H^+ \tag{1d}$$

The bioleaching process progresses at a comparatively sluggish pace, primarily because the growth and metabolic activities of leaching microorganisms are hindered by the toxic influence of elevated metal concentrations. To speed up the reaction, several metal ions catalyst are used as an electron transfer accelerator. In the Co bioleaching process from spent LIB, there was an increase in the leaching process from 43.1 w/t% to 99.1 w/t% in a period of 10 days by adding 0.75 g/L Cu^{2+}.

The same thing was found in the addition of Ag^+ which can increase the leaching process of Co and Ni up to 99.95 w/t% [8]. With addition of 0.75 g/L of copper (Cu^{2+}) ions, bioleaching Co from spent LIB increased remarkably from 43.1 w/t% to 99.1 w/t% in a 10-day leaching period. The mechanism of catalytic process of bioleaching showed in equation below:

$$Cu^{2+} + 2LiCoO_2 \leftrightarrow CuCo_2 + 2Li^+ \tag{2a}$$

$$CuCo_2O_4 + 6Fe^{3+} \leftrightarrow 6Fe^{2+} + Cu^{2+} + Co^{2+} + 2O_2 \tag{2b}$$

$$Ag^+ + LiCoO_2 \leftrightarrow AgCoO_2 + Li^+ \tag{2c}$$

$$AgCoO_2 + 3Fe^{3+} \leftrightarrow 3Fe^{2+} + Ag^+ + Co^{2+} + O_2 \tag{2d}$$

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{A.\ ferroxidans} 4Fe^{3+} + 2H_2O \tag{2e}$$

The effect of the bioleaching processes with *A.ferooxidans* given in the figure 1. After two days, low amount of oxidized iron (34,4% w/t) was observed in non-inoculated control run over 9 days. The efficiency calculated with equation 3:

$$Eff\ (\%) = \frac{Volume x\ Dil.Factor\ x\ Density}{Grams\ of\ WLIB\ (gram)} x100\% \tag{3}$$

Catalysis bioleaching processes shows that efficiency touch percentage until 27% Al, 54% Mo, 98% Ni, 25% Zn, and 32% Cu. The efficiency of Nickel is highest due to high affinity of Ni to bond with oxidizing agent. Fig. 1 shows the leaching efficiency of *A. ferroxidans* in various timestamp.

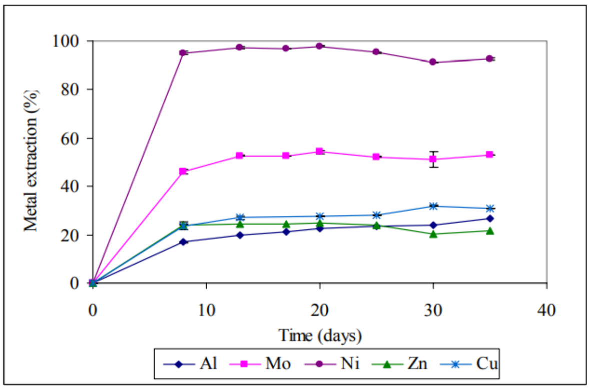


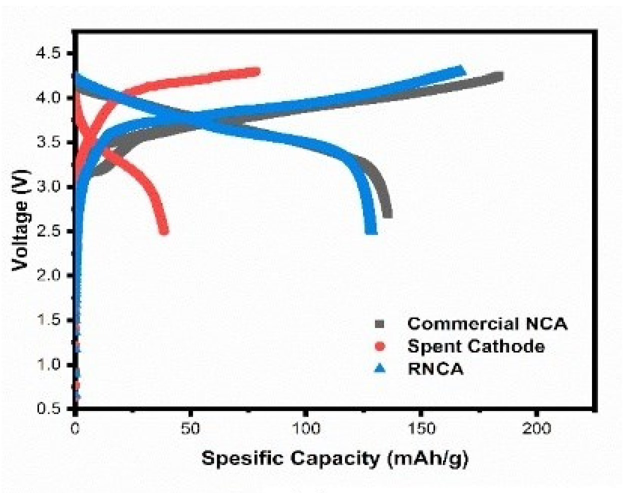
Fig. 1. Efficiency of Bioleaching with *A. ferooxidans*

