

Role of Mechanical Activation in Enhancing Li and Co Recovery from Spent Li-ion Batteries through Citric Acid Leaching

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ABSTRACT

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This study investigates the effect of mechanical activation parameters such as mechanical activation rotation speed (0-550 rpm), mechanical activation time (15-75 min), and solid/ball ratio (1/20-1/50) on the leaching efficiencies in the recycling of lithium-ion batteries. In addition to mechanical activation, the study explores the use of organic acids, specifically citric acid, as leaching agents to enhance metal recovery. A green and innovative recycling process is developed, focusing on optimal conditions of 15 minutes activation time, 450 rpm rotational speed, and a 1/20 solid/ball ratio. The synergistic effect of mechanical activation and organic acid leaching is examined to optimize the process for sustainability and efficiency in recovering valuable metals from lithium-ion batteries. Results indicate that these parameters significantly influence leaching efficiencies, with the highest yields achieved under the identified conditions. This research contributes to advancing sustainable practices in battery recycling by integrating mechanical activation and organic acid leaching as effective and environmentally friendly approaches. The findings highlight the potential of these methods in advancing green technology and materials science, paving the way for more efficient and eco-friendly battery recycling processes.

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1. Introduction

With the increasing use of lithium-ion batteries in portable devices and particularly in automobiles, the demand for sustainable battery components and resources is growing daily. Considering the energy demands in the battery sector, the energy demand, which was 102 GW-hours in 2017, is projected to reach 709 GW-hours by 2026 [1]. Additionally, to reduce carbon dioxide emissions, the sales of electric cars, which were 2 million in 2018, are expected to reach approximately 11 million by 2025 [2].

However, with the anticipated increase in the supply of lithium-ion batteries, while carbon dioxide emissions are reduced, another adverse

effect is looming for the planet. London-based Circular Energy Storage (CES) estimates that China alone produced half a million tons of lithium-ion battery waste by 2020, and this number is expected to reach two million tons annually by 2030 when considering global consumption. Certain materials found in lithium-ion battery waste, such as heavy metals and toxic electrolytes, pose specific threats to ecosystems and human health. Approximately 1,100 tons of the 4,000 tons of lithium-ion battery waste consist of heavy metals, and over 200 tons are toxic electrolytes [1]. Therefore, if lithium battery waste is disposed of through methods other than recycling, it will lead to numerous adverse effects. For instance, if disposed of through solid waste landfilling, the dissolution of

toxic heavy metals into groundwater could cause severe environmental pollution. Similarly, if lithium-ion battery waste is incinerated as general solid waste, it will produce significant amounts of toxic gases, such as hydrogen fluoride (HF), polluting the atmosphere.

Therefore, it is crucial to process waste lithium-ion batteries in the least harmful way to humans and nature. Furthermore, an average waste lithium-ion battery contains 5-20% Co, 5-7% Li, 5-10% Ni, 5-10% Cu, other metals like Al and Fe, 15% organic compounds, and 7% plastics [3]. The significant number of valuable metals in waste lithium-ion batteries, often exceeding the content found in some natural ores, provides substantial economic value [3]. Thus, the primary goal of recycling waste lithium-ion batteries is to reduce or eliminate potential environmental impacts; the secondary goal is to ensure an industrially sustainable and improvable lithium-ion battery industry through the recovery of valuable metals.

Therefore, recycling waste lithium-ion batteries not only complies with environmental requirements but also serves as an alternative source for conserving valuable metals. A lithium-ion battery typically consists of an anode, cathode, binder, electrolyte solution, separator, current collectors, and plastic and metallic outer layers. Besides carbon, other materials like SiO_x , silicon, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be used as anodes, but natural graphite is preferred due to its low cost, high efficiency, and high capacity [4, 5]. The binder, which usually is polyvinylidene difluoride (PVDF), ensures the adhesion of the anode and cathode materials onto copper and aluminum foils [6]. The separator is a microporous film usually made from polymers such as polyethylene (PE) and polypropylene (PP) [7]. The electrolytes used in lithium-ion batteries include LiPF_6 , LiBF_4 , LiCF_3SO_3 , or $\text{Li}(\text{SO}_2\text{CF}_3)_2$.

