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Low melting mixtures from waste as leaching agents for black mass processing

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ABSTRACT

The search for suitable solvometallurgy alternatives to classic hydrometallurgy for the extraction of critical elements such as Li, Co, Ni, and Mn mixed Black Mass (BM) obtained from spent Li-ion batteries is a target of primary importance. This approach, although effective at the laboratory scale, lacks sustainability when applied to the large volumes typical of industrial productions. Herein, a circular fabrication of two leaching agents is presented. Starting from waste cooking oils, which were recycled and subjected to chemical hydrolysis, glycerol and a mixture of long-chain Free Fatty Acids (FFAs) were obtained. The glycerol was mixed with water (1:3 M ratio) to obtain a leaching medium with low viscosity, while the FFAs were combined with menthol to produce a set of low melting mixtures. The determination of their eutectic composition was achieved by DFT calculations and ^{1}H NMR spectroscopy. Both systems were tested as leaching agents for processing a mixed BM showing promising lithium removal rates and selectivity.

1. Introduction

Due to the increasing scarcity of raw materials and the rapid growth in demand for precious elements, developing new processes for the sustainable exploitation of resources has become a primary objective in current research activities, both in academia and in the private sector [1]. One of the most valuable sources of precious raw materials is represented by spent lithium-ion batteries (LIBs). The amount of waste from exhausted LIBs, as well as the exponentially increasing demand for them, is impressive. By 2040, the demand for LIBs is expected to increase at least six or eight times [2], while the stock of electric vehicles will rise from the current 16 million [3] to 150–900 million by 2040 [4]. Among the most used electrochemical configurations for portable devices, $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_{1-x-y}O_2$ (NCM) stand out as the most common cathodic materials, with graphite being used as anode [5]. At the end of their life cycle, when LIBs cannot be reused or healed [6,7], recover of their constituent elements for further applications represents the best sustainable approach, even endorsed by some governments [8]. After discharging the battery and removing the main components such as plastic envelopes, binders, collectors, solvents, and salts, the electrodes are ground to obtain a black powder called black mass (BM) [9]. Depending on the separation procedure of the different kinds of electrodes, it is possible to obtain single or mixed BMs. BM is a powder rich in extremely valuable elements such as Li, Co, Ni, Mn, graphite, Cu, Al, and Fe. The amount of each element can vary significantly for different samples of BM, but it reaches higher values than in any natural ore, making recovery from exhausted LIBs more convenient than natural extraction [10]. As a matter of fact, from mixed LCO + NCM BMs, after quantitative leaching, it is possible to recover up to 7 wt% of Li, 20 wt% of Co, 7 wt% of Ni, and substantial amount of graphite (10–20 wt%) [11]. Currently, industrial facilities recover metals from BMs by chemical processing or pyrolysis. Both the processes are characterized by a high environmental impact [12–14] and many research efforts have been dedicated to the design of suitable alternatives. Nowadays, direct

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recycling, when suitable, is preferred to the recovery of the single elements as it has lower environmental impact (e.g., GHG emissions, energy consumption), shows a higher material recovery rate (nearly 100 %), and it is compatible with a circular battery economy [15].

On the other side, a strongly emerging alternative to hydrometallurgy is represented by the solvometallurgy, which does not involve aqueous solutions of strong mineral acids in the presence of a reductant (such as H_2O_2) typical of hydrometallurgy. In principle, it is possible to replace mineral acids with organic ones (such as oxalic, DL-maleic, ascorbic, formic, salicylic, citric, gluconic, itaconic, succinic, acetic acids) [16,17], or to use eutectic systems for the selective recovery of the main elements. Eutectic solvents can avoid the use of reducing agents like H_2O_2 and provide excellent leaching performance, as demonstrated with betaine hydrochloride:ethylene glycol [18], choline chloride:oxalic acid [19], and choline chloride:thioglycolic acid [20], to name a few examples. Zhu and coworkers have recently reviewed the matter in a very exhaustive way [21]. Despite the excellent results reached by solvometallurgy-based methodologies at laboratory scale, sustainability and economic issues arise when they are considered for industrial scale-up. In this context, utilizing a waste as a raw material and changing the linear economy approach to a circular one, represent an excellent solution for reducing the environmental impact, and for consistently improving the overall sustainability of these production processes [22].

