Heliyon 10 (2024) e40251

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Optimization of resource recovery technologies in the disassembly of waste lithium batteries: A study on selective lithium extraction

Wenbiao Liu, Banglong Wan *, Hang Ma, Jiayu Zhang

Yunnan Yuntianhua Co.Ltd. R & D Center, Kunming, 650228, China

ARTICLE INFO

Keywords:
Decommissioned lithium batteries
Carbonization water leaching
Lithium leaching rate
Roasting modification
Pollution control

ABSTRACT

This study focuses on optimizing resource recovery technology in the dismantling process of retired lithium batteries to mitigate environmental pollution. Addressing the challenge of significant precious metal losses in traditional hydrometallurgical recycling methods, this study employs a reductive roasting-carbonation leaching process to selectively extract lithium from cathode materials using a reducing agent. The study examines the effects of parameters such as roasting temperature, time, and reducing agent dosage on lithium leaching efficiency, and explores additional factors including carbonation leaching time, carbon dioxide flow rate, liquid-to-solid ratio, and leaching temperature in conjunction with multi-stage countercurrent leaching technology. Characterization of the roasting products and leaching process is performed using X-ray diffraction, scanning electron microscopy, and Fourier-transform infrared spectroscopy. The results demonstrate that, under conditions of a 700 °C roasting temperature, a 3-h roasting time, and a 15 % reducing agent dosage, the lithium leaching rate can achieve approximately 90 %. Following multi-stage countercurrent leaching, the lithium leaching rate exceeds 97 %, satisfying the purity requirements for battery-grade lithium carbonate. The innovation of this study is evident in its optimization of the recycling process, effectively separating and recovering cathode materials while reducing environmental pollution. This approach supports environmentally friendly waste treatment and contributes to the sustainable development of the battery industry.

1. Introduction

The rise of electric vehicles has led to a surge in decommissioned lithium batteries, exacerbated by the short lifespan of mobile devices, resulting in frequent battery replacements and a substantial accumulation of discarded batteries in daily life [1,2]. However, conventional wet recycling methods [3] face challenges such as significant loss of valuable metals, management complexities with waste liquids, and environmental pollution. There is an urgent need to explore more effective and environmentally friendly resource recovery technologies. Untreated discarded lithium batteries contain harmful substances like lithium, nickel, cobalt, and other metals, posing potential threats to soil, water sources, and ecosystems [4,5]. Consequently, optimizing dismantling and resource recovery processes through technological advancements has garnered significant interest among scholars across diverse disciplines, aiming to steer the battery industry towards a more environmentally sustainable trajectory.

In the extensive exploration of battery resource recovery, the emergence of various emerging technologies and optimization algorithms has provided diversified choices for addressing the challenges in handling discarded batteries. Some scholars focus on

---

* Corresponding author.
E-mail address: wanbanglong@hotmail.com (B. Wan).

https://doi.org/10.1016/j.heliyon.2024.e40251
Received 16 July 2024; Received in revised form 6 November 2024; Accepted 7 November 2024

supercritical fluid extraction technology, which utilizes fluids in a supercritical state (typically carbon dioxide) as solvents to efficiently extract valuable metals from discarded batteries. For instance, Nshizirungu et al. (2023) [6] concentrated on recovering rare metals from waste nickel-cobalt-manganese cathode materials and simultaneously defluorinating polyvinylidene fluoride in subcritical water. Their innovative approach addressed environmental issues and achieved resource recovery in the context of lithium-ion batteries. Tawonezvi et al. comprehensively assessed the recovery and recycling of valuable metals from waste lithium-ion batteries [7]. Haque et al. investigated the characteristics of extracting oil and amino acids from by-products of yellowtail fish using subcritical and supercritical fluids. This study demonstrated the potential of utilizing advanced fluid technology to extract valuable components from fishery by-products [8]. Li and Chen conducted a comparative analysis of different extraction methods for active ingredients in traditional Chinese medicine and natural products, enhancing the efficiency of pharmaceutical and herbal product development [9].

Existing research indicates that effective selective extraction of lithium can be achieved through methods such as pyrolysis and hydrogen reduction. For instance, Tao et al. demonstrated comprehensive component recovery from waste $LiCoO_2$ batteries through environmentally friendly pyrolysis and hydrometallurgical leaching, achieving leaching rates of 87.9 % for lithium and 99.1 % for cobalt [10]. Tao et al. explored a technique that combined comprehensive component pyrolysis with cathode material reduction, effectively separating lithium and other metal elements, thereby providing a novel approach for the resource recycling of lithium batteries [11]. Additionally, Liu et al. showcased an innovative pathway for selective lithium recovery and the integrated preparation of high-purity lithium hydroxide products, achieving approximately 98 % lithium conversion through reduction roasting, aqueous leaching, and lithium hydroxide crystallization [12]. Zhang et al. utilized an improved method of reduction roasting coupled with simple acid leaching, which not only enhanced the metal recovery rate but also offered an effective route for the sustainable utilization of resources [13]. These advancements demonstrate that optimizing the conditions for pyrolysis and reduction roasting can significantly enhance lithium recovery efficiency while minimizing environmental pollution and resource waste, thereby providing a scientific basis and technical support for the resource recovery of waste lithium batteries.

In recent years, various technologies and optimization algorithms have emerged to address challenges such as significant metal loss, complexities in waste liquid management, and environmental pollution associated with traditional wet recycling methods for lithium batteries. These advancements include supercritical fluid extraction, microbial leaching, and electrochemical recovery [14–16]. While these methods efficiently recover valuable metals, they often prioritize recovery over environmental concerns. The reductive roasting-carbonation leaching process offers notable advantages in the treatment of spent lithium batteries. This method selectively extracts valuable metals, particularly lithium, from cathode materials, thereby minimizing the losses of precious metals often encountered in traditional hydrometallurgical recycling methods. During the high-temperature reductive roasting phase, lithium oxides react more readily with the carbon source to form soluble lithium salts, thereby enhancing the lithium leaching rate. Despite the inherent carbon emissions associated with high-temperature roasting processes, these methods exhibit better performance in terms of environmental benefits and energy consumption compared to pyrometallurgical processes [17,18]. For example, Liu et al. investigated the synergistic enhancement mechanism of mechanical activation-microwave reduction, achieving selective lithium extraction from spent lithium-ion batteries [19]. Zhu et al. employed the carbon thermal shock method to recover valuable metals from spent lithium-ion batteries, highlighting its potential for efficient metal recovery and sustainable battery material utilization [20]. Su et al. successfully recovered valuable metals from spent lithium-ion batteries through zinc powder reduction roasting and cysteine leaching, offering an environmentally friendly and efficient resource utilization method for spent batteries [21]. Additionally, Lu et al. conducted experimental research on utilizing nano-filtration concentrate water in non-fired brick preparation, exploring the feasibility of green building materials and providing empirical support for water resource utilization and environmentally friendly brick production [22]. This approach enhances lithium recovery rates and minimizes energy consumption and environmental impact. Consequently, with the support of these innovations, it becomes feasible to recover valuable metals efficiently while mitigating environmental pollution.