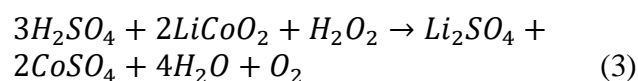
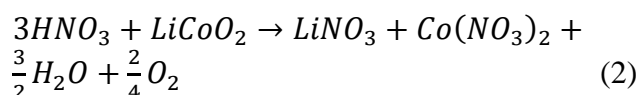
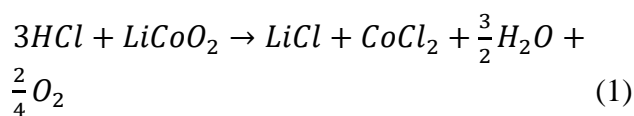
The cathode materials in lithium-ion batteries are primarily lithium intercalation oxides such as LiNiO_2 , LiMn_2O_4 , LiFePO_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, with LiCoO_2 being the most used [8, 9].

Today, three main techniques are employed for recycling lithium-ion batteries: pyrometallurgy,

bio metallurgy, and hydrometallurgy [10]. The pyrometallurgical method does not require pre-processing as organic solvents, plastic coatings, and connectors decompose and burn at the high temperatures applied in this process. The high temperature and capacity used allow for the recycling of large quantities of lithium-ion batteries. However, the disadvantages of the pyrometallurgical method include the emission of hazardous gases such as HF, high investment costs, high energy consumption, and the loss of some metals like lithium and manganese in the slag. The bio metallurgical method, which uses microorganisms for leaching, is less costly and requires less industrial equipment.

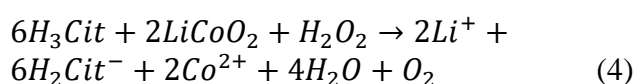
However, due to slower leaching kinetics and efficiencies, it requires much more time for recycling. Hydrometallurgical processes can be faster, provide higher purity, consume less energy, and result in lower gas emissions. Due to the disadvantages of pyrometallurgy and bio metallurgy, hydrometallurgical processes are more commonly used for recycling lithium-ion batteries [11, 12]. Leaching reagents are primarily inorganic acids, organic acids, and alkaline solutions. Inorganic acids like HCl, HNO_3 , and H_2SO_4 have been extensively studied in the recycling processes of lithium-ion batteries.

One of the most valuable components within a lithium-ion battery is the cathode material LiCoO_2 . The leaching (selective dissolution) reactions of LiCoO_2 with HCl, HNO_3 , and H_2SO_4 are as follows [13–15]:



In the absence of a reductant, the leaching efficiency of cobalt is higher with HCl compared to HNO_3 and H_2SO_4 , due to higher reduction potential of HCl. However, as shown in Reaction (3), the addition of H_2O_2 or similar agents can

facilitate the reduction of Co^{3+} when the cathode material is subjected to leaching with H_2SO_4 [16–19]. The leaching process of metals with inorganic acids can be successfully carried out with high efficiency. However, inorganic acids produce environmentally harmful components such as acidic wastewater, Cl_2 , SO_2 , NO_x , and other harmful gases [20]. Therefore, eco-friendly organic acids such as ascorbic acid, citric acid, oxalic acid, formic acid, acetic acid, and tartaric acid are used as leaching agents for metal recovery from waste lithium-ion batteries [21]. In this study, the leaching reaction of the cathode material LiCoO_2 with citric acid, which will be used, is provided in Reaction (4) [22].



Mechanical activation, used prior to leaching, is a widely applied scientific discipline with applications in metal production processes, reaction control in chemical technologies, and more. Heinicke describes this application as “Mechanochemistry, a branch of chemistry that deals with chemical and physical transformations of materials induced by mechanical energy” [23]. Mechanical activation is defined as a process that increases the reactivity of an otherwise unreactive solid, enhancing the dissolution of minerals.

The primary reasons for this enhancement include morphological irregularities, amorphization of mineral particles, the emergence of crystal areas conducive to preferential dissolution, and surface oxidation of minerals during prolonged grinding [24]. An additional fundamental advantage of mechanical activation is its ability to extract low-content, highly dispersed multi-source metal elements from electronic waste with complex compositions and sensitive structures. In the cathode material, cobalt generally exists in the Co^{3+} oxidation state. However, it has been reported that Co^{2+} is more easily soluble in aqueous solutions at room temperature compared to Co^{3+} [25].

Despite numerous reports on the recycling of spent Li-ion batteries, to the best of our knowledge, there have been no systematic

investigations into the effects of the mechanical activation process and its parameters on recycling using organic acids such as citric acid. In this study, the effects of mechanical activation parameters on the process of recovering valuable metals, lithium and cobalt, from waste lithium-ion batteries using an environmentally friendly method of organic acid leaching were investigated, with an emphasis on minimizing the use of toxic substances.

