Circular raw material and waste management: a comparison of biological and chemical approaches for the recovery of metals from spent lithium-ion batteries

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Abstract: Modern production processes are characterized by the extensive demand for metal in the manufacture of lithium-ion batteries used in electronic equipment and electric vehicles. These products are essential for the functioning of today's society, therefore the demand for metallic raw materials increases annually and their natural resources are overexploited. The solution to this issue is the recovery of raw materials from polymetallic waste, which includes spent lithium-ion batteries. The extraction of metals from this type of waste material has already been implemented on an industrial scale, but the priority now is to create technologies that will not only be effective in terms of metal recovery but also environmentally friendly following sustainable development goals and the principles of a circular economy. Concerning the need for alternative ecological methods of waste processing, the concept of recovering Co, Cu, Li and Ni from waste lithium-ion batteries using a biotic and mild chemical approach was proposed. It has been determined that the biological approach to metal recovery may be a promising process in the recycling of lithium-ion battery waste since within 7 days, at a pulp density of 1% and using *Acidithiobacillus thiooxidans* bacteria, comparable results were obtained for the recovery of Co (25.7%), Li (48.8%) and Ni (28.3%) as for leaching with mild organic citric acid. Moreover, the fungus *Aspergillus niger* may be a promising microorganism used in the bioleaching of electrode powder from spent lithium-ion batteries, although the process using it requires the optimization of bioreactor parameters.

Keywords: bacteria, fungus, bioleaching, lithium-ion batteries, recovery of metals

INTRODUCTION

The constantly growing demand for small-size mobile devices and the developing sector of the automotive industry has led to an increase in the amount of lithium-ion batteries (Li-ion batteries, LiBs) being produced and which, in turn, results in a constant increase in the generation of waste. Battery waste must be treated appropriately due to the presence of various chemical substances that pose a potential threat to living organisms and the water and soil environment. Recycling waste LiBs is also economically beneficial. Li-ion batteries are made of many components that can be successfully recovered and, after appropriate preparation, reused, e.g., in the production of new batteries. The most valuable components of waste Li-ion batteries are critical raw materials, especially metals contained in the battery black mass-powdered electrode materials (Sethurajan & Gaydardzhiev 2021, Lebrouhi et al. 2022, Windisch-Kern et al. 2022). The anode is graphite, while the polymetallic cathode occurs in the form of lithium metal oxide, including cobalt ($LiCoO_2$), manganese ($LiMn_2O_4$), nickel and manganese ($LiNi_xMn_yCo_zO_2$), nickel, cobalt and aluminum ($LiNiCoAlO_2$) or iron and phosphorus ($LiFePO_4$) (Thompson et al. 2020, Hantanasirisakul & Sawangphruk 2023, Zhu et al. 2023). The recovery of metals is particularly important, as their over-exploitation can lead to the depletion of natural resources (Arndt et al. 2017). Recycling batteries through the recovery of the metal contained in them is also in line with sustainable development goals and the assumptions of the circular economy model (Sheth et al. 2023, Tripathy et al. 2023). To maximize the recovery of metals, it is necessary to properly and effectively prepare the material in advance for further processing. For this purpose, the first stage of battery recycling, i.e. the mechanical treatment of the accumulated waste material, plays a crucial role (Colledani et al. 2023, Leal et al. 2023, Vieceli et al. 2023). The industrial mechanical treatment of waste batteries includes automatic crushing, grinding and then sieving individual fractions until the smallest paramagnetic fraction is obtained, the majority of which is made of electrode powder – anode and cathode containing various types of metals, e.g. Li, Co, Ni, Mn (Reinhart et al. 2023, Yu et al. 2023, Zhang et al. 2023). Before the actual metal recovery processes, the electrode powder is most often subjected to thermal or chemical pre-treatment to remove potential contaminants, such as remnants of foil, separators, or graphite (Wei et al. 2023).

For the recovery of metals contained in the LiB electrode powder waste, pyrometallurgical or/and hydrometallurgical methods are mainly used on a global industrial scale (Sommerville et al. 2021, Baum et al. 2022, Jin et al. 2022, Raj et al. 2022, Zhao et al. 2024). Pyrometallurgy is based on the thermal transfer of components to the solid phase (usually metal alloys) or the gas phase with subsequent condensation, while hydrometallurgy is acid (with the use of mineral or organic acids) or alkaline leaching, during which metals are transferred from the battery powder to the liquid solutions and then selectively recovered (Chandran et al. 2021). However, despite the great popularity of pyrometallurgy and hydrometallurgy, solutions that are not only effective but also beneficial for the environment are constantly being sought. A promising alternative for recycling battery waste are biological leaching processes using various types of microorganisms that have the ability to recover metals. Bioleaching is a process in which metals and their compounds are converted with the participation of appropriately selected microorganisms into more water-soluble forms (Li et al. 2023). Various microorganisms have already been used to recover metals from spent Li-ion batteries, mainly bacteria and fungi, which can biologically produce acids (Abdollahi et al. 2024, Gerold et al. 2024). Using such a process for leaching polymetallic electrode powder has numerous advantages including reduction of secondary pollution (e.g. no emission of toxic gases), high efficiency, safety and low cost of the process (Alipanah et al. 2023, Biswal & Balasubramanian 2023, Moosakazemi et al. 2023, Panda et al. 2024). However, despite its competitiveness to chemical methods in terms of environmental impact, bioleaching constantly requires improvement in the scope of microorganisms or their consortiums used and optimization of the basic process parameters, such as pulp density, duration and the reactor configuration, especially concerning scaling the technology for use in the batteries recycling industry (Moosakazemi et al. 2003, Xin et al. 2016, Li et al. 2023).