Therefore, this article delves into the reduction roasting-carbonization leaching process, exploring its advantages in the recovery of discarded lithium batteries and seeking a more comprehensive solution. By technically optimizing the dismantling and resource recovery process of discarded lithium batteries, this approach improves the efficiency of valuable metal recovery, reduces resource wastage, and alleviates the negative environmental impact. This initiative promotes the battery industry toward a more

Table 1
Common waste lithium battery recycling technology table.

Method	Features	Advantages	Shortcomings
Organic solvent leaching	Dissolves valuable metals using organic solvents	Wide solvent selection, versatile applicability	Potential environmental impact of solvents
Supercritical fluid extraction	Extracts using supercritical fluids	Environmentally friendly, inorganic solvents	High equipment cost, complex operation, high energy consumption
Smelting	Melting and separating battery materials	Effective metal separation	Possible emission of harmful gases, high energy consumption
Roasting	Volatilization and metal extraction at high temperatures	Specific waste battery applicability	High temperature may cause metal loss, high energy consumption
Acid and alkali leaching	Leaching with acid-base solutions, converting metals into solutions	Simple, low operating costs	Treatment of waste liquids, environmental impact
Reduction roasting-carbonized water leaching	Combined reduction roasting and carbonization-water leaching processes	Selective extraction, low energy consumption, environmentally friendly	Complex operation, requires systematic experimental optimization

environmentally friendly and sustainable direction, aligning with the urgent societal demand for green and environmentally friendly technologies. This article provides crucial support for the sustainable development of the battery industry.

2. Reduction roasting-carbonization-water leaching process for optimizing spent lithium battery recovery

2.1. *Analysis of recovery processes for spent lithium batteries*

Recovery technologies for spent lithium batteries fall into two main categories: wet methods and dry methods. Wet methods include organic solvent leaching, acid-base leaching, and supercritical fluid extraction [23]. Dry methods encompass smelting, roasting, and gas-solid reactions [24]. Table 1 provides an overview of common recovery technologies.

As illustrated in Table 1, a comparison of various methods for recycling spent lithium batteries reveals distinct strengths and limitations for each approach. However, the reduction roasting-carbonization-water leaching process stands out with several advantages. Firstly, the reduction roasting stage facilitates the selective extraction of lithium from the positive electrode material, thereby enhancing recovery efficiency and minimizing interference from other metals. Secondly, incorporating multi-stage countercurrent leaching technology, the carbonization-water leaching phase further boosts the lithium leaching rate [25]. Precise control of parameters like leaching time, carbon dioxide flow rate, liquid-solid ratio, and temperature ensures the extraction of high-purity battery-grade lithium carbonate. Consequently, compared to conventional wet methods, the reduction roasting-carbonization-water leaching process boasts lower energy consumption, reducing resource usage and aligning with sustainability principles.

Thus, the optimized reduction roasting-carbonization-water leaching process outlined in this article efficiently recycles spent lithium battery resources and offers environmentally friendly and sustainable solutions, thereby significantly contributing to waste management efforts. Fig. 1 depicts the overall process flow of the optimized method applied to spent lithium battery recycling.

2.2. *Reduction roasting process condition experiment*

The experiment utilizes positive electrode materials from spent lithium-ion batteries, obtained from the J Electronics Factory in Shaanxi, and coke with a carbon content of 89.52 % and a particle size below 1 mm as the reducing agent. Table 2 presents the chemical composition of the positive electrode material.

The spent lithium battery materials are initially mechanically crushed to obtain fine positive electrode powder. The positive electrode powder is then mixed with coke powder in ratios of 5 %/10 %/15 %/20 %/25 %/30 %, respectively, and evenly distributed in alumina crucibles. These crucibles are subsequently placed in a box-type atmosphere furnace and heated to temperatures of 600 °C/650 °C/700 °C/750 °C/800 °C under a nitrogen atmosphere for roasting. Roasting times range from 1h to 6h. Upon completion of the roasting process, the crucibles are cooled, and the roasted products are collected, crushed into powder, and characterized using Fourier transform infrared spectroscopy analysis and scanning electron microscopy (SEM) to examine the chemical phases and morphology of the reduction roasting products [26]. The carbon content of the roasted material was determined using Eq. (1).

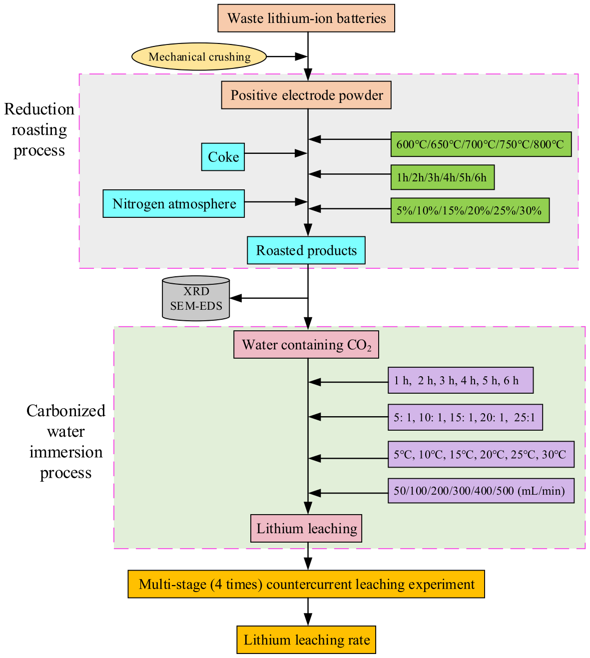

Fig. 1. Schematic representation of the optimized process flow for spent lithium battery recycling.

Table 2
Composition of positive electrode material (wt/%).

Chemical Component	Li	Co	Ni	Mn	Al	C
Content (wt/%)	6.92	26.79	11.48	3.42	4.72	2.22

$$q_0 = \frac{q_1 \times m_1 + q_2 \times m_2}{m_1 + m_2} \times 100\% \tag{1}$$

In Eq. (1), q_0 denotes the carbon content (%) in the roasted material; q_1 represents the mass fraction (%) of carbon in the pre-treated positive electrode active material; m_1 indicates the mass (g) of positive electrode active material added to the roasted material; q_2 signifies the mass fraction (%) of carbon in the coke; m_2 denotes the mass (g) of coke added to the roasted material.

2.3. Experimental conditions of carbonation water leaching process

In the carbonation water leaching experiment, roasted products obtained under various roasting conditions are utilized as raw materials. These products are immersed in pure water within a beaker, with continuous CO_2 injection into the experimental setup. CO_2 presence promotes carbonate generation, facilitating lithium dissolution. To ensure favorable conditions for carbonation water leaching, a liquid-to-solid ratio of 1:1 is maintained, along with adequate reaction time (1.5 h), and a leaching temperature of 100 °C to enhance lithium dissolution. The impact of different roasting conditions (temperature, time, and product composition) on lithium extraction efficiency via carbonation water leaching is systematically explored, aiming to identify optimal roasting conditions for maximizing lithium extraction efficiency.