2. General Methods

All experiments utilized powders derived from spent lithium-based waste batteries. To fully understand the components of a cylindrical Li-ion battery extracted from a laptop battery, a spent Li-ion battery based on LiCoO_2 (LCO) was manually disassembled (Figure 1).

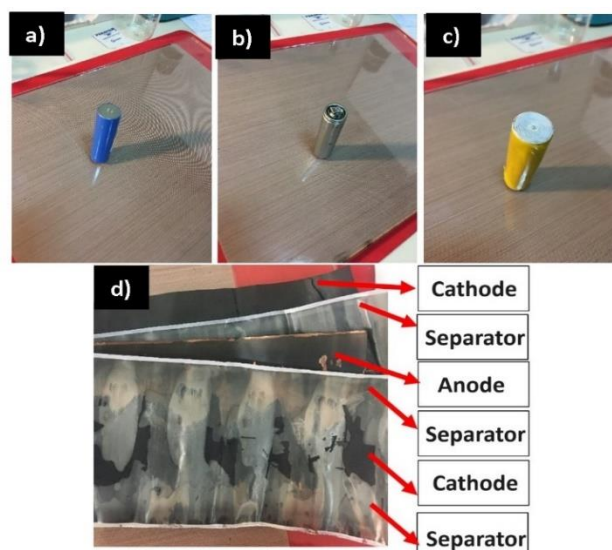


Figure 1. Manual disassembly of waste lithium-ion batteries: a) outer plastic layer, b) metal casing, c) inner plastic layer, and d) internal components of the battery

Prior to all experiments, the waste powders (comprising graphite, LCO, activated carbon, electrolyte, and PVDF) were initially homogenized in a ball mill using a stainless-steel ball-to-waste powder mass ratio of 1:20 at a mixing speed of 300 rpm for 12 hours. A primary powder blend (mixture) was obtained for use in all experiments. To better understand the metallic content of the waste powders and to remove the binder (PVDF) and carbon-based materials (graphite and carbon black) from the samples, a calcination process was conducted at $700\text{ }^\circ\text{C}$ for 3 hours.

To analyze the Li and Co content after calcination, the powders were subjected to dissolution in aqua regia (1/3 nitric acid and 2/3 hydrochloric acid) for 24 hours. Subsequently, the Li and Co contents by weight were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). After the calcination process, it was determined through ICP-OES analysis that the calcined LCO powders contain 5% Li and 31.3% Co. To understand the effects of mechanical activation, a planetary ball mill from Fritch was utilized.

The samples (calcined LCO powders) were subjected to dry mechanical activation in a container made of WC using WC balls with a diameter of 10 mm.

For the identification of compounds in the powders, X-ray diffraction analysis (XRD) was performed using a Rigaku d/MAX 2000 model instrument with CuK α radiation in the range of 10-90°. Morphological analyses before and after calcination were obtained using a Jeol JSM-6060 LV model scanning electron microscope (SEM). To observe the effects of mechanical activation, experiments were conducted at different planetary mill rotation speeds (0, 300, 350, 400, 450, 500, and 550 rpm), various mechanical activation times (15, 30, 45, and 60 minutes), and different sample/WC ball weight ratios (1/20, 1/30, 1/40, and 1/50).

Table 1. Parameters of leaching processes of calcined LCO powders with citric acid leaching agent

	Mechanical Activation Parameters		Leaching Parameters
Mechanical Activation Rotation Speed	0 rpm	Mechanical activation time:	1 M citric acid
	300 rpm	15 min.	30 min. leaching time
	350 rpm	Solid/WC ball ratio: 1/20	1/80 solid/citric acid ratio
	400 rpm		50 °C
	450 rpm		
	500 rpm 550 rpm		
Mechanical Activation Time	15 min.	Mechanical activation	1 M citric acid
	30 min.	rotation speed: 450 rpm	30 min. leaching time
	45 min.	Solid/WC ball ratio: 1/20	1/80 solid/citric acid ratio
	60 min.		50 °C
	75 min.		
Mechanical Activation Solid/WC Ball Ratio	1/20	Mechanical activation time:	1 M citric acid
	1/30	15 min.	30 min. leaching time
	1/40	Mechanical activation	1/80 solid/citric acid ratio
	1/50	rotation speed: 450 rpm	50 °C