Several recent studies have investigated the use of deep eutectic solvents (DESs) for black mass processing, particularly combinations of organic acids and hydrogen bond donors such as choline chloride, urea, or menthol. Systems like choline chloride:oxalic acid or betaine hydrochloride:ethylene glycol have shown promising metal extraction efficiencies under mild conditions [23]. Within this context, menthol-based eutectics have also attracted growing attention due to their low toxicity and tunable hydrophobicity, with applications including cobalt and nickel leaching from battery materials [ref]. Our choice to formulate a eutectic system using free fatty acids (FFAs) and menthol builds directly on this body of work, but with the novel incorporation of recycled FFAs sourced from waste cooking oil. This introduces a circular and sustainable aspect while preserving the hydrogen bonding and solvation properties observed in previous menthol-based eutectics. In contrast, the glycerol:H_2O (1:3) system used in our study does not form a eutectic but serves as a low-viscosity, polar, hydrogen-bond-rich solvent system. Glycerol (GLY), derived here from hydrolyzed waste oil, was selected as a water alternative with the potential to coordinate lithium ions and promote selective Li^+ solubilization. While glycerol has been used in other chemical separation contexts, its specific role in black mass leaching has been underexplored. Our approach aims to evaluate its effectiveness in this novel context and benchmark its performance as a green, waste-derived medium.

Considering these aspects, to combine the effectiveness of liquid or low-melting mixtures in extracting critical raw materials from BM with the sustainable use of waste components, glycerol and long-chain fatty acids from waste cooking oils were obtained via hydrolysis [24] and used to prepare two liquid systems: (i) GLY:H_2O in a 1:3 M ratio, and (ii) FFAs:Menthol in a 1:2 M ratio, forming a novel low melting mixture (LMM). In particular, the system FFAs:Menthol was extensively studied by DFT and ^{1}H NMR spectroscopy, which allowed to determine the eutectic composition.

2. Experimental

2.1. Chemicals

Black mass was provided by a local recycling company settled in Lombardia (Italy). The provider declared an anodic graphite content of 20 wt% (determined by thermogravimetry analysis) mixed with LCO and NCM cathodes. Further treatments were not disclosed. According to ICP-MS analysis, the average amount (wt%) of the main elements in samples of black mass as received (BM) was the following (Table 1).

Table 1
Distribution of main elements in the BM.

Element	Amount (wt%)
Co	16.2 ± 0.5
Ni	5.7 ± 0.2
Mn	3.5 ± 0.1
Li	2.8 ± 0.1
Al	2.3 ± 0.1
Cu	1.7 ± 0.1
Fe	0.3 ± 0.01

Waste Cooking Oils (WCO), resulting from food deep frying with sunflower edible oil, were provided by a local catering company settled in Milan (Italy).

Menthol, deuterated dimethylsulfoxide (DMSO-d_6), and tetramethylsilane (TMS) were purchased by Merck Europe.

2.2. ICP-MS analysis

Elemental analyses on pristine and treated BM samples were conducted with a single quadrupole inductively coupled plasma mass spectrometer (ICP-MS, NEXION 2000, Perkin Elmer) in He mode with kinetic energy discrimination.

Sample preparation was carried out via microwave-assisted digestion of the BM (ETHOS EASY, Milestone Srl) in 9 mL of ultrapure aqua regia for 15 min at 230 °C, followed by dilution with ultrapure 1 % nitric acid. Calibration of the spectrometer was performed with multi-elemental standard solutions (I.V. Labs, Inc.) covering the range of analytical interest.

