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SUSTAINABLE WASTE MANAGEMENT & VALORISATION WITHIN THE CIRCULAR ECONOMY ERA

Closed-loop recycling of lithium iron phosphate cathodic powders via citric acid leaching

Martina Bruno[1] · **Carlotta Francia**[2] · **Silvia Fiore**[1]

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Abstract
Lithium recovery from Lithium-ion batteries requires hydrometallurgy but up-to-date technologies aren't economically viable for Lithium-Iron-Phosphate (LFP) batteries. Selective leaching (specifically targeting Lithium and based on mild organic acids and low temperatures) is attracting attention because of decreased environmental impacts compared to conventional hydrometallurgy. This study analysed the technical and economic performances of selective leaching with 6%vv. H_2O_2 and citric acid (0.25-1 M, 25 °C, 1 h, 70 g/l) compared with conventional leaching with an inorganic acid (H_2SO_4 1 M, 40 °C, 2 h, 50 g/l) and an organic acid (citric acid 1 M, 25 °C, 1 h, 70 g/l) to recycle end of life LFP cathodes. After conventional leaching, chemical precipitation allowed to recover in multiple steps Li, Fe and P salts, while selective leaching allowed to recover Fe and P, in the leaching residues and required chemical precipitation only for lithium recovery. Conventional leaching with 1 M acids achieved leaching efficiencies equal to 95 ± 2% for Li, 98 ± 8% for Fe, 96 ± 3% for P with sulfuric acid and 83 ± 0.8% for Li, 8 ± 1% for Fe, 12 ± 5% for P with citric acid. Decreasing citric acid's concentration from 1 to 0.25 M didn't substantially change leaching efficiency. Selective leaching with citric acid has higher recovery efficiency (82 ± 6% for Fe, 74 ± 8% for P, 29 ± 5% for Li) than conventional leaching with sulfuric acid (69 ± 15% for Fe, 70 ± 18% for P, and 21 ± 2% for Li). Also, impurities' amounts were lower with citric acid (335 ± 19 335 ± 19 of S mg/kg of S) than with sulfuric acid (8104 ± 2403 mg/kg of S). In overall, the operative costs associated to 0.25 M citric acid route (3.17€/kg) were lower compared to 1 M sulfuric acid (3.52€/kg). In conclusion, citric acid could be a viable option to lower LFP batteries' recycling costs, and it should be further explored prioritizing Lithium recovery and purity of recovered materials.

Keywords Citric acid · Leaching · Lithium iron phosphate · Lithium recovery · Recycling

Introduction

Lithium ion batteries (LIBs) represent a fundamental technology to achieve European zero emissions' target by 2050 (European Commission 2020). The forecasted increase in the sales of passengers electric vehicles will lead to 65% rise in LIBs demand, from 330 GWh in 2021 to 550 GWh in 2022 (IEA 2023). LIBs encompass economically valuable elements and critical raw materials, with significant environmental impacts and costs associated to their mining and concern about the security of the supply chain (Farjana et al. 2019; Fu et al. 2020; Sun et al. 2019). Hence, recycling End of Life (EoL) LIBs is crucial for supplying secondary materials related to the expected increase of production demand (Zhao et al. 2022).

Among LIBs, Lithium Iron Phosphate (LFP) batteries are becoming increasingly popular in the electric transport sector, since they high stability, increased safety and lower reliance on critical raw materials (Saju et al. 2023), indeed they will exceed 30% of market share by 2030 (Wood Mackenzie 2020). However, the main bottleneck related to LFP batteries recycling is that the economic trade-off between potential revenues and recycling costs is unfavorable at full-scale (Mahandra and Ghahreman 2021). Up-to-date recycling

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technologies prioritize recovery of the most economically valuable elements, as Cobalt, Manganese and Nickel (Chan et al. 2021; Jantunen et al. 2022; Schiavi et al. 2021), while Lithium and Phosphorous have lower market value.

Recycling EoL LFP cathodes involves hydrometallurgy based on inorganic acids (Gerold et al. 2023; Li et al. 2022; Wang et al. 2023;), achieving leaching efficiencies between 97 and 99.9% for Lithium and 98–99% for Iron with sulfuric acid (Vieceli et al. 2021; Yang et al. 2023; Song et al. 2021; Wang et al. 2022a), and 97% for Lithium and 98% for Iron with phosphoric acid (Jiang et al. 2021; Hu et al. 2022)..

Selective leaching has been recently proposed for LIBs' recycling (Kumar et al. 2022). It is based on leaching specific target elements from the black mass—Lithium leaching exceeded 97% (Jin et al. 2023; Wu et al. 2023), while other elements are extracted in consequent steps. Selective leaching involves mild organic acids, as citric (Kumar et al. 2020), formic (Mahandra and Ghahreman 2021), Methyl Sulfonic Acid (MSA) and p-Toluene Sulfonic Acid (TSA) (Prasad Yadav et al. 2020) in combination with an oxidizing agent, as hydrogen peroxide (Chen et al. 2018; Li et al. 2017; Tao et al. 2019; Zhou et al. 2023a), or sodium hypochlorite (K. Liu et al. 2023a, b; Liu et al. 2022; Tang et al. 2020). Recent studies have proposed novel selective leaching processes based on sodium citrate solution, potentially increasing economic feasibility (Zhang et al. 2023a) or monosodium phosphate, reducing the generation of wastewater from recycling (Zhou et al. 2023a). Moreover, due to shorter time required and lower concentration of leaching agents, compared to conventional hydrometallurgy, selective leaching can limit waste generation and reduce environmental impacts and economic costs (Kumar et al. 2022; K. Liu et al. 2023a, b). The environmental benefits of selective leaching could be enhanced by the use of organic acids,(Golmohammadzadeh et al. 2018; Zhou et al. 2023b), which are less persistent than inorganic ones and their application avoids the release of Cl_2, NO_x and SO_3 (Golmohammadzadeh et al. 2017; Meng et al. 2020). Furthermore, organic acids show highest selectivity towards Lithium leaching compared with inorganic acids, such as sulphuric or phosphoric acids (Gerold et al. 2023).

Citric acid was proposed as "green chemical" for LIBs' hydrometallurgical recycling because it is soluble in water and naturally biodegradable (Li et al. 2010). However, despite organic acids are becoming increasingly common for metals' leaching from Nickel Manganese Cobalt (NMC) and Lithium Cobalt Oxide (LCO) cathodes (Golmohammadzadeh et al. 2018; He et al. 2017; Kim et al. 2023; Zeng et al. 2015), they have been rarely applied to LFP recycling (Li et al. 2023; Wang et al. 2022b).

To the best of our knowledge, recycling EoL LFP cathodes via selective leaching with citric acid has not been yet extensively researched, and existing literature (Gerold et al. 2023; Li et al. 2019) focused on the efficiency of the process, overlooking the economic costs. When previous studies (Hu et al. 2024; P. Yadav et al. 2020; Yang et al. 2023) presented the economic analysis of recycling costs and potential profit from the recovery of Iron phosphate and Lithium carbonate, their results were controversial due to differences in functional units, currencies and costs parameters, e.g. reagents, energy, labour and general expenses. Moreover, previous studies often focused only on leaching, which is the initial step of hydrometallurgical recycling, (Jha et al. 2013; Jin et al. 2023) and when the sequential steps for the recovery of lithium carbonates is considered they report only the purity of the recovered carbonates and not the recovery efficiency (Wu et al. 2023).