The mechanically activated calcined LCO sample powders were then subjected to leaching in a 1 M citric acid solution for 30 minutes at a leaching temperature of 50 °C, with a solid-to-citric acid ratio of 1/80 (mechanically activated calcined LCO powder to citric acid). All leaching experiments were conducted in a glass reactor using a thermostat-controlled magnetic stirrer to maintain the reaction temperature within ± 1.0 °C. A water-cooled reflux condenser was used to prevent vapor loss at high temperatures. The stirring speed was kept constant at 300 rpm for

all leaching processes. Table 1 lists all mechanical activation and leaching conditions. After the leaching process, the leach solution was separated from the solid phase using filtration. The factors influencing the recovery of Li and Co from spent powders were investigated under various experimental conditions: (i) mechanical activation rotation speed, (ii) mechanical activation time and (iii) mechanical activation solid/WC ball ratio. The metal contents in the leaching solutions were determined using Atomic Absorption Spectroscopy (AAS) for each

experiment. The recovery efficiency was calculated according to the following equation:

$$E_{Li,Co}(\%) = \frac{C \times V}{P \times M} \times 100$$

where C is the concentration of Li and Co in the leaching solution (g/L), V is the volume of the leaching solution (L), P is the percentage of Li and Co in spent LiBs (%), and M is the amount of the leached solid (g).

3. Results and Discussion

The leaching behavior of waste Li-ion active material during the leaching process is influenced by various mechanical activation parameters. It has been observed that increasing the mechanical activation time, rotational speed, and ball-to-powder mass ratio enhances the leaching efficiencies of cobalt and lithium [26]. Moreover, the leaching efficiencies of metals exhibit a linear relationship with the surface area of the existing structure [27]. The mechanical activation process alters the leaching behavior of valuable metals, resulting in higher leaching efficiencies compared to non-activated samples [28].

The improved leaching efficiency is associated with reduced particle size, increased specific surface area, and the disrupted crystal structure of the activated samples [29]. Mechanical activation also leads to changes in the physicochemical properties of LCO powders, such as reduced particle size, increased specific surface area, and the formation of mesoporous structures. Figure 2 presents the XRD patterns of calcined LCO powders subjected to mechanical activation at different rotational speeds, with a 1/20 solid/WC ball ratio, and a mechanical activation processing time of 15 minutes.

In Figure 2, it is observed that the mechanical activation processes do not result in significant amorphization or reorientation of the crystal structure within short durations such as 15 minutes. However, at rotational speeds of 400 and particularly 450 rpm, changes in the structures of LiCoO₂ and Co₃O₄ peaks are evident. At lower rotational speeds, as seen in the enlarged graph on the right side of Figure 2, the two peaks at 37° and 37.5° 2θ merge into a single

peak. During mechanical activation at 450 rpm, it is observed that the Co₃O₄ structure formed after calcination transforms into the LiCoO₂ structure, reducing or eliminating the amount of Co₃O₄ in the structure.

It is understood that during mechanical activation at 450 rpm, the Co₃O₄ and LiO₂ present in the structure transform into LiCoO₂ due to the high temperatures generated by solid-phase micro-region collisions. Studies in the literature on the production of LiCoO₂ through mechanical activation using LiO₂ and Co₃O₄ starting materials support this claim [26, 27]. During the leaching process, the dissolution of LiCoO₂ and Co₃O₄ involves different chemical mechanisms. For LiCoO₂, the leaching mechanism is controlled by surface chemical reactions [30]. The leaching of cobalt from LiCoO₂ is influenced by the disintegration of the crystal structure and diffusion, whereas the leaching mechanism for Co₃O₄ is significantly affected by the concentration and type of acid used as well as solvent effects [31].

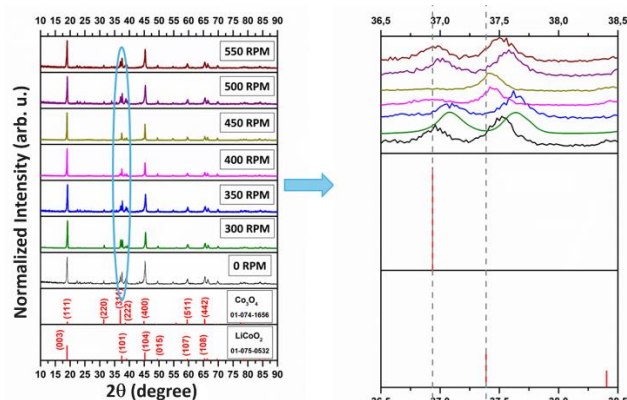


Figure 2. XRD patterns of calcined LCO powders at different mechanical activation rotation speed

SEM images are presented in Figure 3 to examine the impact of different mechanical activation speeds on the morphology of waste calcined LCO powders.

