

## Article

# Direct Sonochemical Leaching of Li, Co, Ni, and Mn from Mixed Li-Ion Batteries with Organic Acids

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**Abstract:** Metals such as nickel, cobalt, lithium, and manganese are widely used in lithium-ion batteries (LIBs) in electronic devices and electric vehicles. It is forecast that there will be a strong increase in the number of electronic devices and electric vehicles in the coming years. (1) Background: In this paper, the application of ultrasound waves on improving Li, Co, Mn, and Ni leaching efficiency from mixed active cathode materials from different types of LIBs is presented. (2) Methods: Environmentally friendly, low-concentrated (0.75 M) organic acids (oxalic acid, citric acid) and, additionally, sulfuric acid, were used in sonochemical and chemical leaching (stirring process) at a temperature of 60 °C. (3) Results: The results showed significantly higher leaching efficiency of metals with ultrasound-assisted treatment, especially when using organic acids. An average of 50% better leaching results were obtained for Li in oxalic acid (99.6%) and for Co (93.1%) in citric acid during sonochemical leaching. (4) Conclusions: Based on the theory of hydrogen peroxide formation during ultrasound wave transition in solutions, the role of H<sub>2</sub>O<sub>2</sub> as one of the most effective reductants used to enhance cobalt, manganese, and nickel leaching from LIBs is indicated.

**Keywords:** lithium-ion batteries (LIBs); sonochemical and chemical leaching; recovery of Li; Mn; Co; Ni



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## 1. Introduction

Lithium and cobalt belong to the group of Critical Raw Materials (CRMs) as essential elements for the development of strategic sectors such as renewable energy, electric mobility, defense, aerospace, and digital technologies [1]. These two metals, together with Ni and Mn, are an essential component of lithium-ion batteries (LIBs). Depending on the type of lithium batteries (LiMn<sub>2</sub>O<sub>4</sub>—LMO, LiCoO<sub>2</sub>—LCO, LiFePO<sub>4</sub>—LFP, LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>—NMC, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>—NCA), the metal content in active cathode material varies: Li: 3.8–7.8%; Co: 6.0–60.2%; Ni: 20.1–48.8%; and Mn: 5.6–60.7% [2–4]. Forecasts for the coming years undeniably confirm the growth tendency of the lithium cell market, electro-plasticity, and the demand for these metals. According to analyses [5] global Electric Vehicle (EV) production is set to increase from 3.4 million vehicles in 2020 to 12.7 million by 2024, and lithium demand will grow from 47.3 kilotons to 117.4 kt. It is estimated the EU will require up to 160 times more lithium and 15 times more cobalt in 2050 compared to levels of demand in 2018 to develop rapid low-carbon strategies [6]. The main thing that attracts attention is lithium, which the European Union recently added to its list of strategic minerals and for which it wants to establish more robust supply chains [7]. The usage, manufacturing rates, end-of-life handling, and recycling of lithium-ion batteries are expected to increase in the coming years as they play a crucial role in

the EU's transition to a climate-neutral economy. Today, lithium recovery in the EU is more limited and the volume of recovered and more economically valuable metals used in battery manufacturing is low. Only 12% of Al, 22% of Co, 8% of Mn, and 16% of Ni used within the EU is recycled [8]. Chemical, physical, and biological processes have been widely discussed [9–12] for the recovery of valuable metals from LIBs. The most popular approaches are hydrometallurgical methods, with strong inorganic acids such as HCl [13], HNO<sub>3</sub> [14], Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and H<sub>2</sub>SO<sub>4</sub> [3,15–18] commonly being used as leaching reagents. Traditional leaching treatments of LIBs rely on expensive reagents and can lead to the release of toxic gases, and the waste acid solution after leaching is a threat to the environment. Therefore, the most sustainable techniques with not-so-aggressive conditions, a closed loop of leaching agents, and improved environmental impact are desired. At the forefront are biological methods (microbial leaching) as important assets in future industrial implementation that are economically sound and have reduced environmental problems (reduced footprint from CO<sub>2</sub> emissions, as well as reduced impact on groundwater and soil quality) [19,20]. An equally important and more environmentally friendly approach is the use of organic acids.

The advantages of this approach relate to biodegradability and non-toxic gas emissions [21,22], the involvement of protonation and chelation reactions that accelerate the dissolution of metals [23], and the reduction of the footprint of recycling processes [24]. Many organic acids have been used to improve the extraction rate of valuable metals from LIBs. Although the acidity (correlated with acidic strength) of organic acids is considerably lower than that of strong inorganic acids, their leaching efficiency is high. This is because organic acids can be used as moderate reducing agents for multivalent transition metals and to stabilize the dissolution of metal ions by forming chelating complexes [25,26]. The most popular is citric acid, usually applied together with a reducing agent in the form of H<sub>2</sub>O<sub>2</sub> [27–30], or ascorbic acids [29]. Other acids, such as oxalic [31], malic [28], formic [32], succinic [33], or glutaric [34] acids, have been used as well. In most studies, the high metal leaching efficiency with organic acid (>95%), comparable to the use of conventional acids (H<sub>2</sub>SO<sub>4</sub>, HCl), has been demonstrated [28,30–32]. However, most experiments have been carried out over a temperature range of 80–100 °C [9,10], while only a few works report lower temperatures bringing equally good metal leaching results [27,32]. In addition to the commonly used factors intensifying or supporting LIB metal dissolution—such as temperature, the addition of a reducing agent, or speed of mixing, a highly enhancing factor—ultrasounds are still among the least used and tested methods in metal leaching. Due to its advantages, ultrasound technology has been widely used in many areas, such as medical diagnostic and therapy [35], micro- and nanomotors [36,37], and hydrometallurgy, where ultrasound is applied to enhance the extraction of metals from precious or rare ores (e-waste e.g., PCB and LCD [38–42]) and releasing metals in a shorter time using acids at low concentration [43] during leaching and bioleaching [41,44–47]. Cavitation and bubbles created by ultrasound waves in the liquid cause high-speed micro-jets (300–1000 m/s) [48], and high local temperature creates localized material erosion, destroys the surface of the grain, enhances mass transfer, accelerates reaction rates, and increases metal recovery during leaching [38,39,42]. Ultrasounds can be introduced into the system by either directly immersing the ultrasound source in a washing medium (direct sonication) or by immersing a vessel containing a mixture of test material and leaching agent in a tank containing an ultrasonically treated liquid, which is usually water (indirect sonication) [43,44]. The available literature and laboratory-scale sonoleaching tests for Li and Co recovery under different sonic conditions are presented in Table 1. The results show that, in direct sonoleaching conditions, the leaching time is significantly reduced compared to that of the method with an ultrasonic cleaning bath/vessels using inorganic acids. The leaching of Co and Li was found to be more efficient with citric acid than with the two inorganic acids [27], remarkable results were achieved for citric acid, whereby nearly 100% of the Co, Li, and Ni were recovered in 35 minute process [45]. It should be noted that these studies used to a cathode material (LiCoO<sub>2</sub>) selected from one type of battery, limiting the analyzed composition to Li and Co.