2.3. NMR analysis

The samples were transferred to 5 mm NMR tubes. For samples with no deuterated solvents (GLY:H_2O and FFAs:Men), a coaxial insert containing DMSO-d_6 and TMS was used as lock signal and chemical shift reference, respectively. High-resolution liquid-state NMR measurements were performed at 298 K without sample spinning with a Bruker NEO 500 console (11.74 T) equipped with a direct observe BBFO (broadband including fluorine) iProbe and a variable-temperature unit (^{1}H, ^{19}F, ^{31}P and ^{7}Li resonance frequencies of 500.13, 470.59, 202.46 and 194.37 MHz, respectively). The instrument was carefully tuned, shimmed, and the 90° pulses calibrated. 1D ^{1}H spectra were collected with 16 scans using 16,384 points, over a spectral width of 15 ppm. 1D ^{19}F spectra were collected with 128 scans using 65,536 points. 1D ^{7}Li spectra were collected with 16 scans using 32,768 points. 1D ^{31}P spectra were collected with 2048 scans using 8192 points.

2.4. Leaching procedure

2 g of BM were placed in an Erlenmeyer flask equipped with a magnetic stirrer. The appropriate amount of leaching agent was added (substrate/leaching agent ratio 40 g/g), and the mixture was stirred at 80 °C for 2 h. Once cooled down to room temperature, the mixture was filtered under vacuum and the residue dried overnight at 80 °C.

2.5. DFT calculations

Density Functional Theory (DFT) calculations were carried out to analyse the nature of the intermolecular H-bond interactions within the FFAs:Menthol system, using TURBOMOLE software. For this purpose, minimal clusters of FFAs:Menthol with increasing Menthol molar ratio were evaluated. In this case, oleic acid was considered as being the most abundant FFA among the recycled oil, provided that DFT calculations are limited to few hundreds of atoms. Thus, 1:2, 1:3, 1:5, 1:7 and 1:9 minimal clusters of oleic acid:Menthol, consisting of 3, 4, 6, 8 and 10 molecules, respectively, were investigated. D-Menthol and two different

conformations of the oleic acid molecule were considered (Fig. 1) after performing a conformer search following a global optimization procedure based on the artificial bee colony algorithm in ABCluster [25] software employing xTB semi-empirical quantum chemistry method by Grimme [26].

The same method was used to obtain the initial configurations of oleic acid:Menthol minimal clusters. The DFT calculations were performed employing PBE functional and def2-TZVP basis set plus D3 Grimme dispersion contribution [27]. For the analysis of the main contributing forces to the overall interactions, Bader's Quantum Theory of Atoms in Molecules [28] (QTAIM), electron localization function (ELF) using Core-Valence Bifurcation (CVB) index [29] and Non-Covalent Interaction (NCI) analysis [30] were applied using MultiWFN program [31].

2.6. Determination of the viscosity

Rheological measurements were performed on pure GLY and GLY:H_2O solution with a 1:3 M ratio using an Anton Paar MCR502 modular compact rheometer. The instrument was equipped with a Peltier Plate and Hood thermal control system to maintain a constant temperature of 25 °C. A cone and plate geometry (50 mm diameter, 1° angle, and 99 μm truncation) was used for the measurements.

Shear rate was varied following a logarithmic ramp profile, ranging from 10 Hz to 100 Hz, with data points collected at a density of 15 points per decade. Then, viscosity values were determined through regression analysis.

3. Results and discussion

3.1. Preparation and characterization of the FFAs:Menthol system and GLY:H_2O

The preparation of the eutectic system composed of a mixture of FFAs and Menthol (1:2) is herein reported for the first time. It is known that Menthol can form eutectic systems with long-chain fatty acids as stearic, myristic, lauric [32], and oleic acids [33]. Nevertheless, when sustainability assessments are conducted, e.g. through green metrics or EcoScale [24], the possibility of obtaining one or more raw materials from waste reduces considerably the environmental impact. In this context, a highly sustainable and circular synthesis of this system was developed. WCO, recycled according to a previously described protocol [34,35], was chemically hydrolyzed to yield pure glycerol and the mixture of FFAs which were then separated as described in Fig. 2.