Concerning the current trends in waste batteries recycling and critical raw materials management, research on the biological and chemical recovery of metals from waste LiBs has been carried out. The aim of the bioleaching experiments conducted was to investigate complex scenarios of recovery processes taking into account a broad spectrum of chemical and biological factors for battery electrode powder recycling. In particular, the research included the analysis of the used microorganisms – *Acidithiobacillus thiooxidans* bacteria and *Aspergillus niger* fungus affecting the leaching of critical metals (Co, Cu, Li and Ni) to determine the potential and applicability of biotic techniques. Moreover, for comparative purposes, a series of acid leaching experiments using mild organic citric acid were performed as a simulation of a potential hybrid process based on biologically-produced citric acid. The choice of the

Acidithiobacillus thiooxidans bacteria and the *Aspergillus niger* fungus for experimental research was justified because (a) microorganisms have been repeatedly identified in polymetallic waste landfills, hence they constitute a realistic model of microorganisms adapted to rigorous conditions where we can expect high concentrations of toxic elements, (b) the microorganisms generate an acidic environment, hence they simulate the conditions under which microorganisms excrete various acidic metabolites, (c) these microorganisms show good tolerance to high metal content in the environment, hence the presence of these particular microorganisms in the bioleaching system would be expected not to inhibit microbial activity, and thus battery powder leaching. In turn, 2 M citric acid was selected as a mild organic leaching agent that (a) occurs naturally in the environment; (b) is one of the metabolic products in the growth phase of the *A. niger* fungus (Gerold et al. 2024), which simulates the acidic conditions it generates, (c) is a relatively cheap organic chemical reagent, which positively affects the costs of conducting the process on a semi-technical and technical scale compared to the currently most commonly used mineral acid leaching (mainly with sulfuric acid).

MATERIALS AN METHODS

Mechanical treatment and material characteristics

The mechanical treatment of waste Li-ion batteries (18650 type) began with the manual disassembly of the outer battery casing to separate individual battery cells. Then, each cell was separated into parts such as a steel casing, plastics, copper and aluminum foils, a separator and battery black mass – a powdered graphite anode and a polymetallic cathode. A sample of the separated battery powder was subjected to thermal treatment – calcination at 750°C for 12 hours to check the loss of impurities, mainly graphite, and to determine the appropriateness of introducing additional pre-treatment processes in the context of the achieved metal recovery rates. The calcined sample was analyzed for morphology as well as quantitative and qualitative composition using scanning electron microscopy (SEM) coupled with the energy-dispersive X-ray spectroscopy detector (EDS; JSM-IT100 In-Touch-Scope, JEOL) and X-ray powder diffraction (XRD; D8 Advance, Bruker). The sample was also mineralized (DigiPREP Jr system) to obtain a solution in which the initial concentrations of metal ions (Al, Co, Cu, Fe, Li, Mn, Ni and Zn) were determined by optical emission spectrometry with inductive coupling in plasma (ICP-OES; Agilent 720, Agilent Technologies).

Leaching experiments

The battery powder was evaluated via a biohydrometallurgical and chemical approach under the following experimental configurations: (1) bioleaching with *A. thiooxidans*, (2) bioleaching with *A. niger* and (3) acidic leaching with 2 M citric acid.

The growth medium dedicated for studied microorganisms and for bioleaching was: (1) for *A. thiooxidans*: 2 g $(NH_4)_2SO_4$, 0.25 g $MgSO_4{\cdot}7H_2O$, 0.1 g K_2HPO_4, 0.1 g KCl and 1% (wt./v) elemental sulfur (S) per 1 L ultrapure water. The pH was adjusted to value 2.5 and (2) for *A. niger* (DSM 2466): 100 g saccharose, 1.5 g $NaNO_3$, 0.025 g KH_2PO_4, 0.025 g $MgSO_4{\cdot}7H_2O$, 0.025 g KCl, 1.6 g yeast extract and pH adjusted to 4.0.

First 0.5 g, 2.5 g, and 5 g of calcinated battery powder were weighed in triplicate (for biotic, control and acid leaching samples) and transferred to the sterile and metal-free culture flasks made of transparent polystyrene (PS) equipped with a "Vent" cap with a hydrophobic filter (with a 0.22-micrometer membrane). Then, 50 mL of sterile medium inoculated with 2 vol.% of biomass/2 M citric acid solution or 50 mL of sterile medium (bioleaching control tests) were added to the tested samples, obtaining pulp density (PD) of 1%, 5% and 10%. Leaching experiments were extended up to 21 days (for single stage approach) with a sampling interval fixed at 7, 14 and 21 days. The flasks were placed on a horizontal shaker set at 60 rpm. The process temperature was 35°C. After collection, the content of Co, Cu, Li and Ni metals in the leachates was determined using the ICP-OES method (Agilent 720, Agilent Technologies). The efficiency of metal extraction was expressed as percentage recovery rates concerning the initial content of metal ions and their concentration obtained in the solutions after leaching, taking into account the leaching solution volume and the processed waste material mass.

RESULTS AND DISCUSSION

Qualitative and quantitative composition of the tested battery powder

The results of XRD analysis (Fig. 1) showed that the separated electrode powder material consists primarily of a compound in the form of $LiCoO_2$ – a characteristic cathode material for cylindrical Li-ion batteries type 18650. The battery powder also contains carbon coming from the graphite anode of the batteries. Moreover, the electrode powder is a polymetallic material with the highest content of Co, Cu, Li, Fe and Ni, as shown by the analysis of solutions after mineralization using the ICP-OES method (Table 1). Since Fe and metallic Al are not critical raw materials, the metal recovery stage focused on the extraction of Cu, Co, Li and Ni.