The current market and technological trend are related to the lowering use of expensive cobalt in the composition of the batteries in favor of a greater concentration of Ni and mixed metal cathode production [10,49]. This forces extending the battery recycling process by focusing not only on cobalt but, for more practical operation, also on other metals derived from cobalt-deficient cathodes and from a mixture of different cathode materials. In our study, we focused on combining the potential of high-efficiency metal recovery using organic acids (0.75 M oxalic and 0.75 M citric acids) with the application of ultrasound waves to shorten process time and improve metal's leaching rate. A mixture of a variety of cathode active materials (containing Li, Co, Ni, Mn) was used and the extraction efficiency of these metals at the temperature of 60 °C was determined.

**Table 1.** Experimental conditions of the ultrasound-assisted leaching of metals from LIBs described in the literature.

Type of Material	Leaching Agent	Type of Sonic Source/Power	Leaching Conditions	Leaching Effectiveness	Ref.
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 5% H <sub>2</sub> O <sub>2</sub>	direct/360 W	0.5 h, 30 °C, 100 g/L	Co: 91.6% Li: 92.7%	[50]
LiCoO <sub>2</sub>	citric acid + H <sub>2</sub> O <sub>2</sub> ,	indirect	0.5 h, 40 °C	Li: 100% Co: 100% Ni: 100%	[45]
LiCoO <sub>2</sub>	0.5 M C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> + 0.55 M H <sub>2</sub> O <sub>2</sub> ,	indirect/90 W	5 h, 60 °C, 25 g/L	Co: 96.1% Li: 98.4%	
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 0.55 M H <sub>2</sub> O <sub>2</sub>	indirect/90 W	5 h, 40 °C, 25 g/L	Co: 45.7% Li: 97.0%	[27]
LiCoO <sub>2</sub>	2 M HCl	indirect/90 W	5 h, 60 °C, 25 g/L	Co: 76.4% Li: 98.2%	
LiCoO <sub>2</sub>	0.3 M C <sub>6</sub> H <sub>12</sub> O <sub>7</sub>	indirect/300 W	1 h, 180 °C, 3 g/200 mL	Co: 96.0% Li: 98.0%	[51]
LiCoO <sub>2</sub>	0.5 M CH <sub>3</sub> COOH + 0.2 M C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> + bagasse pith	direct/450 W	40 min, 50 °C, 20 g/L	Co: 98.6% Li: 99.6%	[52]
LiCoO <sub>2</sub>	CH <sub>4</sub> O <sub>3</sub> S + sugarcane molasses	direct/400 W	1 h, 90 °C, 20 g/L	Co: 97.0% Li: 97.0%	[53]
LiCoO <sub>2</sub>	1 M DL C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> + H <sub>2</sub> O <sub>2</sub>	indirect/90 W	0.5 h, 80 °C, 5 g/L	Co: 97.3% Li: 98.0%	[54]

## 2. Materials and Methods

### 2.1. Materials

Li-ion cells from used cell phones (Samsung prismatic cells) and portable computer equipment (laptop) (cylindrical batteries, type 8858) were used in our research. Common cell compositions based on information in the Material Safety Data Sheet (MSDS) provided by the manufacturer are presented in Table 2.

**Table 2.** Composition of lithium-ion battery LG Chem, Ltd. (Wrocław, Poland) and Samsung (Yongin, Korea) SDI lithium-ion cell/battery [47,48].

Ingredient	Content, %
Aluminum Foil	2–10
Metal Oxide (proprietary)	20–50
Polyvinylidene Fluoride (PVDF)	<5
Copper Foil	2–10

Table 2. Cont.

Ingredient	Content, %
Carbon (proprietary)	10–30
Electrolyte (proprietary)	10–20
Stainless steel, Nickel and inert materials	residue

The batteries were first manually dismantled. Next, cathode active material with lithium transition metal oxides (Co, Ni, Mn) on Al foil was separated from the rest of the components (steel cases, conductive carbon particles, polymer binder). Then Al collector foil with the active cathode material was cut into small pieces ( $1 \times 1$  cm) and was ground by a knife mill (ChemLand FW135, Stargard, Poland). Ground mixed materials were washed with H<sub>2</sub>O demi water, and left to dry for 24 h at 50 °C. Sieve analysis was used to divide the granular material into smaller size by applying an electromagnetic sieve shaker (Multiserw-Morek LPzE-2e, Marcyporeba, Poland) equipped with sieves of standard sizes: >2.0, 1.0, 0.5, 0.2, 0.1 and <0.1 mm. Separating the material into individual fractions allowed for a significant separation of the cathode active material from the shredded aluminum foil (Figure 1). Material with the finest fragmentation (<0.1 mm), characterized by the largest contact surface, was selected for further leaching tests. A particle size analysis of the initial samples and residues was performed by using a Malvern Mastersizer 3000 laser (Malvern, UK) particle size analyzer.

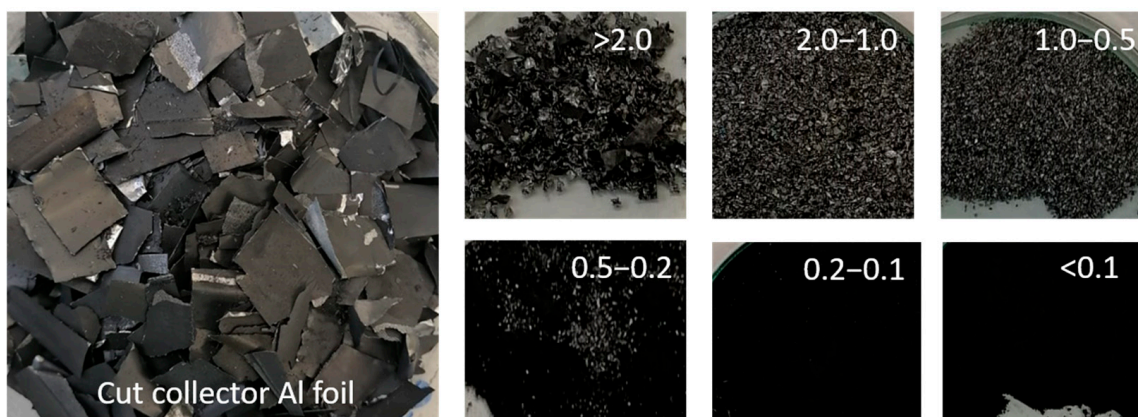


Figure 1. Active cathode material separated from Al foil.