Characterization of Li_2CO_3 give result: nearly all the cobalt (99,9 w/t%) goes into solution after 6 days in the presence of 0,75 g/l copper ions, while only 43,1% dissolution of cobalt is achieved after 10 days without the use of copper ions [11]. Li gave good results with an efficiency of 94% at a solid/liquid ratio (S/L) of the efficiency decreased as the S/L ratio increased. The purity of Li_2CO_3 produced by bioleaching is the same as pure Li_2CO_3 and higher than commercial Li_2CO_3.

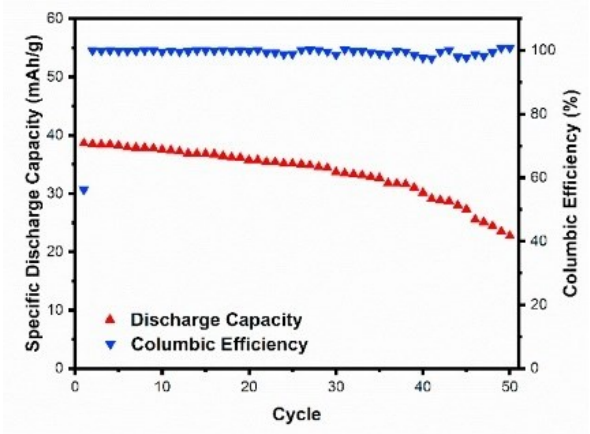
A review of environmental aspects shows that the process of recycling used LIB for cathode regeneration which produces weak organic acid waste is more environmentally friendly than the cathode synthesis process from metal precursors which produces strong acid inorganic waste. With impacts of processes are regarded as the environmentally preferred choice, closely by the 27,9 $kg{\cdot}CO_2\text{-equiv}{\cdot}kg_{cathode}^{-1}$ emission than conventional leaching (With impacts of 25,1 and 26,2 $kg{\cdot}CO_2\text{-equiv}{\cdot}kg_{cathode}^{-1}$, inorganic acid-leaching (HCl and H_2SO_4/H_2O_2) [10].

In this study, the bioleaching sample which it called RNCA was utilized as the cathodes in a cell of lithium-ion batteries (LIBs). Graphite material from LIBs was employed as the counter anode. As a comparison, NCA cathode (one of the commercial batteries) and the spent cathode sample were also used as cathodes. The charge-discharge curves of the RNCA spent cathode and the commercial NCA cathode illustrate on Fig. 2a. At a current rate of 0,1C, the specific discharge capacities of the bioleaching sample, spent cathode, and commercial NCA cathode were 128, 38, and 133.40 mA h/g, respectively, with Coulombic efficiencies of 71,1%, 50%, and 71,2%, respectively. This number indicates the significance of treating spent cathode materials to enhance their usability by 337% [7].

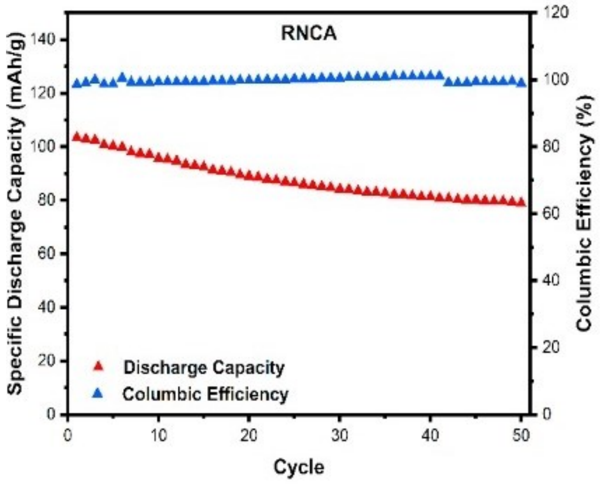
Under the current rate of 1C, the discharge capacity of the bioleaching sample was 102 mA h/g, and it could retain approximately 79% of its initial capacity after 50 continuous cycles. The NCA cathode used in commercial applications displayed a discharge capacity of 115 milliampere-hours per gram (mAh/g), maintaining 82.6% of its capacity after undergoing 50 cycles at a 1C rate. Conversely, the capacity of the spent cathode reduced to only 50% of its initial capacity after 50 cycles at a much slower 0.1C rate. The performance of the spent cathode, alongside the bioleaching sample and commercial NCA cathode, is illustrate in Fig. 2b, 2e, and 2d. From the figure, we know that all metals have ability to give high specific capacity with the same composition in NCA or RNCA.