The results of SEM-EDS analysis (Fig. 2) confirm the quantitative and qualitative characteristics of the tested battery material obtained from XRD and ICP-OES measurements. The electrode powder obtained from spent Li-ion batteries after initial thermal treatment has a granular, relatively homogeneous structure. The powder composition showed the presence of elements typical for Li-ion batteries with LCO cathode, i.e. Co and O (due to the limitations of the method, Li is not detected), as well as C from the anode material, P and F – electrolyte components and Al, which may be residues of the aluminum foil on which the cathode is deposited.

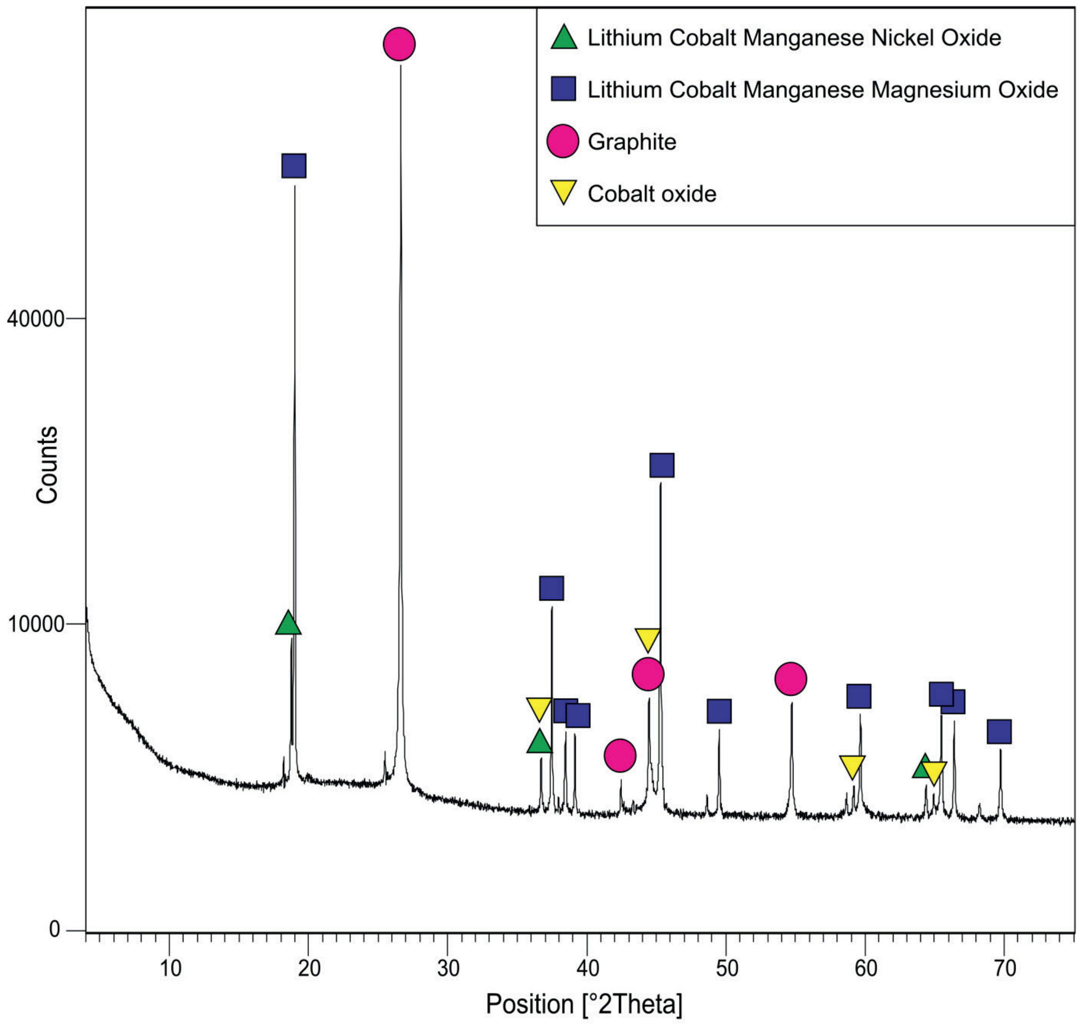

Fig. 1. XRD analysis of electrode powder obtained from tested waste Li-ion batteries with thermal pretreatment

Table 1
Chemical composition of the tested battery powder obtained by ICP-OES analysis

Metal	Al	Co	Cu	Fe	Li	Mn	Ni	Zn
Content [%]	4.60	22.80	11.45	2.93	3.62	1.03	1.49	1.12