The main objective and element of novelty of this study is the comparison of two closed-loop recycling routes applied to EoL LFP cathodes: selective leaching with citric acid at 25 °C and conventional leaching with sulfuric acid at 40 °C, both followed by recovery via chemical precipitation and solid-state synthesis of the recycled LFP phase, considering technical performance and economic analysis of the processes. Moreover, in this work the economic analysis has been performed both for a conventional hydrometallurgical process and for selective leaching on the same sample, considering the cost of reagents and energy consumption, during leaching and precipitation, with primary data measured during experimental activity.

Conventional leaching with sulfuric acid allowed to recover Li, Fe and P by multiple steps of chemical precipitation, whereas selective leaching with citric acid and hydrogen peroxide recovered Fe and P as residual material after leaching and used chemical precipitation only to recover Li, reducing the number of steps required for material recovery. The regeneration of recovered materials was carried out comparing two products: (i) Li, Fe and P precipitated after conventional leaching with sulfuric acid and (ii) Fe and P from the residues of selective leaching with citric acid and hydrogen peroxide and precipitated Li.The two routes of conventional leaching with sulfuric acid and selective leaching with citric acid and hydrogen peroxide have been assessed based on technical performances (leaching and recovery yields, and purity of recovered precursors to produce recycled LFP cathodes), and on associated costs referred to the treatment of 1 kg of EoL LFP cathodic powders.

Materials and methods

Materials and reagents

This study involved LFP cathodes provided by an Italian company, dismantled from EoL cells. The following reagents were used in the experimental tests: sulfuric acid (CAS:

7664–93-9, > 96% purity, Carlo Erba Reagents); citric acid (CAS: 77–92-9, > 99.5% purity, Sigma Aldrich); hydrogen peroxide (CAS: 7722–84-1, 30%v.v., Carlo Erba Reagents); sodium hydroxide (CAS: 1310–73-2, > 98% purity, Honeywell/Fluka); sodium carbonate (CAS: 497–19-8, > 99.8% purity, Sharlab); D(+)Glucose anhydrous (CAS: 50–99-7, > 97.5% purity, Carlo Erba Reagents).

Analytical equipment

Before characterization, the samples were rinsed with deionized water and dried at 60 °C overnight in an ARGO LAB TCN 30 oven. A benchtop pH-meter (GEASS, PH8 + DHS) was used during leaching and chemical precipitation tests. The samples and recovered products have been characterized through: X-ray Fluorescence (XRF) spectroscopy (Rigaku, NEX-DE), X-ray Diffraction (XRD) spectroscopy (PANanalytical X'Pert) and Flame Atomic Absorption (FAA) spectroscopy (Schimadzu, GFA-EX7). Samples underwent microwave digestion before FAA spectroscopy in a microwave digestion system (MILESTONE, ETHOS UP), treating 500 mg with 50 mL of HNO_3 (0.2 M) and HCl (0.8 M) at 230 °C for 25 min. XRF spectroscopy was used to measure the concentration of Al, Ca, Cl, Co, Cr, Cu, Fe, Ni, P, S, Si, V and Zn. Lithium was analysed through AAS. Iron was also analysed via AAS for consistency. It should be noticed that XRF directly analysed the powders, while AAS analyses were preceded by microwave acid digestion.

Overview of the experimental approach

According to a previous study on pre-treatments (Bruno and Fiore 2024., in preparation), the LFP cathodes' powders have been detached from the Aluminum current collectors via thermal treatment at 250 °C for 30 min in a Prederi ZE V220 muffle furnace, then ball milled for 5 min at 14 Hz in 50 mL Zirconia jars with two Zirconia beads (10 mm diameter) in a Retsch MM200 ball mill, and finally manually sieved to eliminate particles having dimensions above 1 mm.

The experimental activity applied in this study (Fig. 1) followed two recycling routes: conventional leaching and selective leaching. Conventional leaching involved 4 consequent phases: (i) leaching, (ii) Fe and P recovery via chemical precipitation with 10 M NaOH, (iii) Li recovery via chemical precipitation with 10 M Na_2CO_3, (iv) carbothermal reduction of LFP powders at 700 °C. While selective leaching involved 3 consequent phases: (i) leaching, (ii) Li recovery via chemical precipitation with 10 M Na_2CO_3, (iii) carbothermal reduction of LFP powders at 700 °C. All processes have been explored in triplicates. pH values adopted during Li, Fe and P recovery are detailed in the following.

Sulfuric and citric acids were compared as leaching agents for conventional leaching (Fig. 1A). Besides, citric acid in various conditions was combined with hydrogen peroxide in a selective leaching process (Fig. 1B). The experimental conditions applied (Table 1) are based on literature (Kumar et al. 2022; Qin et al. 2019; Sattar et al. 2019; Takahashi et al. 2020; Vieceli et al. 2021; Yue et al. 2018). Leaching tests have been carried out in a temperature-controlled Pyrex reactor placed on an AREX-6DIGITAL PRO heating magnetic stirrer and equipped with a VTF EVO digital thermoregulatory, both from VELP Scientifica. The solid residues have been recovered by a Hermle Labor Technik Z 206 A centrifuge, rinsed with deionized water, dried at 70 °C in an Argo Lab TCN 30 oven, and analyzed through XRF and XRD spectroscopy. The leachates have been filtered at 0.45 µm with GVS syringe filters and analyzed by FAA spectroscopy. pH of the leachates was increased by adding 10 M NaOH to precipitate Iron Phosphate (pH 2) and Iron Phosphate·$8H_2O$ (vivianite, pH 5.5), then recovered via centrifugation. Lithium was recovered as phosphate, by adding 10 M NaOH to the leachate up to pH 11, then as Li_2CO_3 by adding 10 M Na_2CO_3 at 95 °C for 2 h. The recovered powders have been combined according to the stoichiometric ratio Li:Fe:P = 1:1:1, adding 20%wt. D(+)glucose as carbon source, and ball milled in a Retsch MM400 mill for 3 h at 20 Hz. Finally, the recovered powders have been thermally treated at 700 °C for 4 h in a Carbolite MTF 12/38/400 tubular furnace under Argon to obtain recycled LFP.

The overall efficiency of the investigated processes has been assessed via two performance indicators, e.g., leaching efficiency (η_{leach}) and recovery efficiency (η_{rec}):

$$\eta_{leach}(\%) = \frac{c_i(mg/l) \bullet V_i(l)}{m_i(mg)} \bullet 100$$

$$\eta_{rec}(\%) = \frac{\Sigma m_{prec}(mg)}{m_i(mg)} \bullet 100$$

where c_i is the concentration of Li, Fe and P in the leachate (mg/L), V_i is the leachate volume (L), m_i is the mass of Li, Fe and P in the initial sample (mg) and $m_{rec.}$ is the mass of Li, Fe and P in the recovered powders (mg). Moreover, the purity of the recovered compounds was investigated via chemical and XRD analyses.