## 2.2. Methods—Leaching Procedure

Data in the literature reports that a concentration of organic acids in the range of 1–2 M is most commonly used in LIBs cell leaching experiments [9,27,50–55]. In the present study, lower acid concentrations were applied. i.e., 0.75 M oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) and 0.75 M citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), these concentrations were nonetheless sufficient to ensure significant acid reactivity, especially in the case of oxalic acid, which is one of the strongest carboxylic acids [56]. For comparison, 0.75 M H<sub>2</sub>SO<sub>4</sub> was used as an example of inorganic acid, that has been widely used as a high-potential leaching agent. In our experiment, no additional reducing agent was used. Leaching was carried out with a sample density of 50 g/L, at a temperature of 60 °C or 4 h. One leaching test with 0.75 M oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) was performed additionally at room temperature (22 °C) and 40 °C for 4 h.

Experiments were conducted under two different conditions, i.e., —the mixed cathode material was subjected to acid leaching:

- (i) mechanical stirring leaching—in closed cylindrical reaction vessels with a thermostatic jacket and mechanical stirrer (300 rpm) (Lenz with Heidolph SN stirrer and thermostat Grant LT Ecocool 150 SN, Royston, UK),

- (ii) sonochemical leaching—in closed vessels with immersed titanium probe conductive ultrasound produced by an ultrasonic generator at 20 kHz frequency, and amplitude range 65% (SONOPhULS HD 4200, Bandelin, Berlin, Germany). Under the assumed operating parameters of the generator, the sonotrode generated a temperature of 60 °C in the solution, which was maintained as a constant value in the sonochemical leaching experiments.

Table 3 shows the conditions for the mixing and ultrasonic leaching experiments. To test the pH, a pH-Eh-meter (Hydromet CP-505, Gliwice, Poland) was used. The progress of leaching was monitored by taking 5 mL samples at different time intervals and analyzing the metal contents after filtration. For the analysis of the Ni, Co, Mn and separate Li concentrations, a Microwave Plasma Atomic Emission Spectrometer (Agilent MP-AES 4200, Santa Clara, CA, USA) and Atomic Absorption Spectrometer (ContraAA300, Analytik Jena, Germany) were used, respectively. Analysis of the morphology and structure of the ground samples and leaching residues were made with a Hitachi S-4200 scanning electron microscope (Naka, Japan) using secondary electron detectors (SE). Chemical composition tests were performed using an X-ray energy dispersion spectrometer (EDS) from Thermo Noran (System Seven) at a voltage accelerating the electron beam of 15 keV.

**Table 3.** Conditions of the experiments.

Type of Acid	Leaching System	Temperature, °C	Initial pH of Leach Liquor
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Mechanical stirrer	22	0.68
		40	
		60	
	Ultrasound	60	
C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	Mechanical stirrer	60	0.94
	Ultrasound	60	
H <sub>2</sub> SO <sub>4</sub>	Mechanical stirrer	60	−0.25
	Ultrasound	60	

The metals leaching efficiency was calculated by the following equation:

$$E = \frac{C_v \cdot V}{m_0 \cdot C_0} \cdot 100\% \quad (1)$$

where E is leaching efficiency of metal (%); C<sub>v</sub> is metal concentration in leachate (mg/L); V is volume of leach solution (L); m<sub>0</sub> is the initial mass of sample (g); and C<sub>0</sub> refers to metal content in leaching material (%).

### 3. Results and Discussion

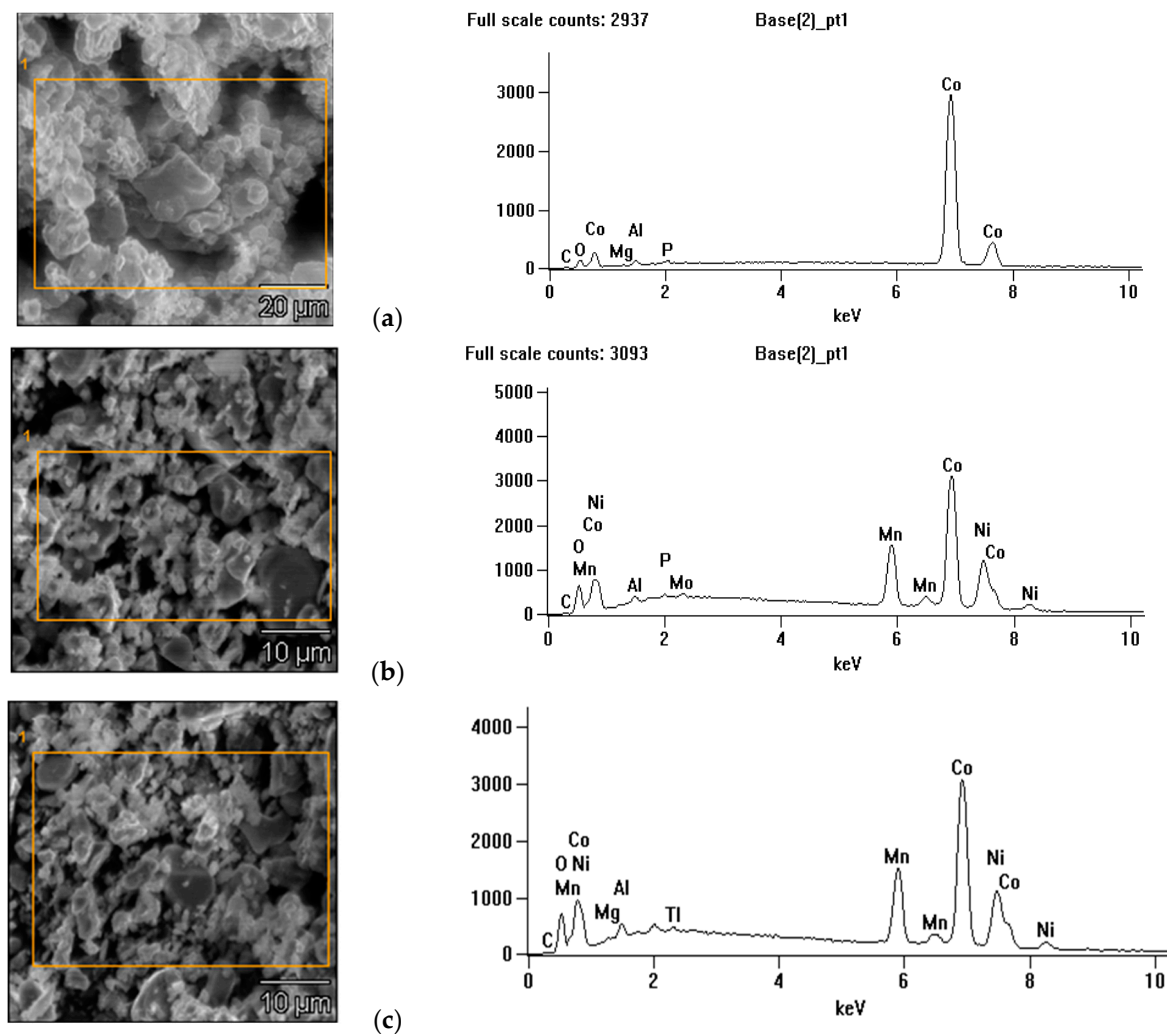
#### 3.1. Cathode Active Material Characterization