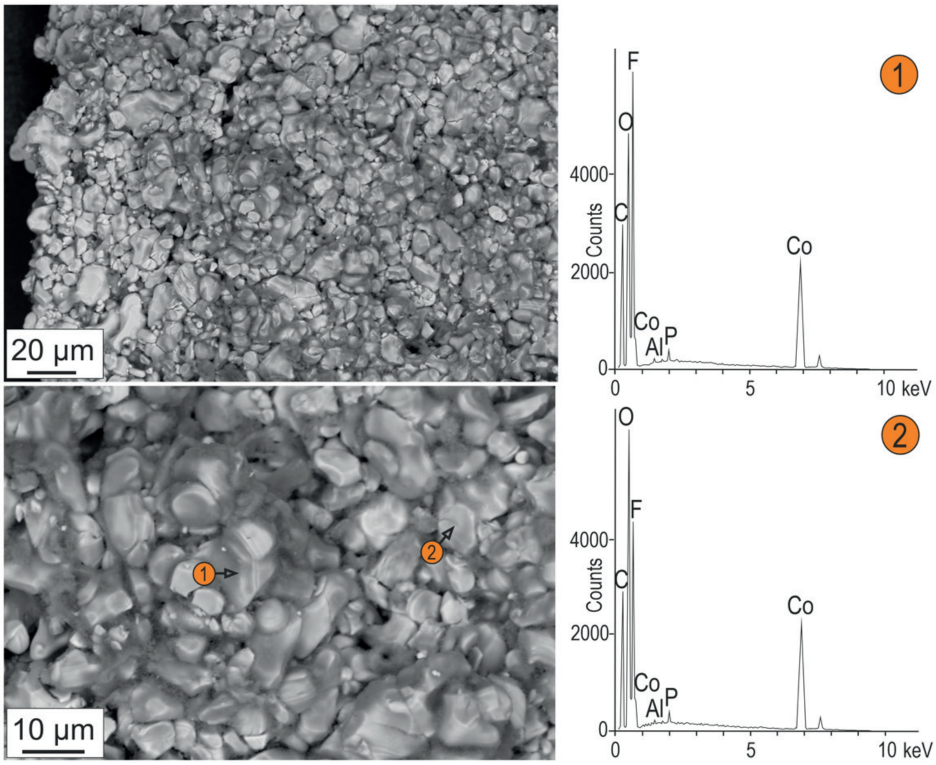

Fig. 2. *SEM-EDS analysis of thermal pretreated electrode powder obtained from tested waste Li-ion batteries (1, 2 – measurement points for EDS analysis)*

Metals recovery efficiency

In a series of bioleaching experiments using *Acidithiobacillus thiooxidans* bacteria (Fig. 3), the highest recovery rates were obtained after 7 days of extraction for the lowest pulp density (PD 1%), respectively: Co – 25.7%, Cu – 2.4%, Li – 48.8%, and Ni – 28.3%. Low pulp density (PD 1%) enables the efficient contact of the solid with a leaching solution which results in good leaching efficiency. On the other hand, economic process would rather require higher pulp densities in order to increase potential reactor processing rates. In turn, the leaching of battery powder in the control experiment (abiotic sample with sterile medium without bacteria) allowed us to achieve maximum recovery of 1.3% Co, 2.2% Cu, and 1.6% Ni within 7 days for PD 1% and 12.7% Li within 21 days for PD 5%. Therefore, biotic experiments (i.e. using bacteria) allowed us to significantly increase the extraction level for Co, Li, and Ni. Such behavior was mostly due to the different pH conditions observed for biotic and abiotic incubations (Table 2). It proves that bacteria *A. thiooxidans* is an efficient acid producer and yet this microorganism is able to handle even the stringent conditions caused by the toxic character of battery powder and its buffering capacity which results in a rise in pH. The lowest recovery rates in biotic experiments were demonstrated for Cu (Fig. 3B), where, regardless of the pulp density used and the process duration, 3% recovery was not exceeded.