Economic preliminary analysis

The economic analysis of the investigated processes was based on 1 kg of LFP powder and accounted the costs of recycling (Table 2), considering the costs due to energy demand and reagents. This analysis should be considered purely preliminary and aimed at just comparing the

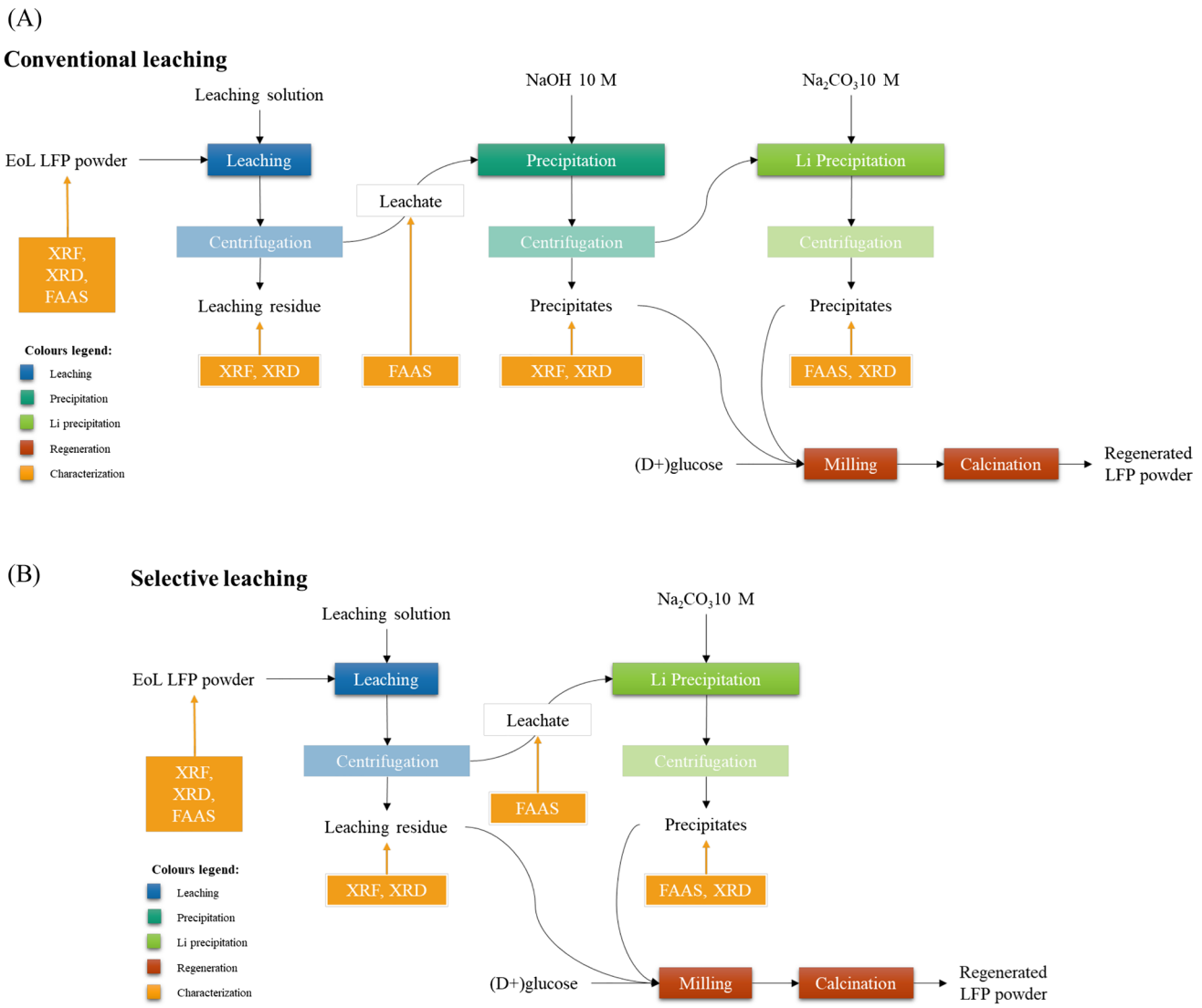


Fig. 1 Outline of the experimental approach (**A**) with conventional leaching and (**B**) with selective leaching

Table 1 Leaching conditions (concentration of leaching agent and hydrogen peroxide, temperature, contact time, S/L: solid to liquid ratio) applied in this study

Leaching agent	Concentration (M)	Concentration H_2O_2 (%vv.)	Temperature (°C)	Time (h)	S/L ratio (g/L)	Reference
sulfuric acid	3	4	50	0.5	0.05	Sattar et al. 2019
sulfuric acid	3	0	70	1.5	10	Qin et al. 2019
sulfuric acid	2.25	0	80	0.5	100	Yue et al. 2018
sulfuric acid	2	0	-	1	20	Vieceli et al. 2021
sulfuric acid	1.2	0	25–50	4	0.2	Takahashi et al. 2020
citric acid	0.25	6	25	1.5	67	Kumar et al. 2022
sulfuric acid	1	0	40	2	50	This study (S_0)
citric acid	1	0	25	1	70	This study (C_0)
citric acid	1	6	25	1	70	This study (C_1)
citric acid	0.5	6	25	1	70	This study (C_2)
citric acid	0.25	6	25	1	70	This study (C_3)

Table 2 Costs accounted in the preliminary economic analysis

Costs	Market value	m.u
Energy	0.199	€/kWh
Deionized water	$8.08 \cdot 10^{-5}$	€/kg
Sulfuric acid	0.06	€/kg
Citric acid	0.78	€/kg
Hydrogen peroxide	0.47	€/kg
Sodium hydroxide	0.19	€/kg
Sodium carbonate	0.24	€/kg

economic aspects associated to the compared routes. The energy consumption of the lab equipment was measured with a PM10 Maxcio power meter. The analysis accounted the average European price of electricity for non-households consumers, equal to 0.1986 €/kWh (Eurostat 2023). The costs of reagents and deionized water have been retrieved from Ecoinvent database (Ecoinvent 2023).

Results and discussion

Samples' characterization

According to the characterization's results (Fig. 2), the EoL LFP cathodic powders have been identified as Lithium Iron Phosphate and Li-Mg-Mn Iron Phosphate. Their chemical composition was: 1.6 ± 0.01%wt. Li, 29.64 ± 1.32%wt. Fe and 14.80 ± 0.4%wt. P, in agreement with literature (Gaines et al. 2018; Yagci et al. 2021; Yang et al. 2018; Zhang et al. 2022). Aluminium impurities from the current collector were 0.092 ± 0.06%-wt., proving the efficiency of the applied detachment process.

Leaching processes

The results of leaching tests (Fig. 3) were as follows. Sulfuric acid was the most effective leaching agent, extracting 95 ± 2% of Li, 98 ± 8% of Fe, and 96 ± 3% of P. Similar values have been reported by a previous study (Zheng et al. 2016), which leached 97% of Li and 98% of Fe with higher sulfuric acid concentration and longer contact time but lower solid-to-liquid ratio. Citric acid exhibited comparable leaching efficiency: 90 ± 0.6% of Li, 99 ± 13% of Fe, and 69 ± 10% of P. Aside from the fact that sulfuric acid is stronger than citric, the lower performance of citric acid, compared to sulfuric, may be due to the milder leaching conditions (25 °C applied for 1 h vs. 40 °C and 2 h).

The leaching mechanisms involved in the leaching process with sulfuric acid and citric acid are provided in Eq. 1 and Eq. 2. While the selective leaching mechanism, due to the presence of hydrogen peroxide which acts as an oxidant agent, is reported in Eq. 3.

$$2LiFePO_4 + H_2SO_4 \rightarrow 2FeSO_4 + Li_2SO4 + 2H_3PO_4 \quad (1)$$

$$3H_3cit + 3LiFePO_4 \rightarrow Fe_3(cit)_2 + Li_3cit + 3H_3PO_4 \quad (2)$$

$$2H_3cit + 3H_2O_2 + 6LiFePO_4 \rightarrow 6FePO_4 + 2Li_3cit + 6H_2O \quad (3)$$

The selectivity of Li leaching is achieved by the effect of hydrogen peroxide, which oxidize Fe^{2+} into Fe^{3+},