Moreover, the roasted products obtained under optimal conditions serve as leaching materials for the carbonation water leaching condition experiments, aiming to further enhance lithium leaching efficiency by optimizing the carbonation water leaching process. In carbonation water leaching, the duration of leaching directly impacts the extent of the reaction, while leaching temperature and liquid-to-solid ratio, to some extent, regulate the rate and effectiveness of the reaction [27,28]. Additionally, the CO_2 ventilation rate, a crucial atmospheric parameter, helps maintain alkaline conditions, promotes lithium dissolution, and simultaneously inhibits aluminum dissolution, thereby enhancing lithium leaching effectiveness [29]. This experiment investigates the effects of different leaching durations, temperatures, liquid-to-solid ratios, and CO_2 ventilation rates on lithium leaching rate to achieve maximal lithium leaching efficiency. The carbonation reactions involved in the process are described by Eqs. (2)–(4):

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \tag{2}$$

$$H_2CO_3(aq) \rightarrow HCO_3{}^{-}(aq) + H^{+}(aq) \tag{3}$$

$$HCO_3{}^{-}(aq) \rightarrow CO_3{}^{2-}(aq) + H^{+}(aq) \tag{4}$$

For lithium-containing cathode materials, such as lithium transition metal oxides (e.g., $LiCoO_2$), the carbonation leaching process can be represented by Eq. (5):

$$LiCoO_2(s) + H_2O(l) + CO_2(g) \rightarrow Li_2CO_3(aq) + Co(OH)_2(s) \tag{5}$$

This equation describes the process in which lithium transition metal oxides (e.g., $LiCoO_2$) react with water and carbon dioxide during the carbonic acid leaching process to produce soluble lithium carbonate and transition metal hydroxides.

The underlying principles of this equation are as follows.

(1) Formation of Carbonic Acid: In the carbonic acid leaching process, carbon dioxide (CO_2) reacts with water (H_2O) to form carbonic acid (H_2CO_3), which is a reversible reaction.
(2) Dissociation of Carbonic Acid: Carbonic acid (H_2CO_3) further dissociates into bicarbonate ions (HCO_3^-) and hydrogen ions (H^+). Subsequently, bicarbonate ions can further dissociate into carbonate ions (CO_3^{2-}) and additional hydrogen ions (H^+).
(3) Leaching of Lithium: Carbonate ions (CO_3^{2-}) react with lithium ions (Li^+) from lithium transition metal oxides ($LiCoO_2$) to form soluble lithium carbonate (Li_2CO_3).
(4) Precipitation of Transition Metals: Transition metals (Co) precipitate out in the form of hydroxides ($Co(OH)_2$).

Further dissolution of lithium carbonate is represented by Eq. (6):

$$Li_2CO_3(s) + H_2O(l) \rightarrow 2Li^{+}(aq) + CO_3{}^{2-}(aq) \tag{6}$$

Here, lithium carbonate dissolves in water, producing lithium ions and carbonate ions.

The equation for calculating the lithium leaching rate α is shown in Eq. (7).

$$\alpha = \frac{c_1 \times v_1}{y_0 \times m_0} \times 100\% \tag{7}$$

Here, α refers to the percentage of lithium leached; y_0 represents the lithium content in the material before leaching (%); m_0 denotes the mass of the material before leaching (g); c_1 signifies the lithium concentration in the leachate (g/L); v_1 stands for the volume of the leachate (mL).

2.4. *Multi-stage countercurrent leaching experiment*

In the multi-stage countercurrent leaching experiment, the optimal conditions of carbonization leaching are maintained while experiments on leachate and leach residue under different liquid-to-solid ratios are conducted. This approach allows for a thorough investigation of the leaching effect of multi-stage countercurrent leaching on lithium and impurity metals during the carbonization leaching process. The experiment controls the liquid-to-solid ratios of the leachate at 5:1, 10:1, 15:1, and 20:1, with a constant leaching time of 1.5 h, CO_2 gas flow rate of 200 mL/min, and leaching temperature of 20 °C for carbonization leaching. After each leaching cycle, the leachate is used as the leaching agent for the subsequent cycle.

Similarly, multiple cycles of leachate circulation experiments are conducted with liquid-to-solid ratios of 5:1, 10:1, 15:1, and 20:1, maintaining a leaching time of 1.5 h, CO_2 gas flow rate of 200 mL/min, and leaching temperature of 10 °C. Following each leaching cycle, the leach residue serves as the leaching material for the next cycle. After several cycles of leachate circulation, a lithium-rich leachate is obtained. This leachate underwent thermal decomposition, evaporation, and crystallization processes to produce high-purity Li_2CO_3. The lithium concentration and other impurity metal concentrations in the leachate are determined using the Inductively Coupled Plasma method, and their theoretical concentration and leaching rate are calculated.

2.5. *Characterization analysis and detection methods*

In XRD analysis, the roasting and leaching residues' phase compositions were determined using the Empyrean Multipurpose X-ray Scatterer from Marvin Panaco (Fig. 2a), providing insights into their crystalline structure. Scanning electron microscopy with SEM analysis, conducted with the Bruker's S8 TIGER X-ray fluorescence spectrometer (Fig. 2b), allowed for detailed investigations into the microstructure and composition of the roasting residue, elucidating surface morphology and element distribution.

For the reduction roasting process of positive electrode waste, the Netzsch STA449F3 synchronous thermal analyzer was employed to comprehensively understand thermal behavior in high-temperature environments, which is crucial for elucidating chemical reactions and material transformations during roasting.

Lastly, the Thermo Fisher Nicolet iS50 Fourier-transform infrared spectrometer was utilized to analyze the molecular structure and composition of the ternary positive electrode waste powder and roasting products, aiding in the identification of changes in organic components within the waste and the structural characteristics of the products.