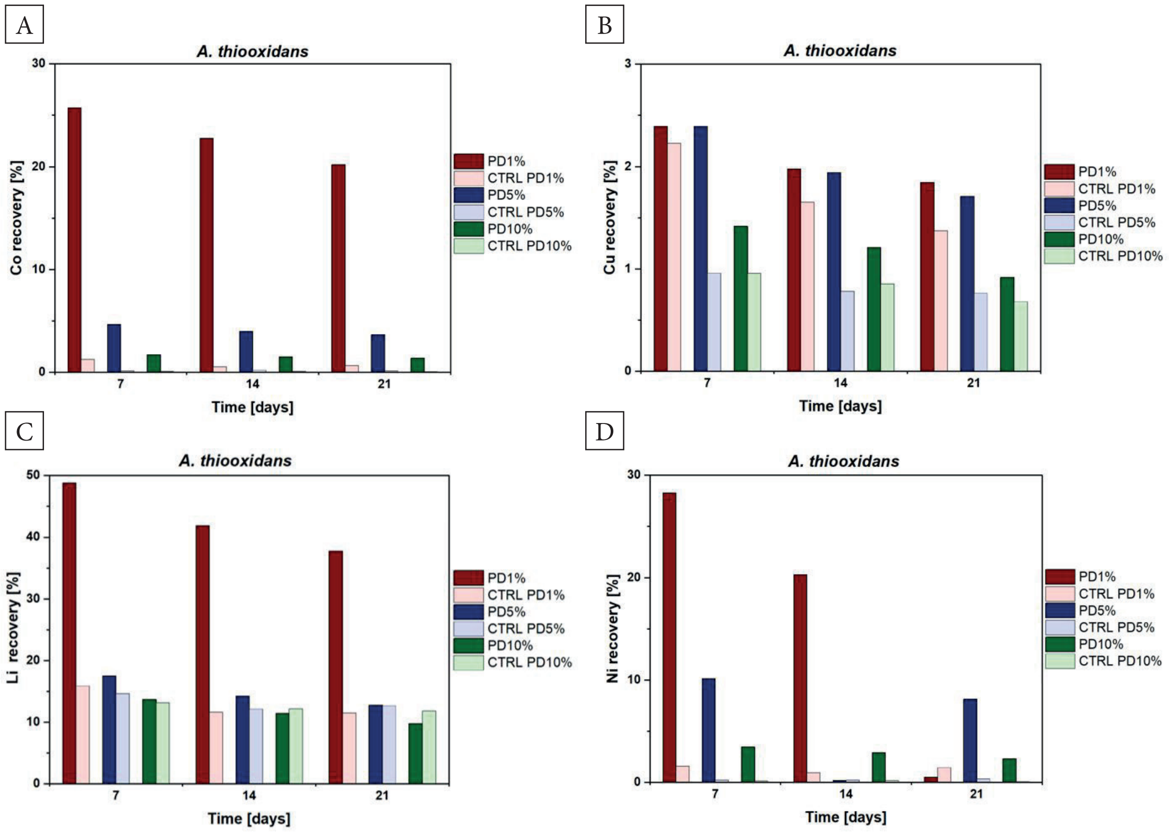

Fig. 3. *Recovery rates of Co (A), Cu (B), Li (C), and Ni (D) obtained in bioleaching with A. thiooxidans bacteria (PD – pulp density, CTRL – control sample)*

This is most likely due to the influence of the pH value of the sample with bioleached powder and bacterial culture solution on the Cu recovery rates. In this paper, the medium was adjusted to an acidic pH of 2.5, with the initial pH of the battery powder being alkaline. Noruzi et al. (2022) show that the initial pH for electrode powder obtained from waste Li-ion batteries from laptops is 11.8. It can therefore be assumed that similarly to the research of Biswal et al. (2018) on Li-ion batteries, as well as that of Isildar et al. (2016) on polymetallic printed circuit boards, the addition of waste material increased the pH value of the sample at the beginning of the process. Moreover, Cu is extracted more effectively by the *A. thiooxidans* bacterial culture at a pH not exceeding 2. It should also be emphasized that acidophiles develop optimally at a pH below 2.5, which also affects the effectiveness of the metal bioleaching process over a longer extraction period (Isildar et al. 2016). This statement is confirmed by the obtained test results – for all of the tested metals, a decrease in recovery efficiency was observed with the extension of leaching time, with the lowest results obtained for samples with the highest pulp density (PD 10%) and those leached the longest – for 21 days. Undoubtedly, as time progressed, the buffering potential of battery powder increased. Consequently, the pH variations of the solutions showed an increasing trend (Table 2). In turn, the decrease in leaching rates during the entire bioleaching cycle (for 21 days) is particularly visible for Co, Li, and Ni in PD 1%. The extraction rate also decreases for other pulp densities, but the differences in recovery rates are not that notable. In the case of Cu extraction, the decrease in recovery efficiency during 21 days of the process is minimal for each of the pulp densities tested due to the relatively low efficiency of the biotic process. Therefore, in addition to the pH value of samples during extraction, the selection of pulp density parameters and process duration are crucial in the context of the recovery rates obtained in the bioleaching process using *A. thiooxidans* bacteria.