(a)



(b)



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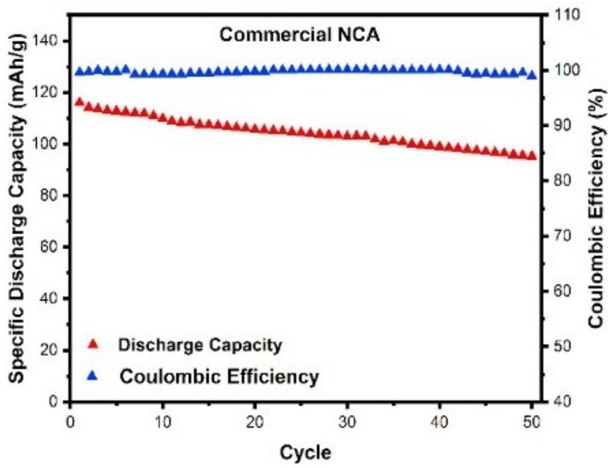

(d)

Fig. 2. Electrochemical Performances Test Curve Behavior: (a) formation curve cycle performances of (b) spent NCA, (c) RNCA, and (d) commercial NCA.

After discuss about advantages using the bioleaching processes, this study will discuss further about the process flow diagram and unit operations of the advanced bioleaching processes. The Process flow diagram shown in Fig. 3.

All of the process is the same with methods in the previous chapter, yet in the bigger scale. Unit operations of the pilot plant considered in bioleaching processes are based on current technologies that were quoted from

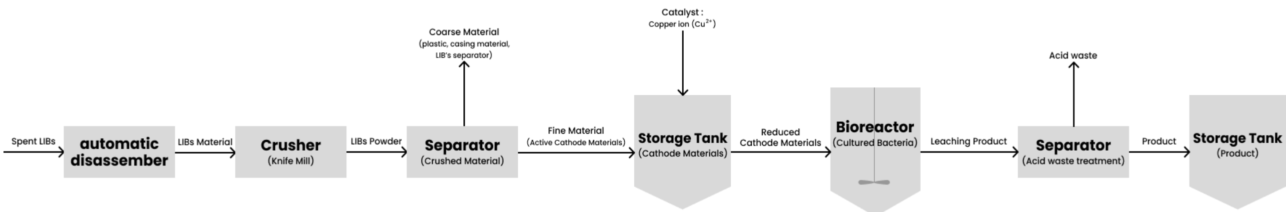

Fig. 3. Process Flow Diagram of Pilot Scale Bioleaching from Spent Lithium-Ion Batteries.

industrial data. The description of these processes are as follows:

Automatic Disassembler

The machine has a total power consumption of 1.2 kW. This machine operates at a fixed cutting speed of 5~250mm/s, with a maximum diameter of the material to be removed (lithium batteries) set at 250 mm. As a result, it separates the positive and negative parts of the batteries with a width of 300 mm and an adjustable length ranging from 1 to 9999 mm, achieving a precision level of ± 0.3 mm.

Crusher

The material from Lithium-Ion Batteries (LIBs) that has been separated by the automatic disassembler will be further refined into powder using a crusher. The knife mill, operates with an efficiency of 86.5% and use power of 1.5 kW. By continuously operating at a speed of 1745 rpm, it will produce LIBs powder, which will be further processed through a separator.