The FFA mixture obtained from WCO has been characterized by semiquantitative ^{1}H NMR analysis [36], and its chemical profile was assessed, revealing the high purity of the product (Fig. 3).

The known methodology reported by Popescu and coworkers [37] for the determination of the fatty acids relative distribution in triglycerides mixtures was herein adapted to our FFAs mixture as reported in Table 2.

The main constituent of our FFAs mixture is the mono-unsaturated oleic acid (about 75 %), while the content of linolenic and linoleic acids is, respectively, 4.3 % and 1.8 %. A relevant amount of SFAs is also present (about 14 %), probably in part derived from the oxidation of the parent edible oils.

The FFAs obtained were used to synthesize a series of low melting mixtures (LMM) in combination with Menthol. Exploratory tests revealed that the mixture of the two compounds formed a low melting system for the following ratios FFAs:Menthol: 1:2, 1:3, 1:5, 1:7 while increasing the amount of FFAs the mixture resulted solid at room temperature.

To choose the system to be tested as leaching agent among those reported above, two different approaches (DFT calculation and ^{1}H NMR spectroscopic analysis) were used to determine the eutectic molar ratio between FFAs and Menthol. This choice is related to the possibility to design a leaching medium with a melting point as low as possible and thus extending the operating temperature window of the leaching process.

Regarding the DFT calculations, as the FFAs mixture is mainly composed by more than 75 % of oleic acid (vide ultra), the monomers oleic acid and Menthol were considered. With the main purpose of revealing the oleic acid:Menthol optimal molar ratio, the strength and topology of H-bond developed between the acceptor and donor within LMM at different oleic acid:Menthol molar ratios was evaluated employing DFT quantum calculations. For the considered minimal clusters, H-bonds developed between H_1 of oleic acid and O_M of Menthol molecules, as well as secondary H-bonds, such as H_M(MENTH2)-O_2(OA) when considering conformer 1 of oleic acid and H_M(MENTH2)-O_M(MENTH1) when considering conformer 2, were evaluated (Fig. 1).

The geometry optimization of the considered minimal clusters (Fig. 4) leads to different bond distances, $d_{H\text{-}bond}$, and bond angles, $\varphi_{H\text{-}bond}$ (Fig. 5a and b, respectively).

For the H_1(OA)-O_M(MENTH1) H-bond, $d_{H\text{-}bond}$, were found to be in the range of 1.55–1.7 Å, where 1.55 Å is the minimum for the 1 to 5 oleic acid:Menthol molar ratio, while angles were ~174°, meaning moderate ionic H-bonds according to Steiner [38] and Grabowski [39]. The QTAIM analysis of intermolecular forces was conducted through the properties of electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho$) at bond critical points (BCPs, type (3–1) in QTAIM), Fig. 4c and d, respectively. The electron density and its Laplacian at the H-bond BCP enable the quantification of the strength of oleic acid – Menthol H-bond. It has been demonstrated that electron density values, ρ, in the range of 0.002 to 0.014 a.u. (a.u.) and Laplacian values, $\nabla^2\rho$, from 0.014 to 0.139 a.u. are indicative of hydrogen bonding [40]. Higher values within these ranges correspond to stronger H-bond. Reported ρ and $\nabla^2\rho$ values for the considered CP, Fig. 4c and d, show moderately strong to strong H-bond interactions for the H_1(OA)-O_M(MENTH1) for both oleic acid conformer 1 and conformer 2 systems, and moderately strong for the H_M(MENTH2)-O_2(OA) H-bonds when considering conformer 1 of oleic acid and H_M(MENTH2)-O_M(MENTH1) H-bond when considering conformer 2. The hydrogen bonding regions were also analyzed using ELF, which reveals electron accumulation or depletion around the formed H-bond. CVB index was calculated from the