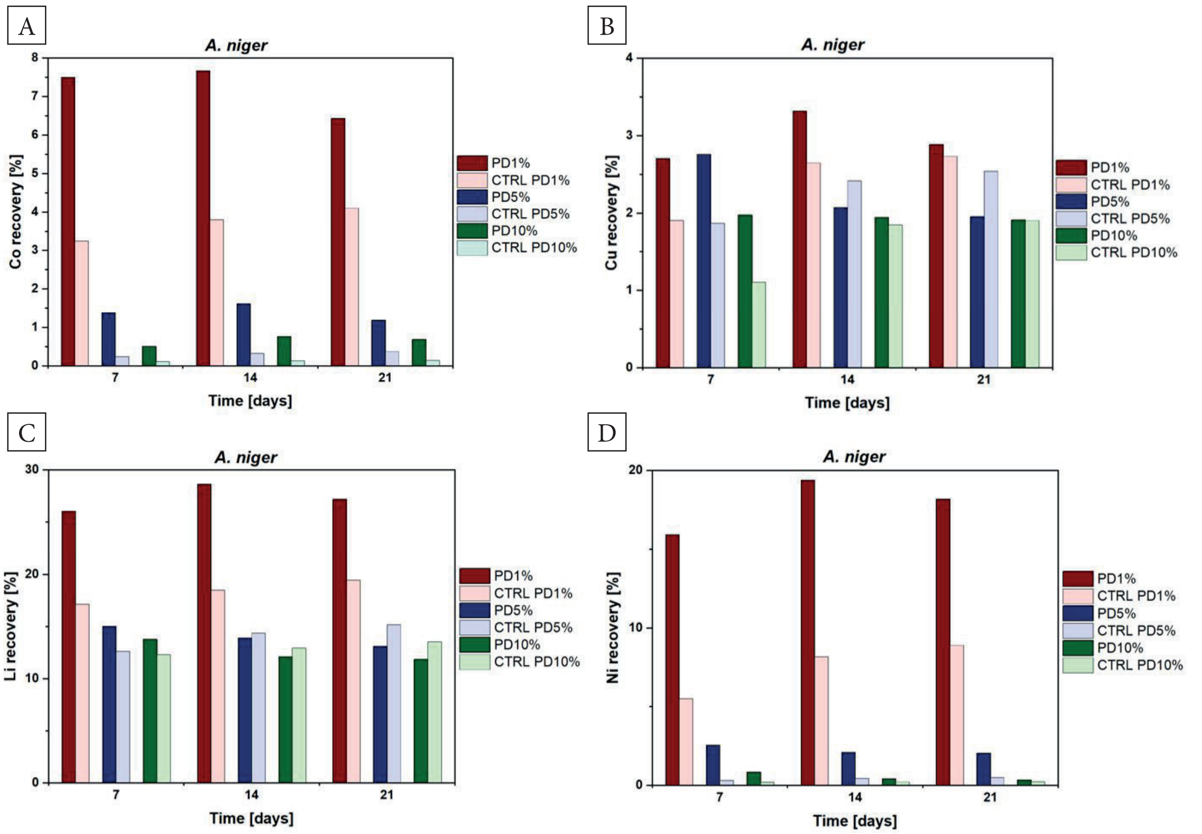

Fig. 4. *Recovery rates of Co (A), Cu (B), Li (C), and Ni (D) obtained in bioleaching with A. niger fungus (PD – pulp density, CTRL – control sample)*

Table 2
Evolution of pH throughout the experiments

Time	***Acidithiobacillus thiooxidans***			**AT Control**		
	PD 1%	**PD 5%**	**PD 10%**	**PD 1%**	**PD 5%**	**PD 10%**
7 days	2.5	3.84	4.57	5.74	7.57	8.11
14 days	2.67	4.15	4.89	6.60	7.30	8.40
21 days	4.24	5.44	7.06	8.00	8.50	9.01
Time	***Aspergillus niger***			**AN Control**		
	PD 1%	**PD 5%**	**PD 10%**	**PD 1%**	**PD 5%**	**PD 10%**
7 days	3.52	4.52	4.81	4.55	8.04	8.13
14 days	3.82	4.82	5.67	5.46	6.78	7.90
21 days	4.10	5.17	6.13	6.30	8.17	8.23
Time	***Citric acid***					
	PD 1%	**PD 5%**	**PD 10%**			
7 days	1.99	2.29	2.54			
14 days	2.00	2.62	3.16			
21 days	2.23	2.88	3.64			

In the case of bioleaching using the fungus *Aspergillus niger* (Fig. 4), the highest levels of metal recovery were obtained for samples with the lowest pulp density (PD 1%) on the 14th day of extraction, respectively: Co – 7.7%, Cu – 3.3%, Li – 28.6%, and Ni – 19.4%, and the extraction of Co, Li, and Ni was lower than for bacterial samples on the 7th day of leaching. The result was only higher for Cu in the biotic tests using *A. thiooxidans*, but this is not a significant difference. Moreover, compared to experiments with bacteria, only 7.7% Co extraction was achieved, which highlights the potential of using the *A. niger* fungus for selective metal recovery, where similar and particularly promising results were obtained for Li and Ni. This is also indicated in the literature, where Ilyas et al. (2024) showed a low, 1% recovery of Co by bioleaching with *A. niger* compared to over 90% recovery of Li in the same process. Moreover, here, in each experiment with *A. niger*, after 14 days the effectiveness of the leaching process decreased for all analyzed metals. Again, the lowest metal leaching was recorded on the 21st day of extraction for the highest pulp density (PD 10%).

As in the case of the use of bacteria, the sample pH during leaching is also important for the *A. niger* fungus. The metabolic processes of the fungus cause the formation of metabolites in the form of organic acids, including citric and oxalic acid, which causes a drop in pH in the solution and likely accounts for a complexation effect. As Bahaloo-Horeh et al. (2018) have shown, the maximum production of organic acids is recorded at a pH in the range of 2.8–3.3, with citric acid being generated at a pH below 3.5, while oxalic acid can be secreted at higher pH. Moreover, a decrease in pH during fungus cultivation from 6 to 4.6 and 3.4 depending on the cultivation conditions was observed (Bahaloo-Horeh et al. 2018). In the metal extraction experiments using the *A. niger* fungus, which was also indicated in the case of bioleaching with *A. thiooxidans*, the addition of alkaline electrode powder significantly increases the pH of the solution during the process. Therefore, even the potential lowering of pH by acidic metabolites of the fungus does not efficiently lower the pH of solutions during leaching to an acidic environment, favoring high levels of recovery of the tested metals, which is confirmed by the obtained analytical results (Fig. 4). This therefore emphasizes the thesis indicated in the bioleaching tests of electrode powder with the *A. thiooxidans* bacteria, that both the pH of the samples influences the effectiveness of metal recovery during the process, as well as the selected pulp density and leaching time. Additionally, for control incubations (sterile medium without fungus culture), maximum recovery rates of 4.1% Co, 2.7% Cu, 8.9% Ni, and 19.5% Li were achieved within 21 days for PD 1%. This means that the use of the *Aspergillus niger* fungus for the recovery of metals from waste Li-ion battery electrode powder is a prospective process that requires the appropriate optimization of extraction parameters.

As a result of additional experiments on leaching battery powder with citric acid simulating a metabolite of the *A. niger* fungus (Fig. 5), it was shown that both process duration and pulp density are important for the recovery of various metals.