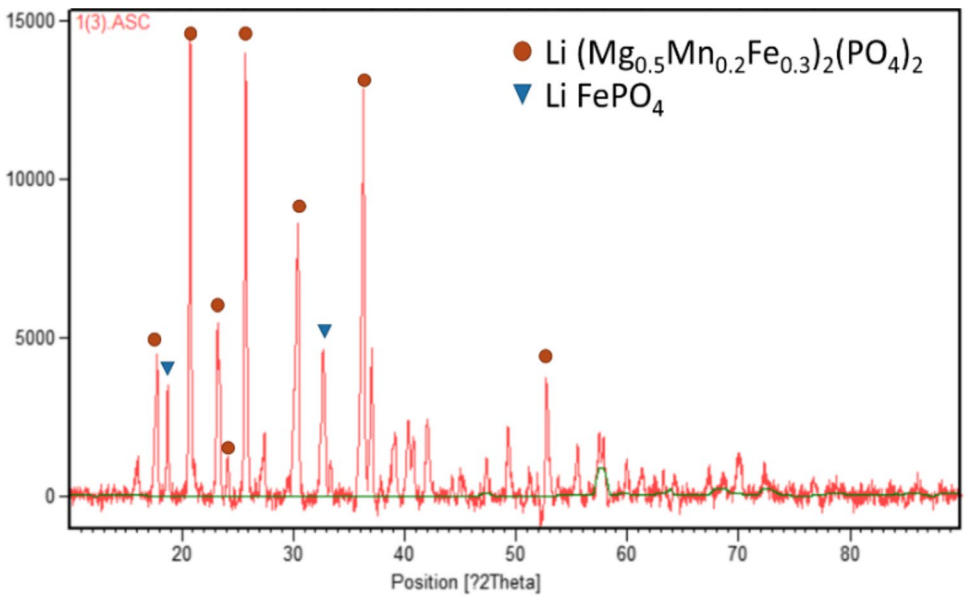


Fig. 2 XRD spectra of EoL LFP cathodic powders

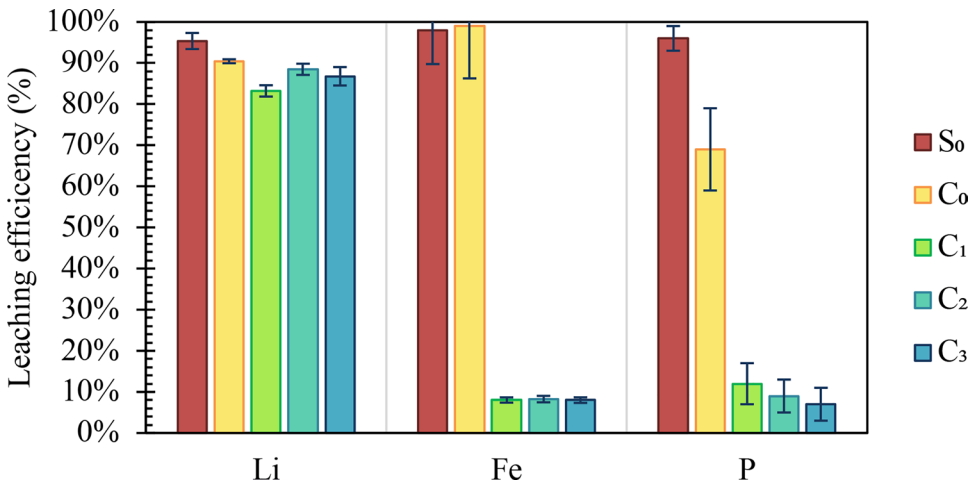


Fig. 3 Leaching efficiency of Lithium, Iron and Phosphorous achieved in the performed tests (S_0 = sulfuric acid 1 M, C_0 = citric acid 1 M, C_1 = citric acid 1 M + 6%v.v. H_2O_2, C_2 = citric acid 0.5 M + 6% v.v. H_2O_2, C_3 = citric acid 0.25 M + 6% v.v. H_2O_2)

strenghtening the olivine structure of $FePO_4$, as reported by previous studies (Niu et al. 2023). A similar result has been presented, without hydrogen peroxide, by using a stoichiometric amount of sulfuric acid, which however was selective towards Fe but still leached 20% of P (Tao et al. 2019).

Contrary to previous studies, which reported an increase of Li leaching efficiency due to the presence of hydrogen peroxide (Mahandra and Ghahreman 2021), it had no effect on Lithium leaching efficiciency. Specifically, the amount of Li leached with 1 M citric acid and 6%v.v. hydrogen peroxide (tests C_1, C_2 and C_3) was 92 ± 2% of Li leached without hydrogen peroxide. On the other hand, it had a detrimental effect on the leaching efficiencies of Fe and P. This study additionally proved that, in presence of 6%v.v. hydrogen peroxide, Fe and P leaching efficiency was unaffected when citric acid concentration decreased, as follows. 83 ± 0.8% Li, 8 ± 1% Fe, and 12 ± 5% P were leached with 1 M citric acid; 88 ± 1% Li, 8 ± 1% Fe, and 9 ± 4% P with 0.5 M citric acid; and 87 ± 2% Li, 8 ± 1% Fe, and 7 ± 4% P with 0.25 M citric acid.

Iron and phosphorous recovery

Following conventional leaching with sulfuric acid, 69 ± 15% Fe and 70 ± 18% P have been recovered at room temperature from the leachates by adding NaOH to precipitate $FePO_4$ at pH 2 and vivianite $FePO_4{\cdot}H_2O$ at pH 5.5 (Fig. 4). In particular, $FePO_4$ obtained at pH 2 didn't display a crystalline structure, thus it was treated at 700 °C for 3 h (Fig. 4A). The recovery of Fe and P via chemical precipitation at room temperature required less than 20 min, with comparable shares of Iron Phosphate obtained at pH 2.2 (53 ± 8%wt. of total precipitates) and Vivianite at pH 5.5 (41 ± 10%wt. of total precipitates) (Fig. 4B).

Chemical precipitation with NaOH was also applied to recover Fe and P after conventional leaching with citric acid and achieved the recovery of 82 ± 6% for Fe and 74 ± 8% for P, as Iron phosphate and hydroxyphosphate (Fig. 5).

Following conventional sulfuric acid leaching, three precipitation processes were carried out, followed by six centrifugation steps, since it was required to repeat the centrifugation to guarantee better separation. The leachate with

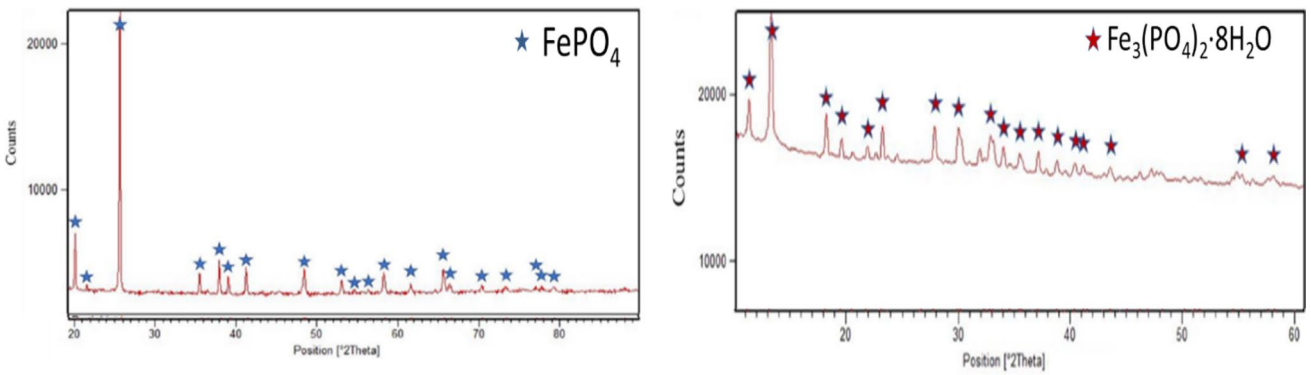


Fig. 4 XRD spectra of the recovered powders obtained from sulfuric acid leaching at (**A**) pH 2 after thermal treatment at 700 °C, and at (**B**) pH 5.5