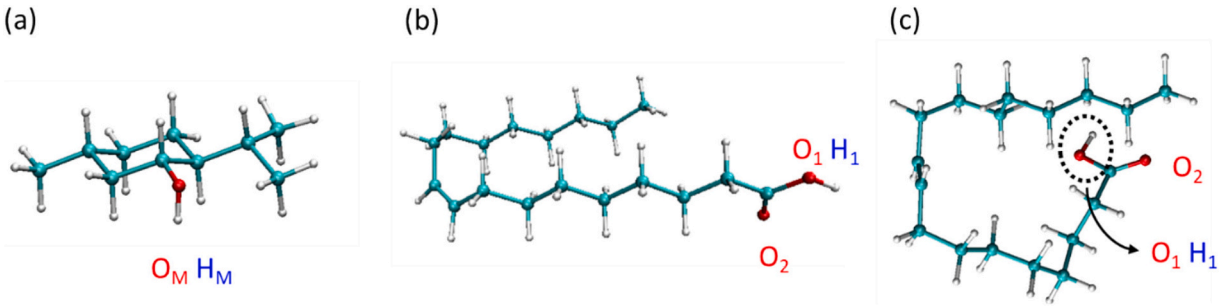

Fig. 1. Molecular structures of menthol (a), oleic acid conformer 1 (b), and oleic acid conformer 2 (c).

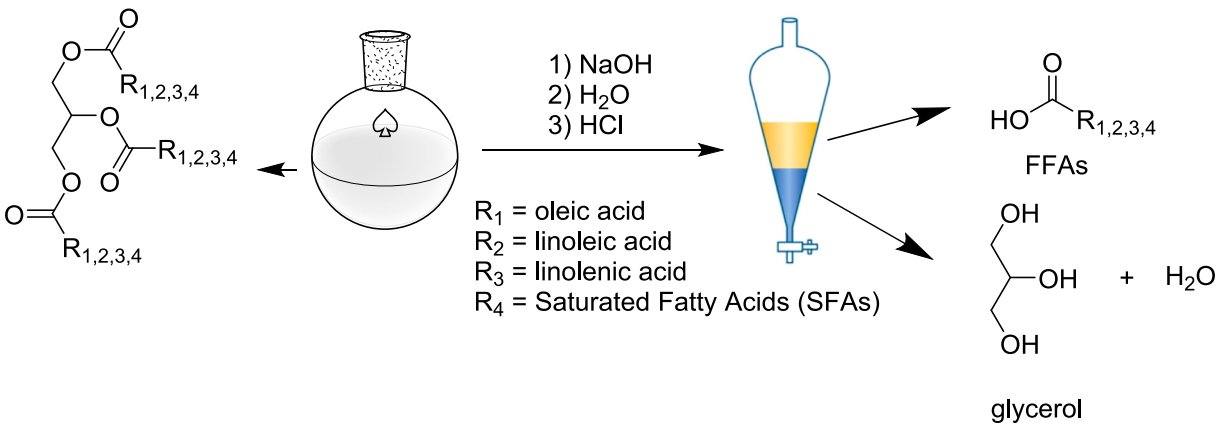

Fig. 2. Recovering of glycerol and FFAs mixture through hydrolysis of WCOs.