The scanning electron microscopy images (SEM) with microanalysis (EDS) samples of the active cathode material from mobile phones and laptops and mixed materials are shown in Figure 2.

The presence of cobalt was particularly noticeable, accounting for 56% of the ground material in the laptop battery, 98% of the material from the mobile phone, and 57% of the mixed material of batteries from both mobile phones and laptops. In the sample of material from a laptop, nickel and manganese were present, with mass fractions of 14% and 24%, respectively, these metals were not detected in the sample from the phone battery. These data verified the model composition of the cathode material of lithium cells used in electronic and electrical devices. In the case of mobile phones, the cathode mass was composed of lithium cobalt oxide (LiCoO<sub>2</sub>) (Figure 2a). For batteries used in laptops, the presence of additional Ni and Mn indicated that it was an NMC battery type,



containing lithium-nickel-manganese-cobalt oxide ( $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ )—Figure 2b. The aluminum present in the SEM-EDS results is a remnant of aluminum foil from cathode material after the process of grinding. Due to the detection limit of the SEM-EDS, Li was not identified, but its content, together with those of other metals (Co, Ni, Mn), was determined by AAS and MP-AES methods, respectively. The content of metals in the mixed cathode active material of laptop and mobile phone batteries intended for leaching experiments is shown in Table 4.



**Figure 2.** SEM-EDS analysis for cathode active material (a) coming from a computer (b) from mobile phones, and (c) a mixed material.

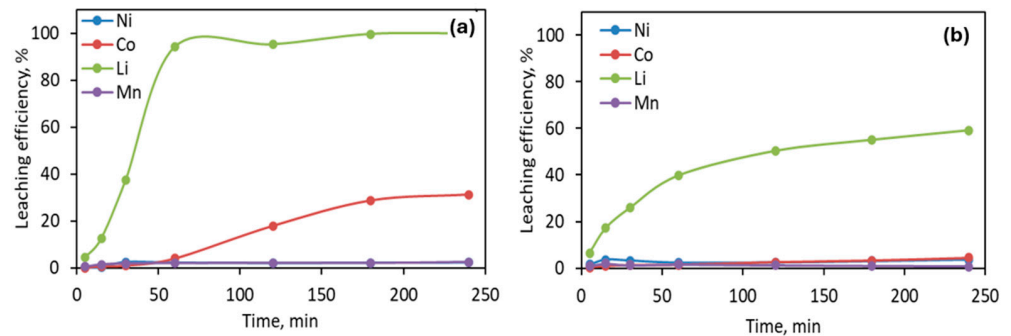
**Table 4.** Chemical composition of homogenized cathode LIBs material.

Element	Co	Ni	Mn	Li	Al
wt%	19.59	5.02	8.90	3.12	0.14

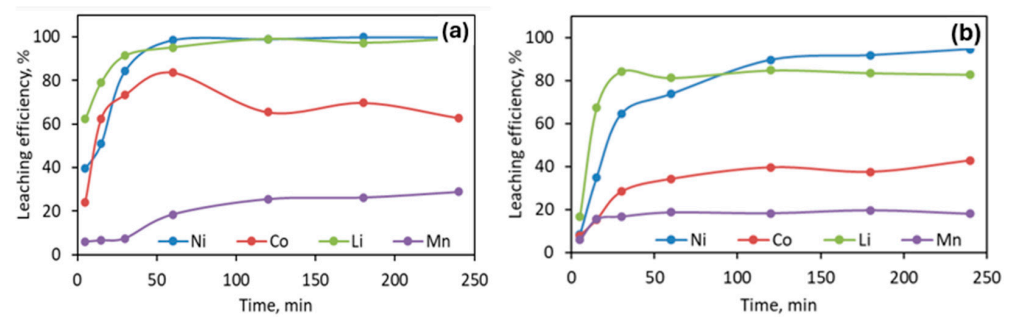
### 3.2. Effect of Time on Leaching Efficiency

In our study, sulfuric acid and 2 organic acids were used: Citric acid recognized as excellent chelating agent, binding metals by making them soluble and the cheapest organic acid [29] and oxalic acid which forms water-soluble oxalate compounds and can be used simultaneously as reducing agent to reduce Co(III) to Co(II) and as effective precipitating agent [9,10,43,57]. Figures 3–5 shows changes in the metals leaching efficiency (Li, Co, Ni and Mn) in inorganic and organic acids over a period of 4 h. Depending on the method

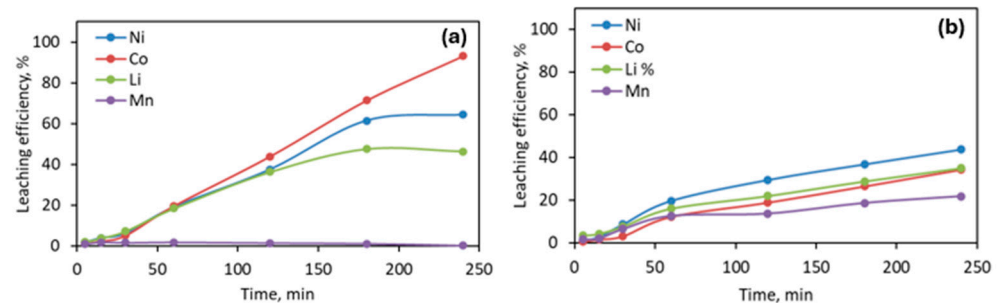
(sonochemical or stirring leaching) and type of acid, different mobilization efficiencies and selectivities of the metals were observed.