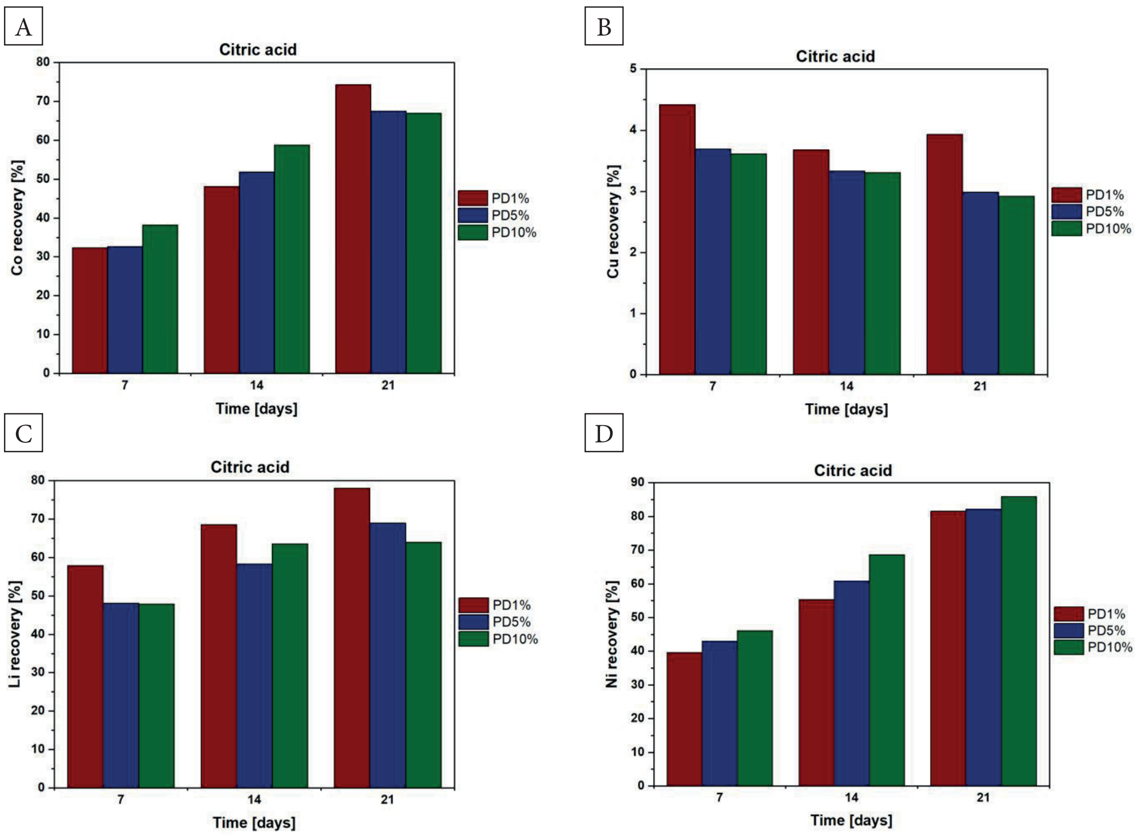

Fig. 5. *Recovery rates of Co (A), Cu (B), Li (C), and Ni (D) obtained in leaching with citric acid (PD – pulp density)*

For Co and Li, the highest recovery rates were obtained on the 21st day of the process for PD 1%, respectively: 74.3% and 78.1%. In turn, the most Ni was extracted (85.6%) on the 21st day of the experiment at the highest pulp density (PD 10%), but this efficiency is not significantly higher than for PD 1% (81.6%) and PD 5% (82.2%) at the same time. It indicates that Ni extraction from a battery powder is independent of pulp density and yet such behavior was due to the relatively comparable pHs, both throughout the experiment and among PDs applied (Table 2). On the 7th day of the citric acid leaching process for PD 1%, the highest rate of Cu recovery was obtained (4.4%). On day 14 of the experiment, the extraction efficiency of Cu decreased and then increased slightly on day 21 – unlike other metals. It can therefore be concluded that for samples leached with organic acid, extending the extraction time is beneficial, especially concerning the recovery of Co, Li and Ni. However, this may affect the scaling of the process to a semi-technical or industrial installation, where a longer extraction time will adversely affect the economic benefits of the technology. Moreover, the pulp density parameter would also require optimization to higher values, which, however, may be potentially simpler than in the case of biotic experiments, especially concerning Ni recovery, for which the highest efficiency was achieved in the highest pulp density (PD 10%). This indicates the great potential of the biological method using the fungus *A. niger*, which generates citric acid as a metabolite. In turn, the biological process using *A. thiooxidans* seems to be a promising green alternative to acid leaching using citric acid as the leaching agent due to the possibility of obtaining the highest rates of metal recovery in a relatively short time – already on the 7th day of the process. Comparing the efficiency of the biotic process with *A. thiooxidans* for chemical leaching, it can be seen that for PD 1%, during 7 days of experiments, slightly lower recovery rates were obtained, especially of Co, Li and Ni (*A. thiooxidans*: 25.7%, 48.8% and 28.3%; citric acid: 32.4%, 57.9% and 39.6%, respectively). Thus, appropriate optimization of other parameters in biological processes (pulp density and pH of samples during leaching) may allow the development of a recycling technology for waste Li-ion batteries that is beneficial in terms of metal recovery efficiency and is safer for the natural environment.

The economic potential and future applications of recycling processes for waste LiBs

The economic potential of the implemented recycling process of waste Li-ion batteries lies not only in the profits resulting from processing batteries as waste but also in the recovery of metals at the stage of the biotechnological process. This, in turn, creates great market potential in the context of a circular economy by obtaining raw materials (metals) from secondary sources, and not from natural deposits as would be the case in a linear economy concept. This confirms the profitability of the process from both an environmental and economic point of view. Therefore, taking into account the reactor capacity, functional parameters, process effect and metal market prices (based on Business Insider and Trading Economics), the total estimated economic potential for the reactor cycle is as follows:

- for the control reactor with medium dedicated for *A. thiooxidans*, \$380/ton of powder per reactor cycle;
- for a biotic reactor with *A. thiooxidans* bacterium, \$2500–3000/ton of powder per reactor cycle;
- for a control reactor with medium dedicated for *A. niger*, \$530–900/ton of powder per reactor cycle;
- for a biotic reactor with *A. niger* fungus, \$1000–1400/ton of powder per reactor cycle;
- for a chemical treatment with citric acid \$3000–9000/ton of powder per reactor cycle.