3. Results and discussion

3.1. *Analysis of reduction roasting conditions*

The analysis commences with an examination of calcination temperature. While maintaining a constant calcination time of 3 h and carbon content in the calcination material at 15 %, the influence of varying calcination temperatures (600 °C/650 °C/700 °C/750 °C/800 °C) on lithium leaching through water immersion is investigated. The results are presented in Fig. 3. Subsequently, the analysis extended to calcination time. With a constant calcination temperature of 700 °C and carbon content in the calcination material set at 15 %, the impact of different calcination times (1 h/2 h/3 h/4 h/5 h/6 h) on lithium leaching through water immersion is examined. Fig. 4 illustrates the research findings. Lastly, the article encompasses an analysis of the carbon content in the calcination material. While maintaining a constant calcination temperature of 700 °C and a calcination time of 3 h, the investigation explores the effect of different carbon contents in the calcination material (5 %/10 %/15 %/20 %/25 %/30 %) on lithium leaching through water immersion. The results are depicted in Fig. 5. Multiple repeated experiments are performed, with error bars representing the variability or

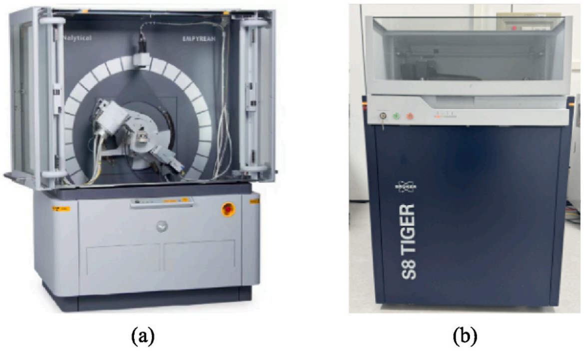

Fig. 2. Characterization analysis equipment (a. Emprean Multipurpose X-ray Scatterer; b. S8 TIGER X-ray Fluorescence Spectrometer).

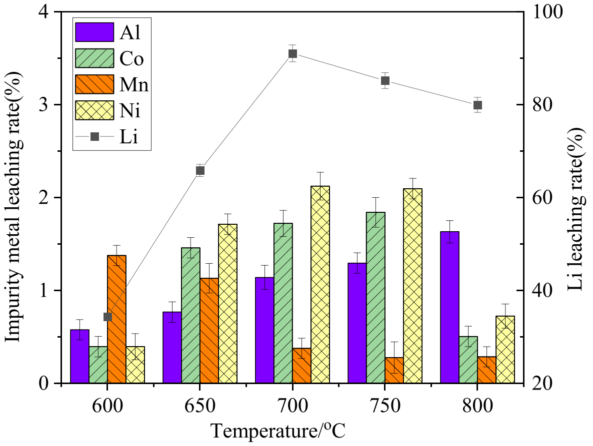

Fig. 3. Relationship between metal leaching rates at different roasting temperatures, with a roasting time of 3 h and a carbon content of 15 % in the roasting material.

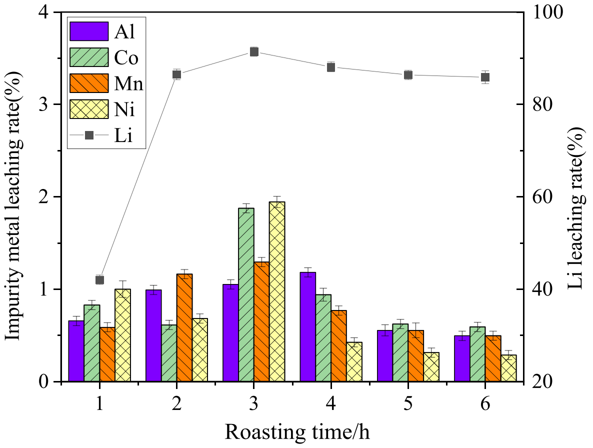

Fig. 4. Relationship between metal leaching rates at different roasting times, with a roasting temperature of 700 °C and a carbon content of 15 % in the roasting material.

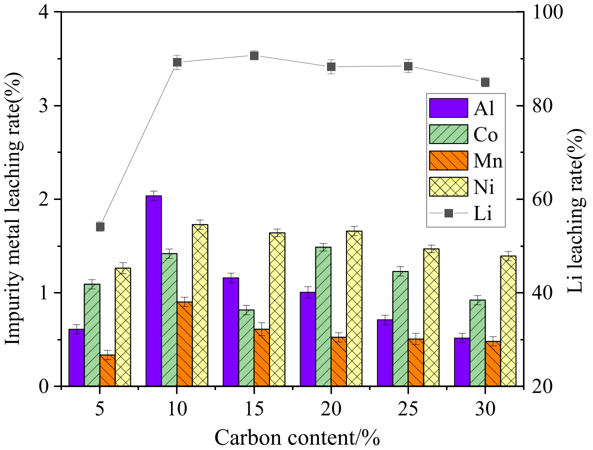

Fig. 5. Relationship between metal leaching rates at different carbon contents, with a roasting temperature of 700 °C and a roasting time of 3 h.

uncertainty of the data. These error bars indicate the dispersion of lithium extraction rates observed under varying experimental conditions.

Fig. 3 illustrates the leaching rates of lithium (Li) and select impurity metals (Al, Co, Mn, Ni) at various sintering temperatures. The leaching rate of lithium increases with higher sintering temperatures, ranging from 34.33 % at 600 °C to 91.05 % at 700 °C. Conversely, impurity metals such as aluminum show variable trends at different temperatures. From a kinetic perspective, roasting temperature significantly influences the reaction rate between lithium oxides and reducing agents in solid materials. At lower temperatures, the reaction rate is slower due to the higher energy required for activation. As the temperature rises, the thermal energy of the reactant molecules increases, leading to a higher frequency and energy of collisions, which accelerates the reduction reaction of lithium and thus enhances the lithium leaching rate. However, excessively high temperatures may damage the structure of the reducing agent or lithium oxides, reducing the effective reaction area or causing over-reduction of lithium oxides, which can decrease the leaching rate. Consequently, an optimal roasting temperature exists at which the lithium leaching rate is maximized. Thus, adjusting the sintering temperature can effectively enhance lithium leaching, with the highest rate (91.05 %) achieved at 700 °C.

Fig. 4 depicts the leaching rates of lithium (Li) and several impurity metals (Al, Co, Mn, Ni) at different calcination times. As the calcination time increases, the leaching rate of lithium gradually rises, reaching 91.43 % at 3 h compared to 42.04 % at 1 h. In contrast, the leaching rates of impurity metals show diverse trends, peaking at different times. For instance, cobalt (Co) peaks at 3 h (1.88 %), while aluminum (Al) and nickel (Ni) peak at 2 h (0.99 % and 1.00 %, respectively). This indicates varying effects of calcination time on lithium and impurity metal leaching. From a kinetic perspective, roasting time plays a crucial role in determining the duration of the reaction between lithium oxides and reducing agents. Insufficient roasting time may result in incomplete reduction of lithium, leading to a lower leaching rate. As the roasting time is extended, more lithium oxides have the opportunity to react with the reducing agent, thereby enhancing the lithium leaching rate. However, once the roasting time exceeds a certain threshold, the reaction approaches completion, and further increases in time yield diminishing returns in the leaching rate. Excessively prolonged roasting times may also cause over-destruction of the material structure, adversely affecting the further release of lithium. Overall, a 3-h calcination time yields higher lithium leaching rates, aiming for efficient lithium extraction while minimizing impurity metal impact.