**Figure 3.** Leaching efficiency of metals with oxalic acid during (a) sonochemical leaching (b) mechanical stirring leaching.



**Figure 4.** Leaching efficiency of metals during (a) sonoleaching (b) mechanical stirring with sulfuric acid.



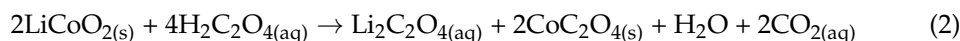
**Figure 5.** Leaching efficiency of metals during (a) sonoleaching (b) mechanical stirring with citric acid.

### 3.2.1. Leaching with Oxalic Acid

Figure 3 confirms the almost complete mobilization of Li after 120 min, where 95.2% of Li was dissolved in oxalic acid (with ultrasound). Cobalt was released in parallel at 31.2%, while Ni and Mn did not dissolve significantly, remaining in the solid phase at 98%. At the same time, 50.3% of Li (with a final value 59.2%) was leached in the system with mechanical stirring (Figure 3b). Ni, Co and Mn were co-mobilized in percentages, not exceeding 1% for Mn and 4.5% for Ni and Co. A similar observation may be found in [28,31,58,59], i.e., when oxalic acid was used to leach transition metals from a cathodes material (Ni, Mn, Co) oxalates were formed that precipitated out of solution.

The oxalate chemistry explains the different behavior of the considered metals. In the presence of oxalic acid, Mn, Ni and Co form water-insoluble oxalate compounds such as  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  [60], while Li goes into solution

easily. Oxalic acid works as leaching and reducing agent simultaneously, releasing  $H^+$  and producing  $CO_2$  from predominant  $H_2C_2O_4$  species at a pH below 1.23 [9,61], as follows:



In many works [5,28,31,59] oxalic acid was applied as a precipitation agent for metals from LIBs with good results. When oxalic acid was used for  $LiCoO_2$  (LCO) cathode active materials, lithium was extracted easily in the leaching solution, while cobalt was precipitated as cobalt oxalate. Zeng et al. [31] reported that 98% of Li was leached into the aqueous phase, while 97% of Co was precipitated out as cobalt(II) oxalate (study conditions: 1 M oxalic acid, 2.5 h, 95 °C, 400 rpm, 15 g/L). Also, positive Li separation results were obtained for the mixed cathode material. Zhang et al. [58] achieved 84% Li recovery in the aqueous phase with a  $LiNi_xMn_yCo_zO_2$  (NMC) cathodes material, while 98% of the Co, Ni, and Mn were precipitated (study conditions: 0.6 M oxalic acid, 2 h, 75 °C, 20 g/L). Our results also confirm the possibility of the selective recovery of Li from mixed cathode material, which is particularly important for practical separation techniques. During the first 60 min of sonochemical leaching, 94.1% Li recovery was achieved while Co stayed in the solid phase (Figure 3a). However, this time, the transition of cobalt onto the solution (31.2%) could be observed. The increased solubility of Co was related to the reduced high valence of Co to lower  $Co^{3+}$  to  $Co^{2+}$ , which was related to the presence of ultrasound in the chemical system. Therefore reaction (2) describes (i) the behavior of Li and other metals in a mechanical stirring system (Figure 3b), where Co and (implicitly), Ni, and Mn also are in the solid phase and (ii) the first 60 min of sonochemical leaching, where we selectively separated Li from a leached mixed active cathode material.

### 3.2.2. Leaching with Sulfuric Acid

The solubility of metals increases with time in most cases. The leaching rate was very fast with sulfuric acid and ultrasounds for Li and Ni, allowing for the transition of these metals into the solution to occur in amounts of >95% during the first 60 min (Figure 4a). Co and Mn were also released from the cathode material, although their extraction was at a lower degree, i.e., 83.7% and 18.5% (after 60 min), respectively.

The leaching of nickel during mechanical mixing was limited in the first hour of the process, where 73.8% Ni was obtained. Only over time did the degree of Ni transition to solution increase. Despite the use of a low concentration of 0.75 M  $H_2SO_4$ , the efficiency of Ni was 89.7% after 120 min, and the final value of the obtained efficiency of Ni was 97.4%. Our results differ from those of Urbańska [55] and Wang et al. [62], who indicated lower efficiencies of Ni leaching. Those authors showed that at temperature of 55–60 °C and 90 °C using 1.5 M or 2.0 M  $H_2SO_4$ , Ni leaching did not exceed 45% within 120 min. On the other hand, Meshram et al. [63], using 1 M  $H_2SO_4$ , 90 °C, 4 h and no reductant agent, achieved a high degree of recovery of Ni 96.3%, Li 94.3%, Mn 50.2%, and Co 66.2% from Commercial LIBs of various compositions. The findings of that study align with our results, showing high extraction efficiency for Ni and Li and lower efficiency for Mn and Co. It appears that a longer processing time and a lower concentration of the applied acid enhance metal extraction. Additionally, the use of  $H_2O_2$  increases the dynamics of Ni extraction as well as the extraction of the less soluble Co and Mn from spent batteries. For instance, as reported in [62], the extraction rate of Ni increases from 48.9% to 83.7% when the concentration of  $H_2O_2$  is raised from 0 to 25 g/L. This suggests that the presence of an additional factor, such as a catalyst for the dissolution reaction, may be responsible for the high efficiency of leaching within the first 60 min, achieving 98.5% for Ni, 95.1% for Li, and 83.7% for Co during sonochemical leaching (Figure 4a).

### 3.2.3. Leaching with Citric Acid

The dynamics of the changes in concentration over time of all metals with citric acid, both in sonochemical leaching and with mixing, proceed much slower, in a characteristic linear manner, compared to oxalic and sulfuric acid were used (Figure 5).



Visible is, however, that, Co, and not Li reached the higher efficiency of transition to the solution (93.1%) after 240 minutes—while Mn did not exceed 1.8% leaching degree in systems with ultrasounds. Also, under in a vessel with stirring conditions, low leaching efficiency of Mn < 22% and other metals (not exceeding 40%) were observed.