Separator

The LIBs powder consisting of plastic, casing material, electrode, and LIBs separator will be separated using the series self-cleaning permanent magnetic separator, leaving only the active cathode material behind. This equipment requires a power of ≤ 1.5 kW with a magnetic intensity capability of ≥ 65 mT, enabling it to separate the active anode material at a speed of ≤ 4.5 m/s.

Storage Tank

The separated active cathode material will be laced into the storage tank. The storage tank has a storage capacity ranging from 0.5 m^3 to 130 m^3. It comes equipped with a machinery test report and video outgoing-inspection, allowing the addition of Cu^{2+} catalyst material as needed and enabling the monitoring of the process inside.

Bioreactor

From the storage tank, the mixed active cathode material with Cu^{2+} will produce reduced cathode materials that are then transferred into the bioreactor. This bioreactor has a container volume ranging from 10 to 100 L with a working volume of of 9.8 to 99 L. Additionally, the bioreactor is equipped with several components that support bacterial culture during the bioleaching process. These components include 2 deep gas inlets and DO control (0 - 150%) to maintain aerobic environmental conditions, an Electrical heating sleeve with bottom water for heating/cooling control at 28-30°C, and pH control (range: 2-12) set at 1-4. Furthermore, the bioreactor features a control system during the bioleaching process, consisting of four peristaltic pumps to flow the reduced cathode material into the bioreactor, as well as agitation control comprising servo motor, PID control, and stepless speed regulation.

The output of the bioleaching process is then directed to another storage tank for further processing into new batteries as alternate cleaner material (RNCA). A methodology for determine are this pilot project feasible to be done is conduct Life Cycle Assessments analysis, using ISO standard 2006. The ISO series of standard requires goal and scope definition, lifecycle inventory analysis, impacts, and interpretation [10]. The summary of Life Cycle Analysis Factors of the project written in Table 1.

Table 1. Life Cycle Assessment of Advanced Bioleaching Processes with A. *ferroxidans* of LIBs

Standards ISO Series LCA Analysis	**Description**
Goal and Scope Definition	Cradle-to-Cradle and Nominal Energy Capacity
Lifecycle Inventory Analysis	Cathode, Anode, Electrolyte, Separator, Container
Impacts and Interpretation	Climate Change (kg $CO_{2\ eq}$) Acidification (mol H^{+}_{eq}) Resource use, minerals, metals (kg Sb_{eq}) Water Scarcity (m^3 world $_{eq}$)

The cradle-to-cradle results showed that the impact category with the highest contribution to the aggregated single score was climate change and water scarcity, which accounted for between 89-93 % of total impact and give net positive impact for the project development. This was mainly due to the minimum usage of acids in the bio-hydrometallurgical process. Climate change, as before only give 27,9 kg·CO_2-equiv·$kg_{cathode}^{-1}$, is the positive impacts to determine that LCA analysis give information for the development of the project plant.

CONCLUSION

In this study, LIBs extracted in the form of Li_2CO_3 electrodes, which will then be recovered using a bioleaching process using *A. ferrooxidans*. Effect of catalysis at bioleaching process using *A.ferooxidans* is dissolve 99.9 w/t% cobalt and gives 94% efficiency at S/L ratio of 6. Electrochemical tests show that recycled Li_2CO_3 has initial capacity respectively of 102 mAh/g and capacity retention of 79% after 50 cycles at 1C while commercial percussors lower. LIBs recycling using bioleaching processes could produce weak organic acid waste and less CO_2eq: 27.9 kg·CO_2-equiv·$kg_{cathode}^{-1}$, more environmentally friendly than the cathode synthesis process from metal precursors. Generally, simple cradle-to-cradle Life Cycle Assessment from laboratory experimental data above has provided significant information about how the advanced pilot project impacts to the environment to achieve cleaner battery production. All the process flow diagram and the unit operations for the pilot plant project descripted in this study. Future studies about the current topic and industrial applications strongly recommended.

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AUTHOR CONTRIBUTION

A. D. Alhaqie, D. M. Damay and M. T. Haidar equally contributed as the main contributors of this paper. All authors read and approved the final version of the paper.

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