In Figure 3a, it is evident that the morphology of the original, non-activated calcined sample shows agglomeration of the powders during calcination. This agglomeration occurs due to chemical changes and attractive forces between the particles during the calcination process. In Figure 3b, at a mechanical activation speed of 300 rpm, partial liberation of the grains is

observed, although the grains are still coarse, indicating that low-scale mill rotations promote and facilitate agglomeration. However, after this stage, the bonds between particles begin to loosen, resulting in a more liberated structure.

This is evident in Figure 3c, where increasing the mechanical activation speed to 450 rpm leads to further liberation and a reduction in grain size. This can be attributed to the particles being subjected to more energy with the increased mill rotation speed of the WC balls, leading to a more loosened structure. However, with the increase in mechanical activation speed, the heating effect caused by collisions and friction between the balls and grains also increases. As shown in the SEM image in Figure 3d, this results in localized sintering and an increase in particle size. The temperatures, which can reach thousands of degrees on a micro scale, cause partial melting, sintering at the contact points of the particles, and an increase in particle size.

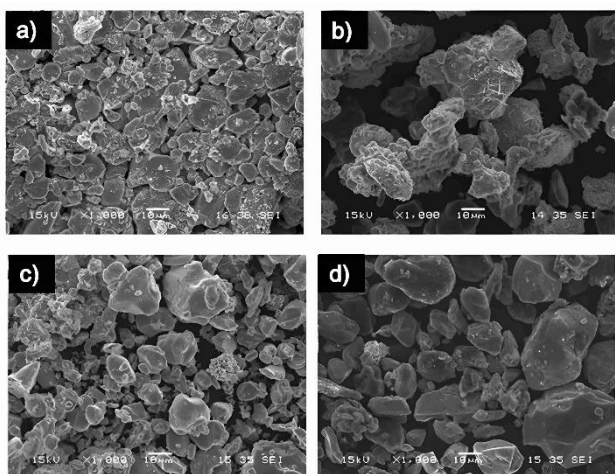


Figure 3. a) Calcined LCO powder (0 rpm) and LCO powders mechanically activated at different rotation speeds b) 300, c) 450, and d) 550 rpm

Figure 4 illustrates the relationship between mechanical activation rotation speed and the leaching efficiencies of Li and Co metals in waste calcined LCO powders.

The fixed parameters used in the leaching processes from which the data in Figure 4 were obtained are provided in Table 1. For the non-mechanically activated sample at 0 rpm, the leaching efficiency was found to be approximately 45% for Li and 10% for Co. With increasing mill speed and mechanical activation,

defects are introduced in the internal structure, enhancing the recoveries of Li and Co. The maximum leaching efficiencies were achieved at 450 rpm, with yields of 87.20% for Li and 24.85% for Co.

However, when the rotational speed of mechanical activation was increased to 500 rpm, significant decreases in leaching efficiencies were observed. This is likely due to the agglomeration of grains at speeds above 500 rpm (as seen in Figure 3d), which reduces the available surface area for leaching. Guan et al. observed the same phenomenon and found that the leaching efficiency significantly increased with the rise in mechanical activation rotation speed. This improvement is attributed to the enhanced kinetic energy transferred to the samples due to the series of collisions among the balls [32]. Additionally, as seen in the XRD patterns in Figure 2, the formation of the LiCoO_2 structure through the reaction of Co_3O_4 with LiO_2 may contribute to the reduced leaching efficiency due to the increased difficulty in dissolving this complex structure. While Co extraction increases with the mill rotation speed similar to Li, no significant increase in Co extraction was observed, which is related to changes in the crystal structure [33].

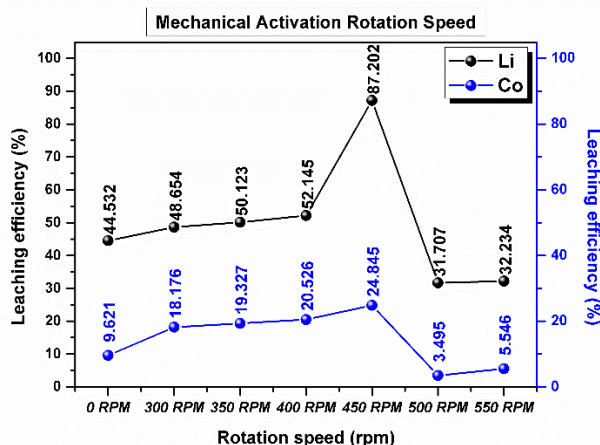


Figure 4. Leaching efficiencies of Li and Co obtained from the leaching process of waste calcined LCO powders subjected to mechanical activation at different rotational speeds

Figure 5 shows the leaching efficiencies of Li and Co obtained from the samples mechanically activated for times ranging from 15 to 75 minutes under the parameters provided in Table 1.