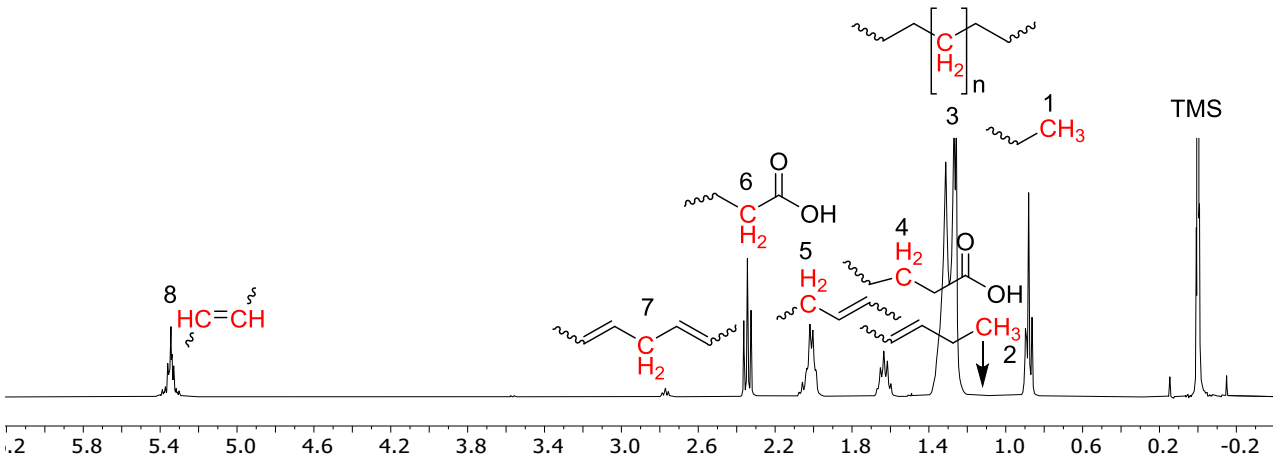

Fig. 3. ^{1}H NMR spectrum of FFAs mixture and peak assignment.

Table 2
Relative chemical composition obtained from peaks integration of ^{1}H NMR spectrum. The numbers in bold in the "Formula" column refer to the peak numbering of Fig. 3.

Component	Formula	Relative amount (mole %)
Linolenic acid	$\mathbf{2}/(\mathbf{2}+\mathbf{1})$	4.3
Linoleic acid	$(3\times\mathbf{7}\text{-}4\times\mathbf{2})/2(\mathbf{2}+\mathbf{1})$	1.8
Oleic acid	$((3\times\mathbf{5})/4\times(\mathbf{2}+\mathbf{1}))$ -linolenic - linoleic	75.3
SFA	$\mathbf{1}/(\mathbf{2}+\mathbf{1})$ – linolenic - linoleic – oleic	14.4

ELFs for the corresponding H-bond atoms, yielding values in the −0.065 to −0.168 range for the H_1(OA)-O_M(MENTH1) H-bonds in systems considering conformer 1 and between −0.036 and − 0.074 when considering conformer 2. These CVB values indicate strong interactions, with higher negative values for the systems where conformer 1 of oleic acid was considered.

The NCI analysis reported in Fig. 5 showed localized spots around the hydrogen bonding sites, confirming the hydrogen bonding, but also large regions corresponding to van der Waals interactions (green spots), thus confirming the stabilizing role of interactions through non-polar sites. H_1(OA)-O_M(MENTH1) H-bond isosurface for the systems considering oleic acid conformer 1 weakens upon Menthol molar ratio increase, Fig. 5a to 5e. NCI index indicates the relation between the sign of the second eigenvalue of the electron density Hessian matrix, λ_2, and the reduced density gradient (RDG) of the electron density. The vanishing of the NCI blue isosurface at H_1(OA)-O_M(MENTH1) H-bond in oleic acid conformer 1 systems, meaning the domination of the electron density gradient over electron density, indicate H-bond attractive interactions weakening upon Menthol molar ratio increase. The characterization of the H-bond developed between oleic acid and Menthol molecules revealed moderately strong to strong interaction forces.

Indeed, NCI analysis in Fig. 6 suggests a gradual weakening of the DFT considered hydrogen bond with the increasing of the Menthol ratio above the 1:2 oleic acid:Menthol mixture.

To gain additional information about the differences in systems with different FFAs:Menthol molar ratios, ^{1}H NMR analysis was conducted to check the chemical shift variation of the average –OH/-COOH signal over the compositional range, taken as indicator of the hydrogen-bond strength of the network (Fig. 7).

Broadly speaking, an upfield shift (i.e. a shift to lower frequencies) is symptomatic of an increase in the shielding of the given proton, indicating a weakening of the hydrogen bond involving the corresponding proton(s) [41–44]. Thus, considering the upfield shift observed for the –OH/-COOH signal with increasing Menthol molar fraction, the molar ratio 1:2 was taken as the one of choice.