Fig. 5 presents the leaching rates of lithium (Li) and selected impurity metals (Al, Co, Mn, Ni) at varying carbon contents. The lithium leaching rate experiences fluctuations, increasing from 54.15 % at 5 % carbon content to 90.75 % at 15 %, followed by a slight decrease. In contrast, diverse impurity metals exhibit distinct responses to changes in carbon content. For instance, aluminum (Al) and cobalt (Co) achieve peak leaching rates at 10 % and 15 % carbon content, respectively. Meanwhile, manganese (Mn) and nickel (Ni) show less fluctuation at different carbon contents. In conclusion, efficient lithium extraction with effective control over impurity metals is attainable at a carbon content of 15 %. Regarding the characterization of reduction-roasting products, the presence of P-O bonds, O-P-O bonds, and C-O bonds indicates diverse reactions between organic and inorganic substances during the roasting process. From a kinetic perspective, carbon content significantly impacts the amount of reducing agent available, thereby influencing the reduction reaction of lithium. Low carbon content may indicate insufficient reducing agent, restricting the reduction of lithium oxides and resulting in a lower lithium leaching rate. As carbon content increases, a greater quantity of reducing agent participates in the reaction, improving the reduction efficiency of lithium and consequently enhancing the leaching rate. However, excessively high carbon content can lead to an overabundance of reducing agent, potentially forming a barrier on the material's surface that impedes the release of lithium ions or causing over-reduction, which may adversely affect the lithium leaching rate. Thus, an optimal carbon content exists where the lithium leaching rate is maximized. Furthermore, well-defined lithium carbonate crystals with a rod-like structure are observed, suggesting that lithium reacts with carbonate to form ordered crystalline substances after roasting.

Thermodynamic analysis of Figs. 3–5 indicates that elevated roasting temperatures promote the structural breakdown of cathode materials, facilitating the release of lithium ions. A roasting temperature of 700 °C is identified as optimal for the reduction of lithium

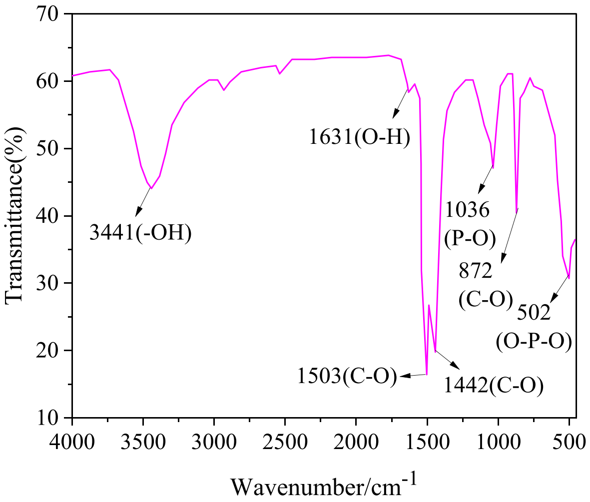

Fig. 6. FTIR analysis of the reduction-baked product under optimal process conditions.

oxides to lithium ions, as it enables the formation of soluble lithium salts through reactions between lithium oxides and the carbon source. Extending the roasting time ensures sufficient duration for the complete reduction of lithium ions, with 3 h potentially representing the point at which reduction and migration of lithium ions reach dynamic equilibrium. Regarding carbon content, a suitable amount of carbon acts as a reducing agent, enhancing the reduction of lithium oxides to lithium ions. However, excessive carbon content can form a surface layer that obstructs further release of lithium ions. Thus, a carbon content of 15 % represents an optimal balance for the reduction reaction and lithium ion release. These findings suggest that optimizing roasting conditions can significantly improve lithium leaching efficiency, offering a theoretical foundation for subsequent lithium recovery processes. Additionally, the small error bars observed indicate better reproducibility of the experimental results and greater data stability.

Additional characterization analysis was conducted on the reduction-baked product under optimal process conditions (700 °C, 3 h, 15 % carbon content). Fourier-transform infrared spectroscopy (FTIR) analysis is depicted in Fig. 6, while SEM images are provided in Figs. 7 and 8 illustrates the XRD analysis.

The characterization analysis of the reduction-baked product, as depicted in Fig. 6, reveals the presence of P-O bonds, O-P-O bonds, and C-O bonds. These bonds signify diverse reactions between organic and inorganic substances during the baking process. The P-O bonds suggest bonding between phosphorus and oxygen, likely originating from phosphorus-containing components in the original ore or introduced external phosphorus sources during baking. The O-P-O bonds represent typical structures of phosphorus oxides, indicating oxygen-phosphorus atom bonding. Additionally, the presence of C-O bonds indicates carbon-oxygen atom bonding, likely resulting from oxidation reactions of organic carbon sources at high temperatures. These interactions between organic and inorganic substances may influence the leaching process of lithium. Furthermore, as observed in Fig. 7, well-defined lithium carbonate crystal phases with a rod-like structure are evident. This suggests that lithium reacted with carbonate post-baking to form crystalline substances, exhibiting relatively ordered crystalline morphology. SEM observations reveal significant alterations in the surface morphology of the material following roasting, including increased porosity and the formation of cracks. These structural changes enhance the leaching efficiency of lithium and other metal ions. FTIR analysis corroborates modifications in the chemical bonding between organic and inorganic substances, indicating the development of a new chemical environment that facilitates lithium leaching during the reduction roasting process. Collectively, these findings demonstrate that a lithium leaching rate exceeding 97 % is achieved under optimized roasting and leaching conditions. The study also provides valuable insights into how structural changes in the material influence lithium recovery efficiency, offering substantial technical support for the resource recovery and environmentally friendly treatment of retired lithium batteries.

As shown in Fig. 8, the X-ray diffraction (XRD) pattern of the reduction roasting products obtained under optimal process conditions—specifically, a roasting temperature of 700 °C, a roasting time of 3 h, and a reducing agent dosage of 15%—is presented. This spectrum clearly reveals the crystal structure and phase composition of the roasting products, providing essential information for understanding the behavior of lithium and other metal ions during the reduction roasting process. The XRD pattern indicates the formation of phases such as lithium carbonate, suggesting that lithium oxides reacted with the carbon source to generate soluble lithium salts during the reduction roasting process. This result demonstrates that under the conditions outlined in this study, selective extraction and efficient recovery of lithium are achieved through precise control of the roasting parameters while minimizing the loss of precious metals. This is of significant importance for enhancing the resource recovery efficiency of spent lithium-ion batteries and reducing environmental pollution.