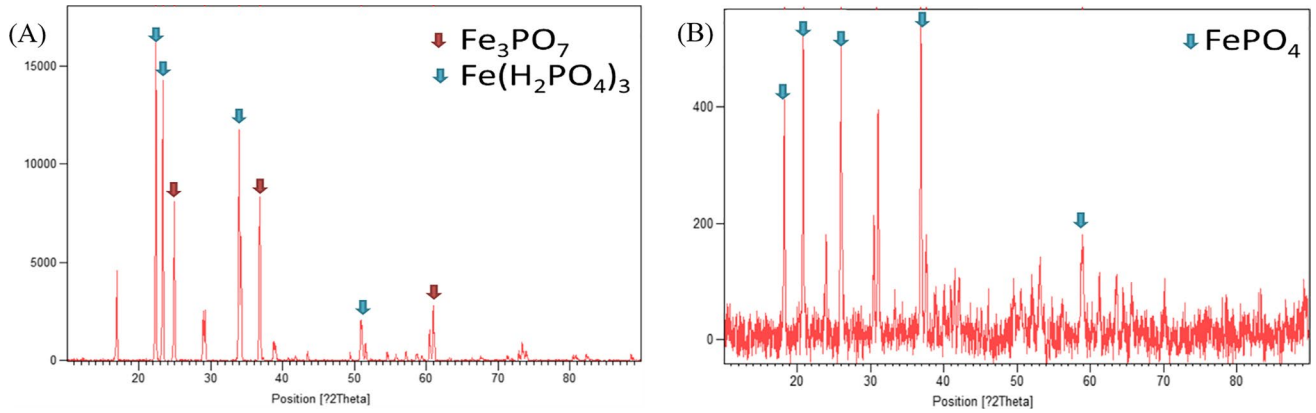


Fig. 5 XRD spectra of the recovered powders obtained from citric acid leaching at (**A**) pH 2 after thermal treatment at 700 °C, and at (**B**) pH 5.5

citric acid instead required two precipitation and four centrifugation steps.

Whereas, selective leaching allowed to recover Fe and P as $FePO_4$ in the solid residues after leaching and the leachate required only one precipitation and centrifugation step to remove Fe impurities (2 ± 1% wt.). Indeed, selective leaching presented the following recovery efficiency: 92 ± 1% of Fe and 88 ± 5% of P with citric acid 1 M and 6%vv. hydrogen peroxide, 92 ± 1% of Fe and 91 ± 4% of P with citric acid 0.5 M and 6%vv. hydrogen peroxide, and 92 ± 1% of Fe and 93 ± 4% of P with citric acid 0.25 M and 6%vv. hydrogen peroxide.

Lithium recovery

Lithium recovery was completed comparing two leaching processes: conventional leaching with sulfuric acid and selective leaching with citric acid and hydrogen peroxide. Lithium recovery happened at 95 °C, in two phases. Firstly, pH of leachates was increased at 12 with 10 M NaOH, then a stoichiometric amount of Na_2CO_3 was added to precipitate Li as carbonate. Depending on the leaching process, different precipitates have been obtained in the first phase (Fig. 6): lithium sulphate (98 ± 12%wt. of recovered Lithium) with conventional sulfuric acid, and lithium phosphate (66 ± 7%wt. of recovered Lithium) with citric acid and hydrogen peroxide. Lithium recovery as Li_3PO_4 from LFP cathodes was previously reported by literature (Mahandra and Ghahreman 2021) and.the precipitation of Li phosphate alongside Li carbonate is attributed to the fact that the solubility constant value is lower for Li_3PO_4 ($2.37 \cdot 10^{-11}$) than for Li_2CO_3 ($8.15 \cdot 10^{-4}$) (Lide 2004).At 95°C, Na_2CO_3 was added to the leachate to precipitate the residual Lithium as carbonate, achieving a total recovery of 21 ± 2% from sulfuric acid route (98 ± 12% as Li_2SO_4 and 2 ± 0.7% as Li_2CO_3) and 29 ± 5% from citric acid and hydrogen peroxide route (66 ± 7% % as Li_3PO_4 and 34 ± 5% as Li_2CO_3). In this study, Lithium recovery efficiency from selective leaching was lower compared to literature considering selective leaching (Kumar et al. 2020) and conventional leaching (Dolotko et al. 2020), which reported values between 70 and 85%wt. A possible explanation of the poor performances of Li recovery achieved in this study may be associated with the relatively low masses involved in this study (4 g of EoL LFP cathodic powders producing 0.86 g of Lithium-rich precipitates from conventional leaching with sulfuric acid and 1.16 g from selective leaching with citric acid and hydrogen peroxide), which were probably affected by material losses during the overall leaching and recovery processes.

The recovery of lithium was carried out, after conventional and selective leaching, with two precipitations steps (after reaching pH 12, and after adding Na_2CO_3 at 95 °C) and two centrifugation steps to separate the precipitates.

Purity of recovered compounds

The performance of the recycling processes was evaluated considering also the concentration of impurities in the Fe- and P-rich powders, through XRF spectroscopy to determine the concentration of other elements in the products of precipitation from conventional leaching (Fig. 7) and the residues from selective leaching (Fig. 8). The concentration of Cu, Ni and Si was below the detectable limit of XRF spectroscopy.

The most prevalent contaminant in the Fe- and P-rich powders recovered from sulfuric acid route was S, which was 8798 ± 3061 mg/kg in Iron Phosphate recovered at pH 2 and 8468 ± 1925 mg/kg in Vivianite recovered at pH 5.5. Other contaminants detected in same powders were Co, mostly leached at pH 2 (153 ± 37 m/kg of precipitate), while Vivianite contained Al (3287 ± 1777mg/kg), V (520 ± 155 mg/kg) and Cl (181 ± 31 mg/kg). In overall,

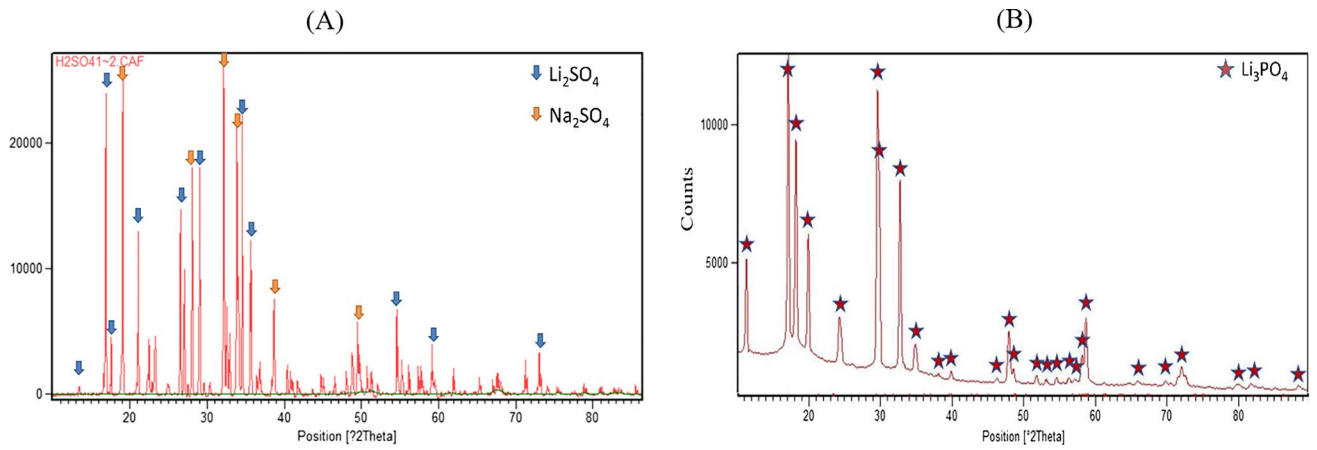


Fig. 6 XRD spectra of precipitates obtained at pH 12 from (**A**) conventional sulfuric acid leachates and (**B**) selective 0.25 M citric acid and hydrogen peroxide leachates