The leaching efficiency of organic acids is directly correlated with their acidic strength (Table 5). From this, it follows that citric acid with triprotic nature, comprising three carboxylic acid groups, compared to oxalic acid, is a highly potent leaching agent. Oxalic acid, despite of diprotic nature, exhibited poor leaching efficiency for Ni, Mn, and Co from LIBs due to the formation of a lowly soluble metal oxalate precipitate [64], this resulted in low recovery values for these metals in vessels with stirring, i.e., not exceeding 1.9% (Figure 3b).

**Table 5.** Acidic strength of applied acids [8,60].

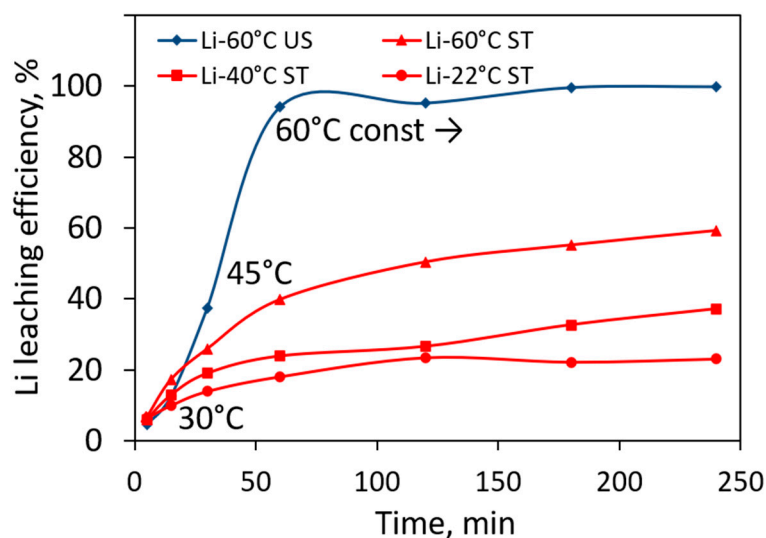
Type of Acid	The Dissociation Constants
H <sub>2</sub> SO <sub>4</sub>	pKa = $1.26 \times 10^{-2}$
C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	pKa1 = 3.08 pKa2 = 4.74 pKa3 = 5.40
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	pKa1 = 1.23, pKa2 = 4.19

Research by Chen et al. [65] and other authors [30] clearly indicates the dependence of metal leaching efficiency on the volume concentration of the introduced H<sub>2</sub>O<sub>2</sub> additive and the concentration of the citric acid. The lack of a reducing agent limited the leaching of Ni, Co, Mn, and Li to 51%, 48%, 43%, and 59%, respectively (time: 60 min, 80 °C) [62], and using a low concentration of citric acid (0.5 M) the efficiency of metal transition to solution did not exceed 60%. Increasing the citric acid concentration to 1.0 M allowed for the recovery of 89%, 86%, 86%, and 80% of Ni, Co, Mn, and Li, respectively [65]. Therefore, it may be concluded that the low concentration of 0.75 M citric acid used in our study and the absence of reducing agent in the system with mechanical mixing were the reasons for the low efficiency of metal recovery.

### 3.3. Effect of Leaching Temperature on Li Efficiency with Oxalic Acid

From hydrometallurgical practice it is known that generally, temperature intensifies the leaching of metals from solid phase. Therefore, the effect of lower temperature on the leaching efficiency of the valuable metals in LIBs was studied only for one case, i.e., using oxalic acid. We compared the mobilization of Li at room temperature (around 22 °C), 40 °C and at 60 °C when mechanical stirring and ultrasound (only at 60 °C) were applied (Figure 6). Due to the low leaching efficiency of Ni, Co, and Mn (<1%) with mechanical mixing, these metals were not included in the chart. As expected, at lower temperatures, the efficiency of Li leaching was at low level of 23.0% and 37.1% respectively, at 22 °C and 40 °C. However, Li extraction increased significantly with leaching temperature in the ultrasound system. Ultrasonic cavitation produces high local temperature, increasing with time from 30 °C after 5 min to a constant of 60 °C after 60 min. This was accompanied by a clear increase in the efficiency of Li leaching from 4.4% after 5 min at 30 °C to 94.1% when the system reached a temperature of 60 °C. This concurs with research by Yoon et al. [66], who showed, that increasing the temperature from 25 °C to 60 °C led to an increase in Li recovery from 7% to 100%. Similar conclusions were found in many works dedicated influence temperature on recover valuable metals from spent lithium-ion batteries [9,10,52,59,62,65,67]. Temperature is a factor, which significantly affects the increase of effectiveness of leaching Li and other metals, i.e., Co, Ni, and Mn, especially when an additional factor, reductant agent, is present [62]. For example, with increasing reaction temperature from 30°C to 50 °C, the leaching efficiency of Li, Ni, Co and Mn improved

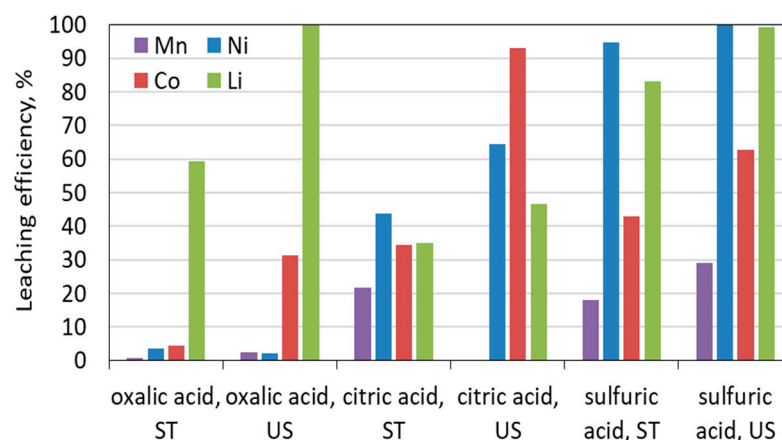
from 90.7%, 87.2%, 87.5% and 87.2% to 98.9%, 94.8%, 95.6% and 94.3%, respectively, [52] Also Okonkwo [53] improved that, compared to conventional mechanical stirring, the application of ultrasonic waves improves the leaching of metals by ~22–74%, with the degree of enhancement dependent on the temperature and the metal. The findings illustrated in Figure 6 confirm the expected results and align with data published in the literature. Specifically, the data demonstrate that lithium (Li) leaching efficiency was significantly higher at 60 °C, as anticipated. The best leaching results were observed at this temperature, particularly when ultrasonic stirring (US) was employed. This corroborates previous studies indicating that increased temperature and the presence of ultrasonic waves enhance Li extraction efficiency. Therefore, maintaining a constant temperature of 60 °C from the very beginning of the process should be considered in further research on the recovery of metals from LIBs.