3.2. Analysis of carbonization water immersion conditions

The analysis of carbon dioxide (CO_2) flow rates is initiated, maintaining a constant leaching time of 3 h, leaching temperature at 20 °C, and a leaching liquid-to-solid ratio of 15:1. The CO_2 flow rates are set at 50 mL/min, 100 mL/min, 200 mL/min, 300 mL/min, 400 mL/min, and 500 mL/min for the leaching experiments. The results are presented in Fig. 9. Subsequently, an analysis of carbonation leaching times is carried out, with a constant CO_2 flow rate of 300 mL/min, leaching temperature of 20 °C, and a leaching liquid-to-solid ratio of 15:1. Leaching times are varied from 1 h to 6 h for the experiments, and the results are depicted in Fig. 10. Following that, an analysis of the liquid-to-solid ratio is performed, maintaining a constant leaching time of 3 h, leaching temperature of 20 °C, and a CO_2 flow rate of 300 mL/min. The leaching liquid-to-solid ratios are set at 5:1, 10:1, 15:1, 20:1, and 25:1 for the experiments, and the results are shown in Fig. 11. Finally, an analysis of leaching temperature is conducted, with a constant leaching

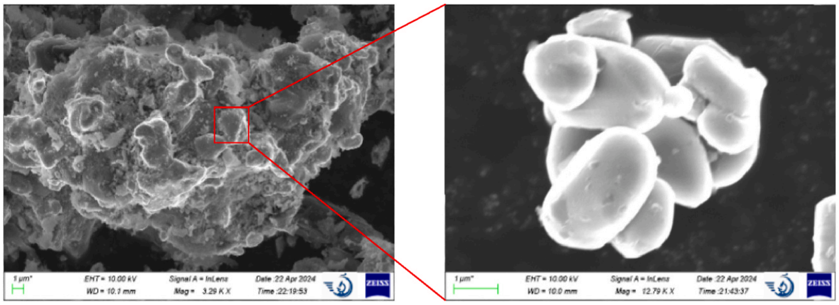

Fig. 7. SEM images of the reduction-baked product under optimal process conditions.

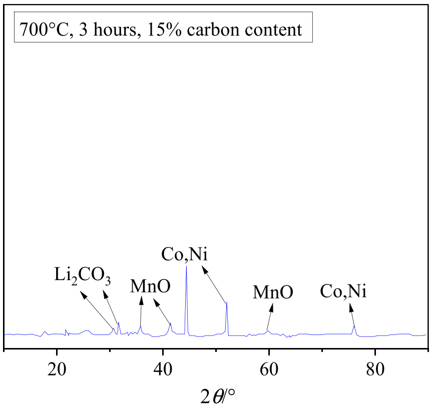

Fig. 8. XRD pattern of reduction roasting products under optimal process conditions.

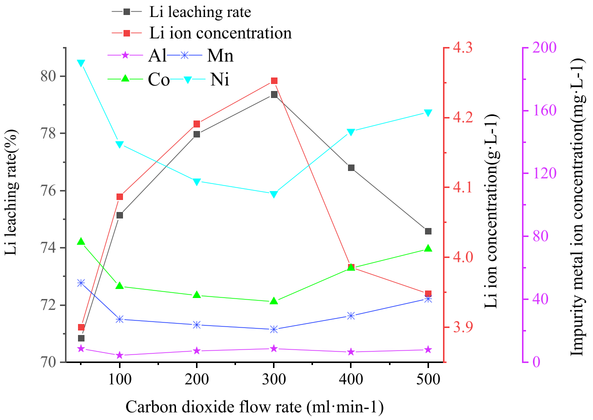

Fig. 9. Relationship between CO_2 flow rate, Li leaching rate, and metal ion concentration.

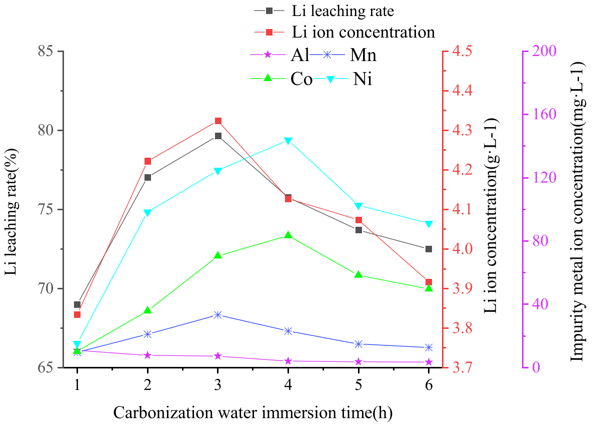

Fig. 10. Relationship between carbonation leaching time, Li leaching rate, and metal ion concentration.

time of 3 h, CO_2 flow rate of 300 mL/min, and leaching liquid-to-solid ratio of 15:1. Leaching temperatures varied from 5 °C to 30 °C for the experiments, and the results are illustrated in Fig. 12.

Figs. 9–12 illustrates the impact of various parameters—carbon dioxide flow rate, carbonation leaching time, liquid-to-solid ratio, and leaching temperature—on the leaching rates of lithium (Li) and impurity metals (Al, Co, Mn, Ni). Analyzing these parameters provides a deeper understanding of the thermodynamic characteristics of the carbonation leaching process.

Fig. 8 demonstrates that the carbon dioxide flow rate significantly influences the lithium leaching rate. As the carbon dioxide flow

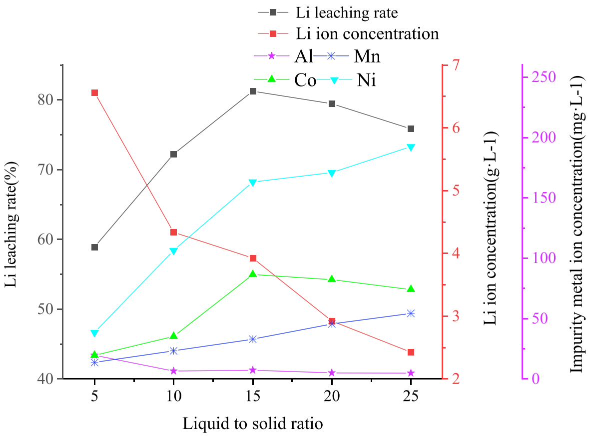

Fig. 11. Relationship between liquid-to-solid ratio, Li leaching rate, and metal ion concentration.

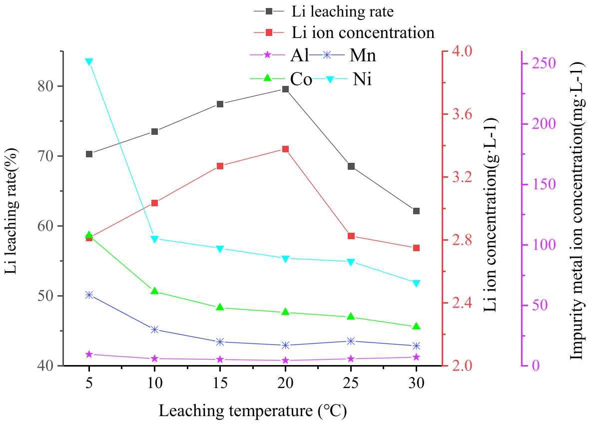

Fig. 12. Relationship between leaching temperature, Li leaching rate, and metal ion concentration.

rate increases, the concentration of carbonate ions also rises, enhancing the solution's alkalinity and facilitating the dissolution of lithium ions. However, beyond a certain flow rate threshold (300 mL/min in this study), further increases in the carbon dioxide flow rate result in diminishing returns for lithium leaching efficiency. This phenomenon may be due to the potential over-saturation of carbonate ions in the solution, which could impede the effective dissolution of lithium ions.