3.2. *Preparation and characterization of the system glycerol:H_2O*

As reported in the Fig. 2, after the basic hydrolysis of recycled waste cooking oils, it is possible to recover from the water phases pure glycerol. The high purity of the chemical obtained by this route was assessed by ^{1}H NMR and recently published by some of us [24]. Regarding the direct application of pure glycerol as solvent for BM processing, its high

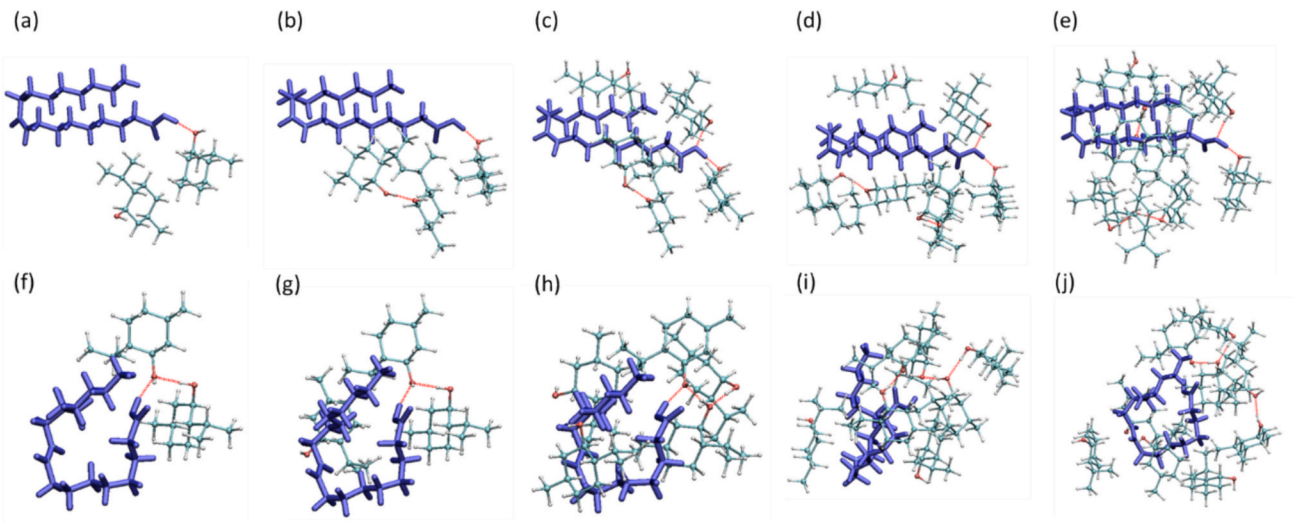

Fig. 4. Molecular structure of the oleic acid/menthol minimal clusters considered in this work after DFT geometry optimization**.** Different molar ratios 1:2 (a, f), 1:3 (b, g), 1:5 (c, h), 1:7 (d, i) and 1:9 (e, j) and configurations, conformer 1 (a-e) and conformer 2 (f-j), are shown. Red dashed lines indicate H-bonds ($d_{\text{H-bond}} < 1.9$ and $\varphi_{\text{H-bond}} > 165°$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

viscosity represented a relevant technological barrier. Rheology measurements reveled viscosity values of 886 ± 11 mPa*s for GLY and 11.53 ± 0.18 mPa*s for the system GLY:H_2O (1:3).

3.3. Leaching experiments

The eutectic system FFAs:Menthol (1:2) and the GLY:H_2O system (1:3) were evaluated as leaching media for processing BM samples. After each leaching experiment, the mixture was filtered, and both the leachate and the residual BM were analyzed using ICP-MS (see Section 2.4). To assess the feasibility of using FFAs:Menthol derived from waste oil recycling, an analogous system composed of commercial oleic acid and Menthol (oleic:Menthol) was also prepared and tested.