**Figure 6.** Effect of temperature on Li recovery in sonochemical (US) and stirring leaching (ST).

### 3.4. Leaching under Sonic Conditions vs. a Mechanical Stirring System

Our experiments were conducted without the addition of reductants such as  $H_2O_2$ , glucose,  $NaHSO_3$  or ascorbic acid, applying ultrasound as the only intensifying factor. In the systems with ultrasounds present, the effectiveness of transitioning metals to a solution was higher in relation to systems applying the stirring leaching method, as displayed in Figure 7.

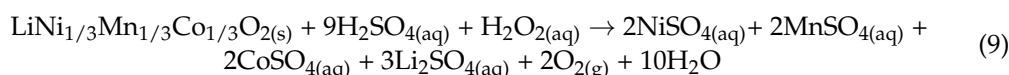
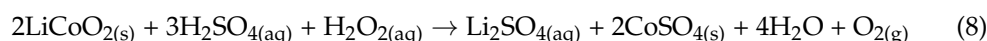
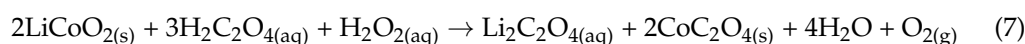


**Figure 7.** Comparison of metals leaching efficiency with different methods (0.75 M acids, 60 °C, 240 min): ultrasound leaching (US) and stirring leaching (ST).

Depending on the leaching medium used, in addition to Li, Co, Ni and Mn also pass into the solution. During the ultrasound process, vacuum holes are produced in the solution, and the formed bubbles are enlarged gradually when the sound pressure increased via the transmission of ultrasonic waves [51,68,69]. Growing bubbles attack the surface of the ground material and finally burst with high pressure accelerating the leaching of metals. Ultrasonic waves promote not only cavitation but also convective motion, which increases the contact area of solid and liquid, providing a large amount of energy, which facilitates the dissolution of material [27]. Ultrasound significantly improves the mass transfer rates by causing cavitation, which leads to the formation of micro-jets and shock waves. This phenomenon enhances the penetration of the leaching agents into the solid matrix. Yan et al. [51] reported up to 10% increase in the leaching efficiency of Li, Co, Ni, and Mn using ultrasound compared to traditional methods. Also other authors [45,50,51,54] using different organic media demonstrated higher ultrasound leaching efficiencies for cobalt and lithium. Importantly, in our research, we also considered the possibility of the presence of an additional effect of ultrasound waves phenomenon—the formation of H<sub>2</sub>O<sub>2</sub>. In the presence of ultrasound, in aqueous systems and organic acids, in addition to the local increase in temperature, pressure formation, and the growth and implosive collapse of bubbles, transient cavitation initiates the formation of hydrogen atoms and free hydroxyl radicals which may recombine to form hydrogen and hydrogen peroxide, depicted by reactions [70–72]:



The creation of free radicals and the presence of H<sub>2</sub>O<sub>2</sub> in systems with ultrasound supports the extraction and the transition of Co, Ni and Mn into solution. Hydrogen peroxide is one of the most effective reductants in terms of enhancing cobalt, manganese and nickel leaching from LIBs in organic [10,28,30,59] and inorganic (H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>) acids [10,62,73,74], as follows:



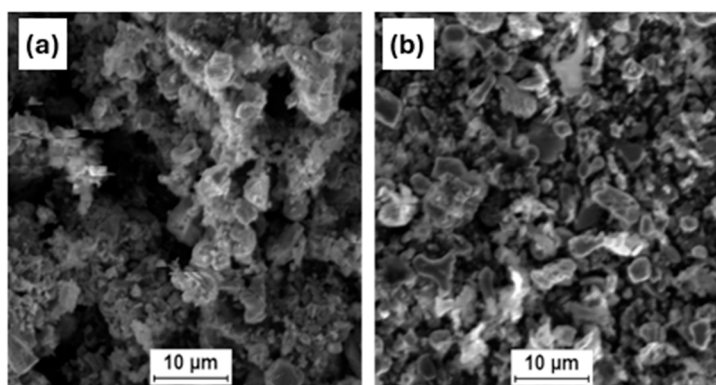
Hydrogen peroxide has been used successfully as a reducing agent to increase the leaching rate Li and Co in leaching systems without ultrasounds. The authors of [75] reported increase in Li, Ni, Co, and Mn leaching efficiencies to over 98% within 30 min by adding H<sub>2</sub>O<sub>2</sub> at a temperature, 50 °C. Bertuol et al. [76] explored the use of H<sub>2</sub>O<sub>2</sub> and showed that at atmospheric pressure, cobalt leaching was favoured by increasing the amount of H<sub>2</sub>O<sub>2</sub> (from 0 to 8% *v/v*) reaching more than 95 wt.% of cobalt during 5 min with H<sub>2</sub>SO<sub>4</sub> and CO<sub>2</sub>. Also, Chen et al. [77] added peroxide to phosphoric acid, increasing Co recovery up to 99%. Comparing the behavior of Co, Ni, and Mn in mixing and ultrasound systems in oxalic acid, it was observed, that only Co transitioned into the solution throughout sonoleaching. It can therefore be concluded, that not only it was this caused directly by the temperature, but that the presence of ultrasound and the effect of the creation of H<sub>2</sub>O<sub>2</sub> may have been responsible for catalyzing the dissolution reaction of Co. Cathode transition metals have low solubility as they exist in <sup>+3/+4</sup> valence states in discharged cathodes and are difficult to leach due to the strong metal–oxide bonds [10,50]. It seems, that the rapid realize of Li first from the solid phase of the cathode causes the rupture of the bond structure of the LiCoO<sub>2</sub> material, followed by the release of Co and the reduction of Co<sup>3+</sup> to Co<sup>2+</sup>, which then goes into solution. Hydrogen peroxide production