Fig. 9 highlights the critical role of carbonation leaching time in influencing the lithium leaching rate. Extended leaching time facilitates a more thorough reaction between lithium and carbonate ions, which enhances the leaching rate. However, beyond a certain threshold (3 h in this study), additional increases in leaching time yield diminishing returns. This plateau occurs as the leaching process approaches equilibrium, rendering further time extensions less effective in improving the leaching rate.

Fig. 10 illustrates the impact of the liquid-to-solid ratio on the leaching rate. A lower liquid-to-solid ratio results in less solution interacting with a fixed amount of solid material, thereby decreasing the opportunities for lithium ions to react with the solution and reducing the leaching rate. Conversely, an increase in the liquid-to-solid ratio enhances the reaction by providing more solution, which improves the lithium leaching rate. Nonetheless, an excessively high liquid-to-solid ratio may dilute the solution, decreasing ion strength and limiting further improvements in the leaching rate.

Fig. 11 demonstrates that leaching temperature has a significant impact on the lithium leaching rate. Within a specific temperature range, increasing the temperature enhances the reaction rate between lithium and carbonate ions, thereby improving the leaching rate. However, when the temperature exceeds the optimal level (15 °C in this study), excessively high temperatures can lead to the decomposition or volatilization of carbonate ions in the solution. This results in a decreased concentration of effective reactants and a subsequent reduction in the lithium leaching rate.

These parameters collectively influence the reaction kinetics and thermodynamic equilibrium between lithium and carbonate ions during the carbonation leaching process, thereby determining the lithium leaching rate. Optimal adjustment of these parameters can significantly enhance the efficiency of lithium leaching while effectively controlling the leaching of impurity metals, leading to more efficient and selective lithium recovery.

3.3. Analysis of lithium leaching rate in a multi-stage circulation process

In-depth analysis is conducted under the conditions of a carbon dioxide flow rate of 300 mL/min, a carbonation leaching time of 3 h, and a leaching temperature of 15 °C to investigate the lithium leaching rate after multi-stage circulation at different liquid-to-solid ratios, as depicted in Fig. 12. Additionally, with the carbon dioxide flow rate maintained at 300 mL/min, the carbonation leaching time at 3 h, and a liquid-to-solid ratio of 15:1, the lithium leaching rate after multi-stage circulation at different leaching temperatures is analyzed, as shown in Fig. 13.

Figs. 12 and 13 illustrate the effects of different liquid-to-solid ratios and leaching temperatures on lithium (Li) leaching rates during a multi-stage countercurrent leaching process. The data reveal that as the number of cycles increases, the lithium leaching rate improves progressively, particularly when the liquid-to-solid ratio is 15:1. After four cycles, the lithium leaching rate can reach 98.40 %. Additionally, varying leaching temperatures also show a significant increase in lithium leaching rates with the number of cycles. This trend can be attributed to the multi-stage countercurrent process, wherein each cycle enhances the transfer of lithium ions from the solid material into the solution. An optimal liquid-to-solid ratio and leaching temperature create favorable conditions for the dissolution and migration of lithium ions. A liquid-to-solid ratio of 15:1 ensures a higher solution volume, which increases the contact area between lithium ions and the solution, thereby enhancing their dissolution. Similarly, a leaching temperature of 20 °C is close to the optimal temperature for lithium ion dissolution, promoting the highest dissolution rate and migration efficiency. Consequently, after four cycles at a liquid-to-solid ratio of 15:1 and a leaching temperature of 20 °C, the lithium leaching rate is maximized. These factors collectively contribute to a substantial enhancement in lithium leaching efficiency over multiple cycles.

A comprehensive elemental analysis of the leach residue was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), as detailed in Table 3.

As shown in Table 3, while lithium content is notably reduced, the leach residue remains rich in transition metals such as nickel, cobalt, and manganese. This indicates that despite the efficient extraction of lithium, the residue retains significant potential for the recovery and reuse of these valuable metals. The relatively high levels of aluminum and iron are likely linked to the original chemical composition of the cathode material and the physicochemical transformations that occurred during the reductive roasting process. The presence of these elements points to the possibility of further processing to recover additional resources from the leach residue. This study not only emphasizes the efficient recovery of lithium but also offers a scientific and technical foundation for the sustainable utilization of the entire cathode material.

4. Conclusion

This study successfully optimizes the lithium recovery process from spent lithium-ion batteries through a reductive roasting and carbonation leaching technique. By carefully controlling the roasting temperature, duration, and dosage of the reducing agent, a lithium leaching rate of approximately 90 % is achieved. The implementation of a multi-stage counter-current leaching process further enhances lithium recovery efficiency to over 97 %, meeting the purity requirements for battery-grade lithium carbonate. Characterization via SEM and FTIR reveals significant structural and morphological changes in the cathode material induced by the reductive roasting process, which facilitates the efficient leaching of lithium and other metals. Additionally, chemical analysis of the leach residue demonstrates that, while lithium content is substantially reduced, valuable metals such as cobalt, nickel, and manganese remained enriched, indicating potential for further resource recovery. These findings provide valuable insights into the comprehensive recovery and environmentally sustainable treatment of the entire cathode material.

Despite significant progress in improving lithium recovery efficiency, several limitations and areas for future enhancement remain. First, the current process primarily targets lithium recovery, while the recovery of valuable metals such as cobalt, nickel, and manganese from the leach residue has not been fully explored. Future research should focus on developing more efficient metal separation

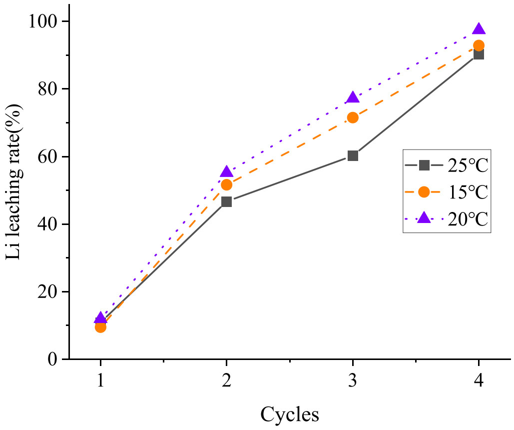

Fig. 13. Results of lithium leaching rate after multi-stage circulation at different leaching temperatures.

Table 3
Elemental composition of the leach residue.

Element	Li	Co	Ni	Mn	Al	Fe
Content (wt%)	0.55	5.32	3.87	1.45	7.21	2.94

and recovery techniques to ensure comprehensive extraction of all valuable components within the cathode material. Second, this study does not address the management and utilization of waste gases and liquids generated during the reductive roasting process, which could raise environmental concerns. Future investigations should prioritize the development of more sustainable roasting technologies and explore the resource recovery of by-products to create a closed-loop, environmentally friendly recycling process for lithium batteries. Advancing these areas will further enhance recycling technologies and contribute to the green transition and circular economy in the battery industry.