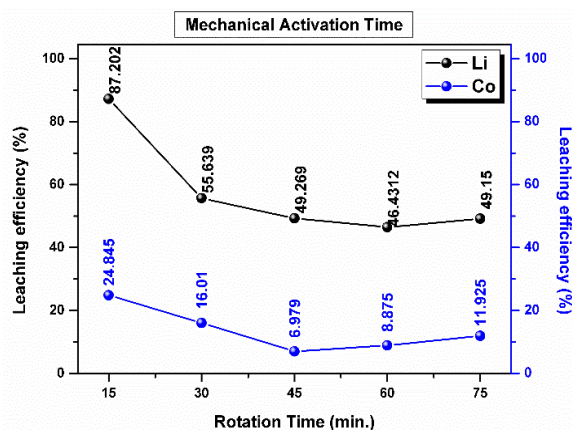


Figure 5. Leaching efficiencies of Li and Co obtained from the leaching process of waste calcined LCO powders subjected to mechanical activation at different activation times

As seen in Figure 5, when the mechanical activation time is increased from 15 minutes to 75 minutes, the extraction efficiencies of Co and Li decrease from 25% to 12% and from 87% to 49%, respectively. The obtained results indicate that mechanical activation time and the rotational speed of the planetary mill are critical factors for the recovery of Co and Li from recycled LIBs. Extending the activation duration beyond 15 minutes leads to a significant increase in the tendency for sintering events, due to local temperature rises, which in turn reduces leaching efficiency. Additionally, the literature explains that the agglomeration caused by cold welding of particles during mechanical activation contributes to this phenomenon [34]. It is clearly observed that excessively long mechanical activation times result in increased particle sizes and reduced surface areas, which decrease the extraction efficiencies of Co and Li.

Figure 6 shows the leaching efficiencies of Li and Co obtained from the leaching process at different solid/WC ball ratios under the fixed leaching parameters provided in Table 1.

As seen in Figure 6, as the solid/WC ball ratio decreases from 1/20 to 1/50, the leaching efficiencies for both Li and Co decrease.

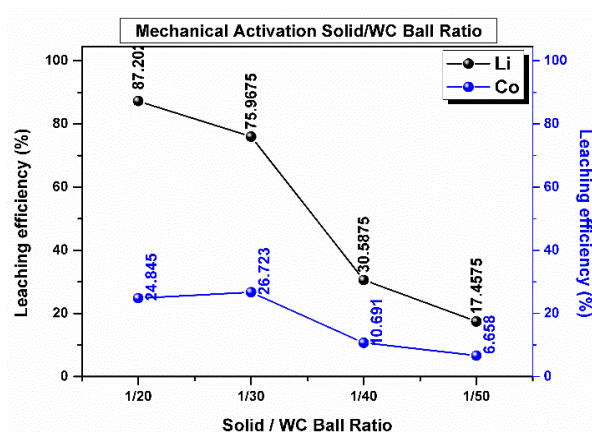


Figure 6. Leaching efficiencies of Li and Co obtained from the leaching process of waste calcined LCO powders subjected to activation at different waste calcined LCO/WC ball ratios

This is attributed to the limited high-speed collisions of the mechanical activation balls with the samples during the mechanical activation process (due to increased ball numbers per unit volume, which reduces collision intervals and strength) and the larger contact area of the grinding balls [33]. An inappropriate solid/WC ratio results in both a waste of mechanical energy and reduced leaching efficiencies of the metals.

4. Conclusion

It has been understood that low-speed and short-time mechanical activation positively contributes to the recovery of Li and Co from waste batteries, while high-speed and long-duration mechanical activation has adverse effects. It has been observed that even with a low concentration of 1 M citric acid in the leaching process, Li can be extracted at levels of approximately 87% and Co at approximately 25%. The conditions with a solid/WC ball ratio of 1/20 have emerged as the ratio at which the highest leaching efficiency is obtained.

Article Information Form

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Authors' Contribution

The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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