during cavitation depends on the intensities of the ultrasonic irradiation and time [72]. It has been indicated that the  $\text{H}_2\text{O}_2$  concentration is higher where the ultrasonic intensity is greater and the time is longer [78,79]. This explains the release of Co after 60 min, i.e., the time needed for  $\text{H}_2\text{O}_2$  to form; this peroxide is then used by the released Co faster than Mn and Ni, which remain bound in the solid phase. Additionally, the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  by  $\text{H}_2\text{O}_2$  might be further accelerated by increasing the temperature; this is in agreement with previous findings [27,30]. It was possible to recover 99.6% of the Li and 31.2% of the Co during sonochemical leaching with oxalic acid, while in the stirring system, it was only 59.2% of the Li and 4.4% of the Co. Ultrasound also supports the dissolution of metals from batteries in citric acid and  $\text{H}_2\text{SO}_4$  solutions. In these cases, however, co-dissolution of all metals with varying efficiency was observed. In addition to the partial dissolution of Co and Mn in the  $\text{H}_2\text{SO}_4$  solution, a slightly higher degree of Ni recovery was obtained, i.e., 99.9% compared to 94.7% in the mixing system. Also for Co, a higher leaching efficiency was achieved during sonoleaching: 62.8% compared to 42.8% during mechanical mixing. Citric acid was shown to be one of the best chelating agents, as it should accelerate the dissolution process [27]. However, compared to  $\text{H}_2\text{SO}_4$  and oxalic acid, chelating only with  $\text{Co}^{2+}$  was s greatly accelerated citric acid by the cavitation action of ultrasound [27] and the possible presence of  $\text{H}_2\text{O}_2$ ; 93.1% of Co was leached with ultrasound, while in the stirring system, it was 42.8%.

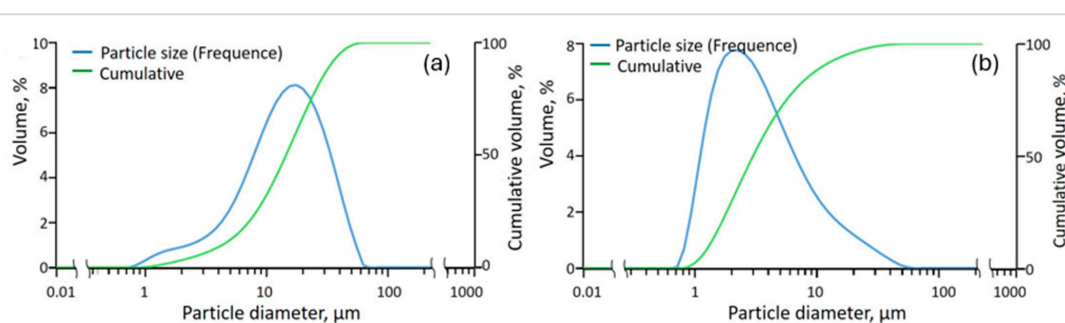
### 3.5. Cathode Active Material after Ultrasound-Assisted Leaching

Figures 8 and 9 present, respectively, SEM pictures and the particle-size distribution of the initial cathode active material following the milling process and mechanical sieving (fraction < 0.1 mm) and the residue after ultrasound-assisted leaching with sulfuric acid. According to Figure 8, the initial material had a dense structure with porous agglomerates, while the residue was looser with visible individual grains of material and smaller particle sizes.

Leached material after the ultrasonic-assisted treatment shows a significant reduction of particle size relative to initial material, what is described in many works [27,80–83]. The results of particle size distribution (Figure 8) also confirm SEM analysis. The resulting curves differ significantly from one another.  $D_{90}$  value is below 35  $\mu\text{m}$ ,  $D_{50}$  below 15  $\mu\text{m}$  for the initial cathode material before leaching and the proportion of the particle diameter below 10  $\mu\text{m}$  was small (Figure 9). Compared with the residue after ultrasound leaching, the particle size below 10  $\mu\text{m}$  of the cathode material was obviously predominant and  $D_{90}$  value was below 11  $\mu\text{m}$  and  $D_{50}$  below 3  $\mu\text{m}$ . Particle size reduction is directly related to the mechanical ultrasound effect and accompanied cavitation phenomenon damaged the solid surface [45,67,79,83]. Ultrasound increases the specific surface area of materials and provides contact of the solid phase with the solvents which accelerates the dissolution reaction and improves the leaching rate.



**Figure 8.** SEM images of cathode active material. (a) before leaching, (b) residue after ultrasound leaching.



**Figure 9.** Particle size distribution of active cathode material (a) before leaching and (b) after ultrasound-assisted leaching.

#### 4. Conclusions

Ultrasound-assisted leaching is a suitable technique for metal recovery, as it significantly improved the efficiency of the Li, Co, Mn and Ni extraction process, particularly with organic acids (citric and oxalic acids), compared to the mechanical stirring leaching process. An average of 50% better leaching results were obtained for Li recovery in oxalic acid and of the Co in citric acid during sonochemical leaching, allowing us to obtain 99.6% of the Li and 93.1% after 4 hours. Oxalic acid, as a leaching and precipitating agent, has a good selectivity in the separation of Li from Co, Ni, and Mn, e.g., in the mixed cathode active material. The optimum Li leach conditions for separation were 0.75 M  $C_2H_2O_4$  at 60 °C for 60 min using ultrasound assistant leaching where 94.1% of Li was recovered. Based on the theory of free hydroxyl radicals and hydrogen peroxide formation during ultrasound waves action in acids solutions, it may be concluded that hydrogen peroxide is a support factor that reduces the high valence of metals to a lower state, enhancing cobalt, manganese and nickel leaching from LIBs.

Future research in ultrasound-assisted leaching should focus on optimizing ultrasound parameters such as frequency, power, and duration to enhance metal recovery efficiency. Further exploration of other organic acids, beyond citric and oxalic, could lead to improved selectivity and recovery rates for various metals. Mechanistic studies are essential to understand the influence of ultrasound on the chemical and physical properties of the leachate and its effect on the dissolution and precipitation of metals. Additionally, assessing the environmental impact and sustainability of the use of organic acids in this process is crucial, including evaluating the potential for recycling these acids to reduce waste and costs.

Scaling up the laboratory processes for industrial applications is another vital area of study, addressing challenges related to equipment design, process control, and energy consumption. The technology's applicability to other battery types and electronic waste (e-waste) containing valuable metals should also be investigated, potentially broadening its scope. Moreover, integrating ultrasound-assisted leaching with other recovery techniques, such as bioleaching or electrochemical methods, could enhance overall efficiency and recovery rates. This research aims to refine and expand the use of ultrasound-assisted leaching, potentially revolutionizing metal recovery from various sources and contributing to more sustainable recycling practices.

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