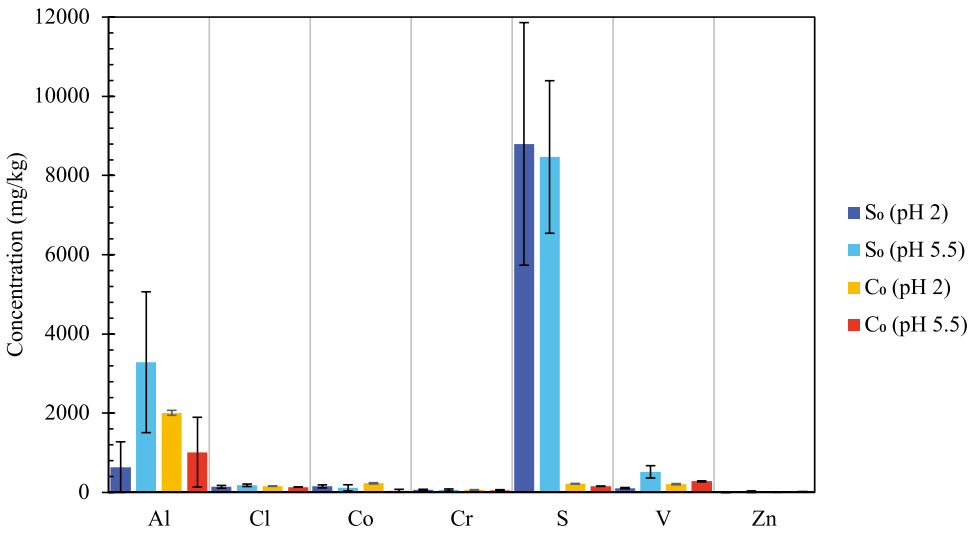


Fig. 7 Concentration of impurities in the precipitates from conventional leaching (S_0 sulfuric acid 1 M; C_0 citric acid 1 M)

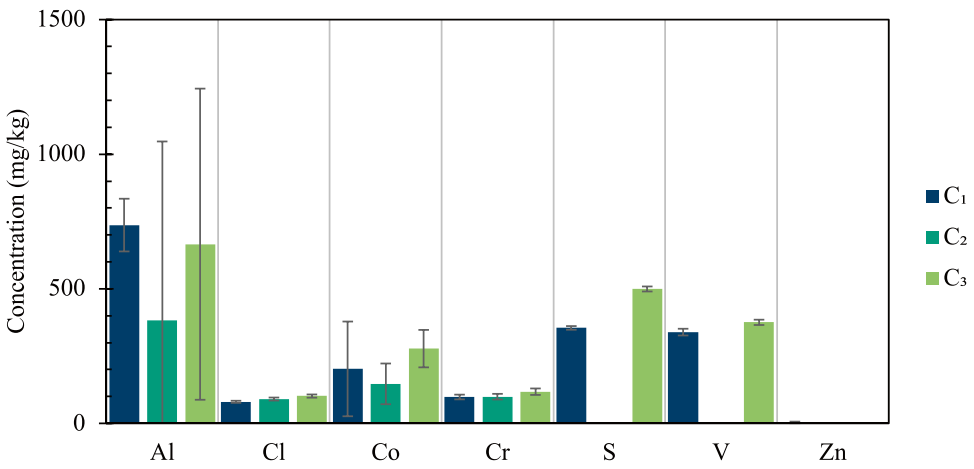


Fig. 8 Concentration of impurities in the solid residues from selective leaching (C_1 = citric acid 1 M + 6%v.v. H_2O_2, C_2 = citric acid 0.5 M + 6% v.v. H_2O_2, C_3 = citric acid 0.25 M + 6% v.v. H_2O_2)

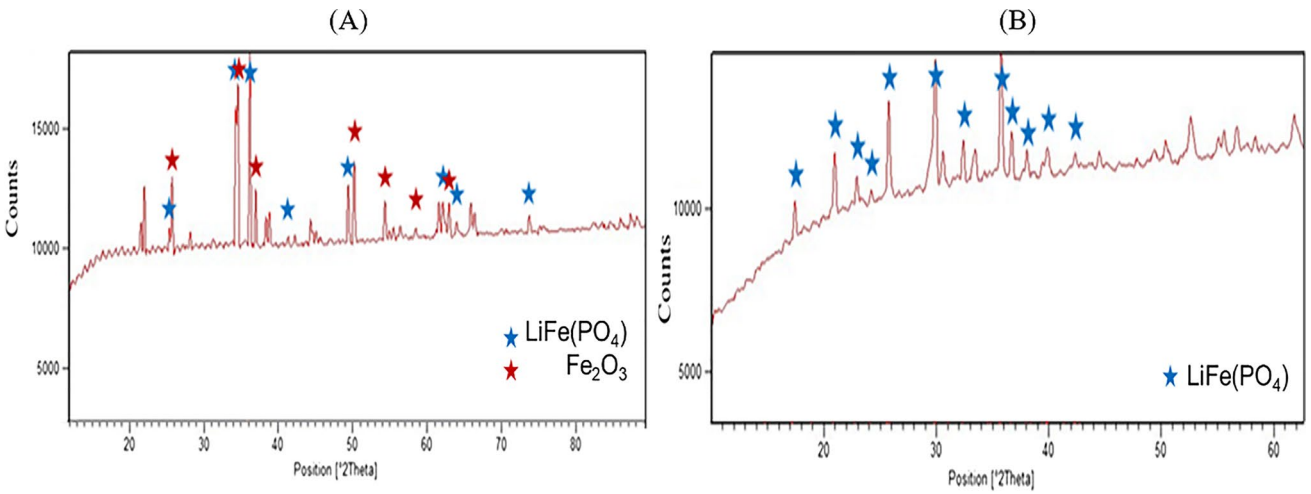


Fig. 9 XRD spectra of recycled LFP powders deriving from (**A**) sulfuric acid route and from (**B**) selective citric acid route

the precipitated fraction from conventional leaching with sulfuric acid presented the following contaminations: 1681 ± 1063 mg/kg of Al, 149 ± 31 mg/kg of Cl, 128 ± 51 mg/kg of Co, 8104 ± 2403 mg/kg of S and 270 ± 71 mg/kg of V.

Powders recovered via conventional leaching with citric acid displayed contaminations of Al (2010 ± 62 mg/kg), V (219 ± 15 mg/kg) and Cl (160 ± 7 mg/kg) at pH 2 and of Al (1016 ± 881mg/kg), V (158 ± 13 mg/kg) and Cl (136 ± 5 mg/kg) at pH 5.5. The totality of contamination in the precipitates from conventional leaching with citric acid were: 1602 ± 381 mg/kg of Al, 149 ± 7 mg/kg of Cl, 155 ± 24 mg/kg of Co, 193 ± 7 mg/kg of S and 234 ± 14 mg/kg of V.