CRediT authorship contribution statement

Wenbiao Liu: Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Banglong Wan:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Methodology, Formal analysis, Data curation. **Hang Ma:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **Jiayu Zhang:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Investigation, Formal analysis, Data curation.

Data availability statements

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by New Energy Material Innovation Consortium Projects of Yunnan Province (202302AB080018).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e40251.

References

[1] V. Chaudhary, P. Lakhera, K.H. Kim, et al., Insights into the eco-friendly recovery process for valuable metals from waste lithium-ion batteries by organic acids leaching, Sep. Purif. Rev. 53 (1) (2024) 82–99.
[2] K.H. Chan, J. Anawati, M. Malik, et al., Closed-loop recycling of lithium, cobalt, nickel, and manganese from waste lithium-ion batteries of electric vehicles, ACS Sustain. Chem. Eng. 9 (12) (2021) 4398–4410.
[3] T. Zhao, W. Li, M. Traversy, et al., A review on the recycling of spent lithium iron phosphate batteries, J. Environ. Manag. 351 (2024) 119670.
[4] S. Wang, J. Yu, A comparative life cycle assessment on lithium-ion battery: case study on electric vehicle battery in China considering battery evolution, Waste Manag. Res. 39 (1) (2021) 156–164.
[5] S. Oh, S. Park, K. Yoo, Isothermal battery calorimetry analysis on a thermal behavior of Li-ion battery for electric vehicle, J. Energy Storage 75 (2024) 109678.
[6] T. Nshizirungu, M. Rana, M.I.H. Khan, et al., Rare metals recycling from spent NCM cathode materials and simultaneous dehydrofluorination of polyvinylidene fluoride (PVDF) in subcritical water, J. Environ. Chem. Eng. 11 (1) (2023) 109160.
[7] T. Tawonezvi, M. Nomnqa, L. Petrik, et al., Recovery and recycling of valuable metals from spent lithium-ion batteries: a comprehensive review and analysis, Energies 16 (3) (2023) 1365.
[8] A.R. Haque, J.S. Park, T.C. Ho, et al., Characterization of oil and amino acids obtained from yellow corvina by-products using subcritical and supercritical fluids, J. Supercrit. Fluids 199 (2023) 105970.
[9] G. Li, D. Chen, Comparison of different extraction methods of active ingredients of Chinese medicine and natural products, J. Sep. Sci. 47 (1) (2024) 2300712.
[10] R. Tao, P. Xing, H. Li, Z. Sun, Y. Wu, Recovery of spent LiCoO2 lithium-ion battery via environmentally friendly pyrolysis and hydrometallurgical leaching, Res. Conserv. Recycl. 176 (2022) 105921.
[11] R. Tao, P. Xing, H. Li, Y. Wu, S. Li, Z. Sun, Full-component pyrolysis coupled with reduction of cathode material for recovery of spent LiNixCoyMnzO2 lithium-ion batteries, ACS Sustain. Chem. Eng. 9 (18) (2021) 6318–6328.
[12] F. Liu, C. Peng, Q. Ma, J. Wang, S. Zhou, Z. Chen, et al., Selective lithium recovery and integrated preparation of high-purity lithium hydroxide products from spent lithium-ion batteries, Sep. Purif. Technol. 259 (2021) 118181.
[13] Y. Zhang, W. Wang, Q. Fang, S. Xu, Improved recovery of valuable metals from spent lithium-ion batteries by efficient reduction roasting and facile acid leaching, Waste Manag. 102 (2020) 847–855.

[14] J. Dutzi, N. Boukis, J. Sauer, Process effluent recycling in the supercritical water gasification of dry biomass, Processes 11 (3) (2023) 797.

[15] Z. Tong, X. Ren, M. Ni, et al., Review of ultrasound-assisted recycling and utilization of cathode materials from spent lithium-ion batteries: state-of-the-art and outlook, Energy Fuels 37 (19) (2023) 14574–14588.

[16] M. Ilić, F.H. Haegel, A. Lolić, et al., Surface functional groups and degree of carbonization of selected chars from different processes and feedstock, PLoS One 17 (11) (2022) e0277365.

[17] K. Yan, Q. Chen, Z. Xiong, et al., A novel method for the recovery of Li from spent lithium-ion batteries using reduction roasting–countercurrent leaching, JOM 74 (10) (2022) 3821–3832.

[18] S. Jin, D. Mu, Z. Lu, et al., A comprehensive review on the recycling of spent lithium-ion batteries: urgent status and technology advances, J. Clean. Prod. 340 (2022) 130535.

[19] C. Liu, J. Long, W. Luo, et al., Synergistic strengthening mechanisms of mechanical activation-microwave reduction for selective lithium extraction from spent lithium batteries, Waste Manag. 155 (2023) 281–291.

[20] X.H. Zhu, Y.J. Li, M.Q. Gong, et al., Recycling valuable metals from spent lithium-ion batteries using carbothermal shock method, Angew. Chem. 135 (15) (2023) e202300074.

[21] F. Su, Q. Meng, X. Liu, et al., Recovery of valuable metals from spent lithium-ion batteries via zinc powder reduction roasting and cysteine leaching, Sci. Total Environ. 912 (2024) 169541.

[22] R. Lu, L. Li, J. Yao, et al., Experimental study on the application of nanofiltration concentrated water in the preparation of burning-free bricks. Energy Sources Part A Recovery Util, Environ. Eff. 46 (1) (2024) 2093–2108.

[23] H. Song, S. Fan, S. Zhang, et al., Strength deterioration prediction of pervious concrete in sulfate and dry-wet cycle environments utilizing ultrasonic velocity, PLoS One 18 (6) (2023) e0286948.

[24] Z. Dobó, T. Dinh, T. Kulcsár, A review on recycling of spent lithium-ion batteries, Energy Rep. 9 (2023) 6362–6395.

[25] S. Kim, S.E. Lee, S.H. Baek, et al., Preparation of activated carbon from Korean anthracite: simultaneous control of ash reduction and pore development, Processes 11 (10) (2023) 2877.

[26] S. Zhang, R. Wang, J. Chu, et al., Vegetable extracts: effective inhibitors of heterocyclic aromatic amines and advanced glycation end products in roasted Mackerel, Food Chem. 412 (2023) 135559.

[27] D. Spagnuolo, V. Bressi, M.T. Chiofalo, et al., Using the aqueous phase produced from hydrothermal carbonization process of Brown seaweed to improve the growth of phaseolus vulgaris, Plants 12 (14) (2023) 2745.

[28] J. Li, L. Ding, Z. Su, et al., Non-lignin constructing the gas–solid interface for enhancing the photothermal catalytic water vapor splitting, Adv. Mater. 35 (45) (2023) 2305535.

[29] S. Rashid, M. Singh, An investigation on carbon dioxide incorporated sustainable ready-mix concrete using OPC and PPC, Arab. J. Sci. Eng. 48 (10) (2023) 14213–14236.