The obtained results clearly illustrate the broad economic potential of the process developed.

The overriding value of material recovery is the possibility of replacing natural resources with secondary raw materials obtained from waste, which leads to a sustainable approach to the environment and reduces the need to exploit natural deposits of elements. This is particularly important in the context of recovering metals from raw material resources such as waste, due to growing consumerism and the demand for new, small-sized electronic devices or electric vehicles. Therefore, the methodology for extracting Co, Cu, Li and Ni presented in this paper is of great importance in the context of meeting formal requirements. The use of mild hydrometallurgical processes using organic acids and bioleaching using microorganisms naturally occurring in the environment, capable of surviving in extreme conditions, e.g. variable pH values or in the presence of high metal concentrations, is in line in particular with the principles of raw materials closed-loop and the circular economy. Effective recycling of battery waste also contributes to the achievement of sustainable development goals, in particular Goal 12 on responsible consumption and production (United Nations, n.d.). Since July 2023, European Union member states have also been required to implement the provisions of the new Battery Regulation on the management of batteries and their waste, which focuses on the entire life cycle of batteries – from ecodesign through production, use and replacement, to waste recycling and the possibility of using secondary raw materials recovered from them in new batteries (European Commission – Directorate-General for Environment 2023, Regulation (EU) 2023/1542). The act also establishes regulations on the use of recovered metals in the production of new Li-ion batteries (European Commission – Directorate-General for Environment 2023), which emphasizes the need to seek out and implement modern methods of metal extraction. Therefore, the use of biological methods that have a smaller negative impact on the environment than chemical methods using inorganic acids or high-thermal pyrometallurgical processes, and at the same time with a high potential to achieve the same metal recovery efficiency, is a promising approach to implementation on an industrial scale in the Li-ion batteries recycling market. After appropriate optimization of the biological reactor parameters (including the reaction time and pulp density indicated in these research), bioleaching can be an attractive alternative to conventional hydrometallurgical and pyrometallurgical methods, thus contributing to the development of innovative recycling methods as well as meeting current and future formal and legal requirements.

CONCLUSIONS

The experimental approach implemented for battery powder treatment showed that:

– bacterium *A. thiooxidans* is a highly prospective microorganism for battery powder treatments, taking into account the relatively high efficiency of Co, Li and Ni recovery (Co: 25.7%, Li: 48.8%, Ni: 28.3%) in the shortest process duration (7 days);
– the fungus *A. niger* showed great potential for selective recovery of Co, rendering it a suitable candidate for future treatments;
– citric acid is an effective extractant, especially concerning scaling the process to industrial technologies due to the promising results obtained for the highest pulp density (PD 10%).

The developed technology presented in this paper is on the border of several areas including environmental technologies, process engineering and biotechnology, thus indicating the interdisciplinary nature of the proposed approach, which is crucial from the point of view of both environmental protection and the closed-loop raw materials systems. Therefore, the approach is broadly consistent with the European Union's assumptions regarding the circular economy and sustainable development goals. It is worth highlighting that the presented technology has also several benefits affecting its competitiveness in the market. Typical process solutions for recycling waste LiBs are based on mechanical methods assisted by high thermal or chemical processing. In contrast, the method presented in this article combines mechanical treatment and biological recovery processes using selected species of naturally occurring microorganisms. This approach is more environmentally friendly, meets the latest EU and national legal requirements, and at the same time demonstrates potentially similar metal extraction efficiency to conventional hydrometallurgical or pyrometallurgical methods. Due to the achieved promising results for biotic leaching in laboratory conditions with the use of *A. thiooxidans* bacteria and *A. niger* fungus, future research should be focused on optimization of reactor parameters – pH and pulp density values and reaction duration – for applications on an industrial scale. As the battery powder tends to buffer the pH, shifting the original value of the parameter (i.e. leaching medium pH) towards higher (alkaline) values, the factor of initial pH of the bioleaching medium has to be taken into consideration. The PD (1%, 5% and 10%) revealed that low pulp density results in better extraction yield. However, PD played a different role depending on the leaching reagent used. Overall, the 7-day long extraction period was found to be suitable, however further optimization of the conditions has a chance to shorten the extraction time, especially in experiments using *A. thiooxidans*. The effect of the leaching agent showed that in the biotic approach *A. thiooxidans* bacteria is the most efficient for the recovery of metals from waste LiBs electrode powder. Nevertheless, *A. niger* fungus is also promising in terms of selective extraction of elements and it is worth expanding research into the adjustment of bioleaching process parameters to the highest extraction efficiency in the presence of this microorganisms. On the other hand, citric acid is a prospective chemical, mild organic reagent if the increase of pulp density to 10% is required, with an extended leaching time of up to 21 days giving improved metal recovery results. The methods of recovering metals from waste LiBs presented in the paper are therefore a promising way to recycle waste towards a closed loop of critical raw materials without the need for excessive consumption of their natural mineral resources. After the proper optimization, they can become the basis for the creation of a complex technology for recovering metals from spent LiBs and be implemented in the global industrial recycling sector of this type of waste.

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The source data for the results presented in this study are publicly available in the Open Data Repository (RepOD): https://doi.org/10.18150/T0HCXO.

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