The residues from selective leaching presented lower concentration of Al, S, Zn and Cl compared with the precipitates from conventional leaching. In particular the contaminations in the leaching residues after selective leaching were: 736 ± 97 mg/kg of Al, 80 ± 4 mg/kg of Cl, 202 ± 176 mg/kg of Co, 354 ± 7 mg/kg of S and 339 ± 12 mg/kg of V with citric acid 1M and hydrogen peroxide 383 ± 663 mg/kg of Al, 91 ± 5 mg/kg of Cl, 146 ± 75 mg/kg of Co, 331 ± 19 mg/kg of S and 328 ± 2 mg/kg of V with citric acid 0.5M and hydrogen peroxide and 665 ± 557 mg/kg of Al, 101 ± 6 mg/kg of Cl, 277 ± 69 mg/kg of Co, 499 ± 10 mg/kg of S and 357 ± 9 mg/kg of V with citric acid 0.25M and hydrogen peroxide.

The Lithium-rich powders from conventional leaching with sulfuric acid contained: 978 ± 853 mg/kg of Al, 417 ± 17 mg/kg of Cl, 51,900 ± 2165 mg/kg of S, detected as Na_2SO_4 (Fig. 6A). The concentration of Co, Cr and V were below detection limits. Whereas the products of lithium recovery from selective leaching with citric acid and hydrogen peroxide presented the following contaminations: 7523 ± 187 mg/kg of Al, 236 ± 71 mg/kg of Cl, 335 ± 19 mg/kg of S and 236 ± 71 mg/kg of V.

Carbothermal reduction of recovered LFP powders

The recovered powders deriving from sulfuric acid and 0.25 M citric acid routes underwent carbothermal reduction to obtain precursors for recycled LFP cathodes. Lithium Iron Phosphate Olivine crystalline structure was detected in the

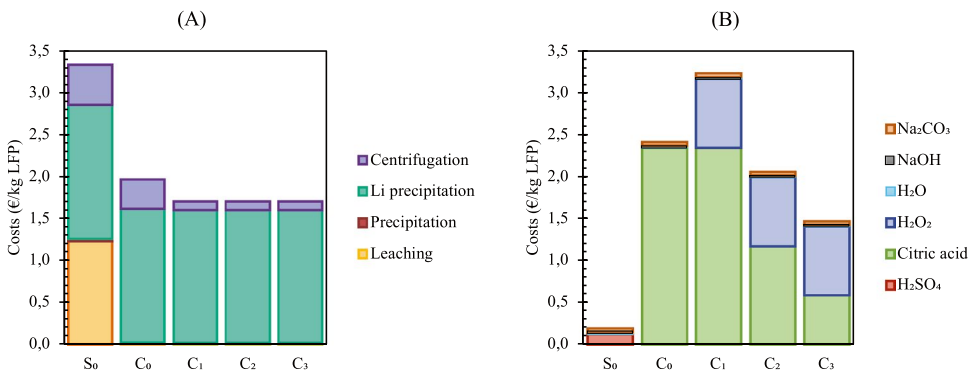


Fig. 10 Costs associated with (A) energy demand and (B) reagents' consumption (S_0 sulfuric acid 1 M; C_0 citric acid 1 M; C_1 citric acid 1 M + 6% H_2O_2; C_2 citric acid 0.5 M + 6% H_2O_2; C_3 citric acid 0.25 M + 6% H_2O_2)

Table 3 Summary of economic analysis results from literature overview on LFP recycling

Functional unit	Process	Costs	Income	Profit	Costs (€)	Considered costs										Process steps					Reference
						Raw materials	Reagents	Energy	Labour	Equipment	Waste management	Fixed charges	Plant overhead	General Expenses	Pre-treatment	Mechanochemical activation	Leaching	Recovery	Electrolysis	Regeneration	
1 kg of LFP (input)	Selective leaching	15.98 $	17.79 $	1.82 $	14.66	x	x	x	x						x		x	x		x	(Zhou et al. 2023a)
	Selective leaching	8.27 $	9.98 $	1.71 $	7.59	x	x	x	x								x	x			(Zhou et al. 2023b)
	Mechano-chemical with Na-citrate	32.8 $	44.7 $	11.9 $	30.09	x	x	x									x	x			(Zhang et al. 2023b)
1 kg of cell (input)	Electrolysis			25.8 $			x	x											x		(Zhao et al., 2024)
1 kg of LFP battery (input)	Leaching	1.65 $	5.97 $	4.32 $	7.0		x					x	x	x			x	x		x	(Jin et al. 2023)
	Leaching with H_2SO_4 and H_2O_2	2.86 $	5.85 $	2.99 $	12.1		x	x	x	x		x	x	x	x		x	x			(Xu et al. 2023)
	Leaching with H_2SO_4 and H_2O_2	15.81 $	19.84 $	4.03 $	66.8	x	x	x									x	x			(Yang et al. 2023)
	H_2O_2 method	1.25 $	8.98 $	7.73 $	5.3		x					x	x	x			x	x		x	(Jin et al. 2023)
	Leaching with CO_2 and H_2O_2	2.38 $	6.13 $	3.75 $	10.1		x	x	x	x		x	x	x	x		x	x			(Xu et al. 2023)
	Leaching with CO_2 and O_2	2.09 $	6.13 $	4.04 $	8.8		x	x	x	x		x	x	x	x		x	x			(Xu et al. 2023)
	Self-catalytic air pressure leaching	1.11 $	9.09 $	7.98 $	4.7		x					x	x	x			x	x		x	(Jin et al. 2023)
	Mechano-chemical	1.85 $	6.62 $	4.768	7.8	x	x	x							x	x	x	x		x	(Liu et al. 2023a, b)

Table 3 (continued)

Functional unit	Process	Costs	Income	Profit	Costs (€)	Considered costs										Process steps					Reference
						Raw materials	Reagents	Energy	Labour	Equipment	Waste management	Fixed charges	Plant overhead	General Expenses	Pre-treatment	Mechanochemical activation	Leaching	Recovery	Electrolysis	Regeneration	
1 t of LFP battery (input)	Leaching with H_2SO_4	1,418 $	2,716 $	1,297 $	5.04	x	x	x									x	x			(Song et al. 2021)
	Selective leaching	26,499 $	40,586 $	7,469 $	94.23	x	x								x		x			x	(Hu et al. 2022)
	Selective leaching	35,700 ¥	54,520 ¥	18,820 ¥	0.86	x	x								x		x	x			(Song et al. 2023)
	Selective leaching and precipitation	1962.4 $	1242.4 $	719.6 $	6.98	x	x	x									x	x		x	(Hu et al. 2024)
	Selective air oxidation leaching	2,051 $	4,081 $	2,030 $	7.29	x	x	x	x	x					x		x	x			(Jin et al. 2022)
	Mechanochemical with $FeCl_3$	1,580 $	6,539 $	4,959 $	5.62	x	x	x								x	x	x			(Wu et al. 2023)
	Electrolysis	2225 $	9148 $	6923 $	7.91	x	x	x											x		(Yang et al. 2024)
1 kg of recovered	Traditional leaching	18.60 $			17.06		x	x													(Du et al. 2024)
	Leaching with citric acid and MSA	4.35 $			3.99		x	x									x				(Kim et al. 2023)
	Selective pressure leaching with H_2SO_4	17.36 $			15.93		x	x													(Du et al. 2024)

Table 3 (continued)

Functional unit	Process	Costs	Income	Profit	Costs (€)	Considered costs									Process steps					Reference
						Raw materials	Reagents	Energy	Labour	Equipment	Waste management	Fixed charges	Plant overhead	General Expenses	Pretreatment	Mechanochemical activation	Leaching	Recovery	Electrolysis	Regeneration	
1 kg of $FePO_4$ leaching residues (input)	Regeneration of battery-grade $FePO_4$ with H_3PO_4 ultrasonic centrifugation	1.25 $	1.80 $	0.55 $	1.15		x	x			x						x	x		x	(Han et al. 2023)
100 kWh	Leaching with methanesulfonic acid (MSA), p-toluenesulfonic acid (Ts	970 $	1,129 $	159 $			x	x	x	x	x			x	x		x	x		x	(Prasad Yadav et al. 2020)

XRD spectra of both materials (Fig. 9), with iron oxides impurities in LFP powders deriving from sulfuric acid route. Since XRF spectroscopy was not able to differentiate the amount of iron present in form of oxides and in form of lithium iron phosphate, it was not possible to quantify the amount of iron oxides impurities.

Economic analysis

Conventional sulfuric acid leaching required one leaching step at 40 °C, followed by three precipitation and six centrifugation steps to recover the precipitates and two precipitation steps (one at pH 12 and room temperature and one at 95 °C) to recover the lithium-rich precipitates; the precipitates were eventually regenerated by carbothermal reduction. Instead, selective leaching required one leaching step at 25 °C, one precipitation and two centrifugation steps to remove residual Fe impurities, and two precipitation steps (one at pH 12 and room temperature and one at 95 °C) to recover Lithium-rich precipitates; the leaching residues and precipitated Lithium were regenerated by carbothermal reduction.

The overall operative costs of the compared recycling routes (Fig. 10) were 3.52 € per kg of recycled LFP for 1 M sulfuric acid leaching, and 4.37 €/kg for 1 M citric acid leaching without hydrogen peroxide. Lowering citric acid concentration and adding hydrogen peroxide reduced the costs of selective leaching: from 4.93 €/kg of recycled LFP for 1 M, to 3.76 €/kg for 0.5 M and 3.17 €/kg for 0.25 M. The most expensive reagents were hydrogen peroxide (0.82 €/kg of recycled LFP) and citric acid (2.34 €/kg of recycled LFP for 1 M, 1.17 €/kg for 0.5 M and 0.59 €/kg for 0.25 M). Due to the increased temperatures necessary to precipitate Li_2CO_3, lithium recovery displayed the highest energy demand (1.59 €/kg).

In overall, sulfuric acid route's costs were mostly (94%) related to energy demand, while chemical reagents H_2SO_4, NaOH and Na_2CO_3 accounted for 0.20 € per kg of recycled LFP. Costs of 1 M Citric acid route were balanced between chemicals (55%) and energy demand (45%). When hydrogen peroxide was added and citric acid concentration decreased to 0.25 M, the costs' partition changed, e.g., 46% was ascribable to chemicals and 54% to energy demand.

Previous studies considered the economic costs and potential profit from recycling LFP batteries (Table 3), their results have been converted into a comparable unit of measurement (€/kg LFP). According to literature, the average cost of LFP recycling corresponds to 15.5 ± 22.4 €/kg. The substantial discrepancy in this result is credited to the fact that each study considered various cost factors (raw materials, reagents, energy consumption, labour, equipment and overhead expenses). and process steps. In particular all the considered studies considered the cost of reagentes, almost 80% considered the costs of energy consumption, 50% considered the price of spent LFP batteries as raw material for the process, below 30% considered additional costs, such as labour cost, equipment maintenance, plant overhead and general expenses and only 8% of them considered the expenses due to waste management. Moreover, less than 38% of the studies considered the costs associated with pre-treatment or final regeneration of the recovered products and only 17% take into account both steps. Our study exclusively concerned the cost of reagents and energy consumption, during leaching and precipitation, since these metrics were collected as primary data during experimental activity.

Therefore, additional expenses that full scale recycling facility have, such as capital investment or operative expenses, e.g. labour cost, equipment maintenance and waste management, were not considered. This limitation prohibits to assess the economic feasibility of the process. Nonetheless, the direct comparison between operative costs of conventional and selective leaching processes allows to quantify the economic benefit of selective leaching towards conventional processes, that required higher process temperature and additional recovery steps.

Conclusion

Despite hydrometallurgical recycling of lithium-ion batteries is widely applied at full-scale and intensively researched, current full-scale technologies are not economically profitable for Lithium Iron Phosphate batteries. This study had the main goal of comparing two closed-loop recycling routes applied to EoL LFP cathodic powders based on conventional leaching with sulfuric acid at 40 °C and on selective leaching with citric acid at 25 °C to recover and synthesize LFP precursors via chemical precipitation and solid-state synthesis of the recycled LFP phase. The comparison involved two objectives: (i) the technical performances of the two routes (yield of leaching and recovery, purity of the recovered powders), and (ii) a preliminary economic analysis, based on experimental data achieved from the study and compared to literature data, referred to 1 kg of end-of-life LFP cathodic material treated. In details, conventional leaching was performed with sulfuric acid and with citric acid, while selective Li leaching was performed with citric acid and hydrogen peroxide. Leaching efficiency of conventional leaching with citric acid ($90 \pm 0.6\%$ for Li, $99 \pm 13\%$ for Fe, $69 \pm 10\%$ for P) was comparable with sulfuric acid ($95 \pm 2\%$ for Li, $98 \pm 8\%$ for Fe, $96 \pm 3\%$ for P) considering that citric acid processes happened at 25 °C (instead of 40) and involved shorter contact time, higher solid to liquid ratio. Selective

leaching, with hydrogen peroxide and lower citric acid concentration (from 1 to 0.25 M) showed comparable Li leaching efficiency (87 ± 2%) and allowed to recover 92 ± 1% of Fe and 93 ± 4% of P in the leaching residues. The route based on conventional leaching with sulfuric acid, was followed by chemical precipitation and recovered 69 ± 15% of Fe and 70 ± 18% of P, with contaminations of Al (1681 ± 1063 mg/kg), Cl (149 ± 31 mg/kg), Co (128 ± 51 mg/kg), S (8104 ± 2403 mg/kg) and V (270 ± 71 mg/kg). Whereas selective leaching with 0.25 M citric acid and 6%vv. hydrogen peroxide allowed to recover 92 ± 1% of Fe and 93 ± 4% of P in the leaching residues with the following contaminations: 665 ± 557 mg/kg of Al, 101 ± 6 mg/kg of Cl, 277 ± 69 mg/kg of Co, 499 ± 10 mg/kg of S and 357 ± 9 mg/kg of V. In total, the route based on conventional leaching with 1M sulfuric acid allowed to recover 21 ± 2% of Li, 69 ± 15% of Fe and 70 ± 18% of P. Objective (i) of the study—i.e. comparison of the technical performances of the two routes—has been achieved, as the performance of selective leaching with 0.25 M citric acid and hydrogen peroxide were better, compared to conventional leaching: 29 ± 5% of Li, 92 ± 1% of Fe and 93 ± 4% of P.

Objective (ii) of the study—i.e. preliminary economic assessment of the two routes—has been also achieved, as follows. The preliminary economic assessment revealed that 0.25 M citric acid route was cheaper (3.17 €/kg) than the one based on sulfuric acid (3.52 €/kg), because of the lower energy demand and fewer process phases. In conclusion, from the point of view of a general perspective, this study proved that selective leaching with citric acid and hydrogen peroxide, compared to sulfuric acid in the recycling of EoL LFP cathodic powders, can be considered a promising recycling route for Li, Fe and P and is worth of further research to improve Lithium recovery.

Author contributions Martina Bruno: methodology, data acquisition, analysis, and visualization; writing-manuscript draft; Carlotta Francia: conceptualization, data analysis, writing-manuscript review; Silvia Fiore: conceptualization, methodology, supervision, writing-manuscript review. All authors read and approved the final manuscript.

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Declarations

Ethical approval. The authors are fully aware of their ethical responsibilities.

Consent to participate All authors contributed to the study conception and design, and consented to participate to the study as authors.

Consent to publish The authors consent to publish the article on Environmental Science and Pollution Research.

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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