The leaching experiments were designed using mild conditions intentionally selected to reflect practical, industry-relevant parameters while avoiding possible solvent degradation. Based on prior studies involving similar black mass compositions and aqueous leaching systems, we adopted a substrate-to-leaching-agent ratio of 40 g/g, a temperature of 80 °C, and a reaction time of 2 h. The chosen temperature avoids potential decomposition of the eutectic mixtures, which is a known risk at elevated temperatures, particularly for DESs. Additionally, longer leaching times were used to ensure completeness, although similar black mass systems are often reported to reach equilibrium in aqueous media within 30 min. [45]

The leaching results, along with the characterization of the residual BMs, are presented, respectively, in Tables 3 and 4.

Table 3 presents the residual metal content in black mass after leaching with the two tested systems, illustrating their markedly different selectivity profiles. The GLY:H_2O (1:3) system achieved the most effective lithium removal (reduction from 28 wt% to 1.6 wt%), while leaving the transition metals largely unaffected, indicative of a highly selective, mild leaching process. Conversely, the FFAs:Menthol (1:2) mixture showed limited lithium removal but moderate capacity of leaching for cobalt and nickel, suggesting weaker overall leaching power but potential for tuning toward multi-metal recovery under optimized conditions. In Table 4, the leaching outcome of GLY:H_2O, FFAs:Menthol and oleic:Menthol systems, considering a substrate/leaching agent ratio of 40 g/g, are reported.

The leaching results presented in Table 4 underscore the promising performance and selectivity of the tested systems, particularly the GLY:H_2O (1:3) mixture. This system exhibited high lithium extraction efficiency, reaching 588.2 ± 17 mg/kg, which is comparable to or even exceeds values reported in the literature using more energy-intensive techniques, such as microwave-assisted leaching [45]. This result is especially significant considering the benign and sustainable nature of the leaching medium, which is entirely derived from waste cooking oil. The observed lithium efficiency of the GLY:H_2O system can be rationalized by considering the chemical environment created by the glycerol-water mixture. While glycerol lacks intrinsic acidity or redox activity, it provides a highly polar and hydrogen-bond-rich medium that facilitates the solvation and transport of lithium ions. The water component in the 1:3 mixture lowers the viscosity significantly and enhances ionic mobility, which is crucial for diffusion-driven processes. Lithium ions, being small and monovalent, are relatively labile in metal oxide lattices and can be released through partial hydrolysis of the Li—O bonds at elevated temperature (80 °C), even in the absence of strong acid or reducing agents. Glycerol's hydroxyl groups may assist in stabilizing solvated Li^+ ions via weak coordination, thus preventing readsorption onto the solid surface. However, the mechanism is largely non-redox and diffusion-limited, which also explains the negligible extraction of transition metals such as Co, Ni, and Mn, whose oxides are more stable and require acidic or reductive conditions for dissolution. Overall, the GLY:H_2O system acts as a selective medium for Li^+ solubilization via a mild, hydrogen-bond-mediated mechanism without significant lattice disruption of other metals.

The key advantage of our approach lies in cost and sustainability. Commercial glycerol (≥99 %) typically costs between €1.5 and €4 per kg depending on purity and supplier, while the glycerol we produced was obtained from waste cooking oil, a material often acquired at zero or negative cost due to regulatory disposal constraints. The alkaline hydrolysis process used to recover glycerol is low-energy and easily scalable. This results in a solvent system that not only matches the chemical performance of commercial alternatives but also drastically reduces environmental impact and material costs, reinforcing the circular and sustainable nature of our proposed leaching strategy.

Moreover, the selective leaching of lithium over other metals such as Co, Ni, and Mn indicates a strong potential for targeted recovery applications, aligning well with current strategies in critical raw material management.

The FFAs:Menthol (1:2) eutectic system, while showing a lower lithium extraction efficiency (140.8 ± 2.3 mg/kg), still demonstrates clear potential, particularly in terms of its capacity to co-extract Co (32.0 ± 0.5 mg/kg) and Mn (28.3 ± 0.5 mg/kg), which could be advantageous in multi-metal recovery schemes. The comparable performance of this

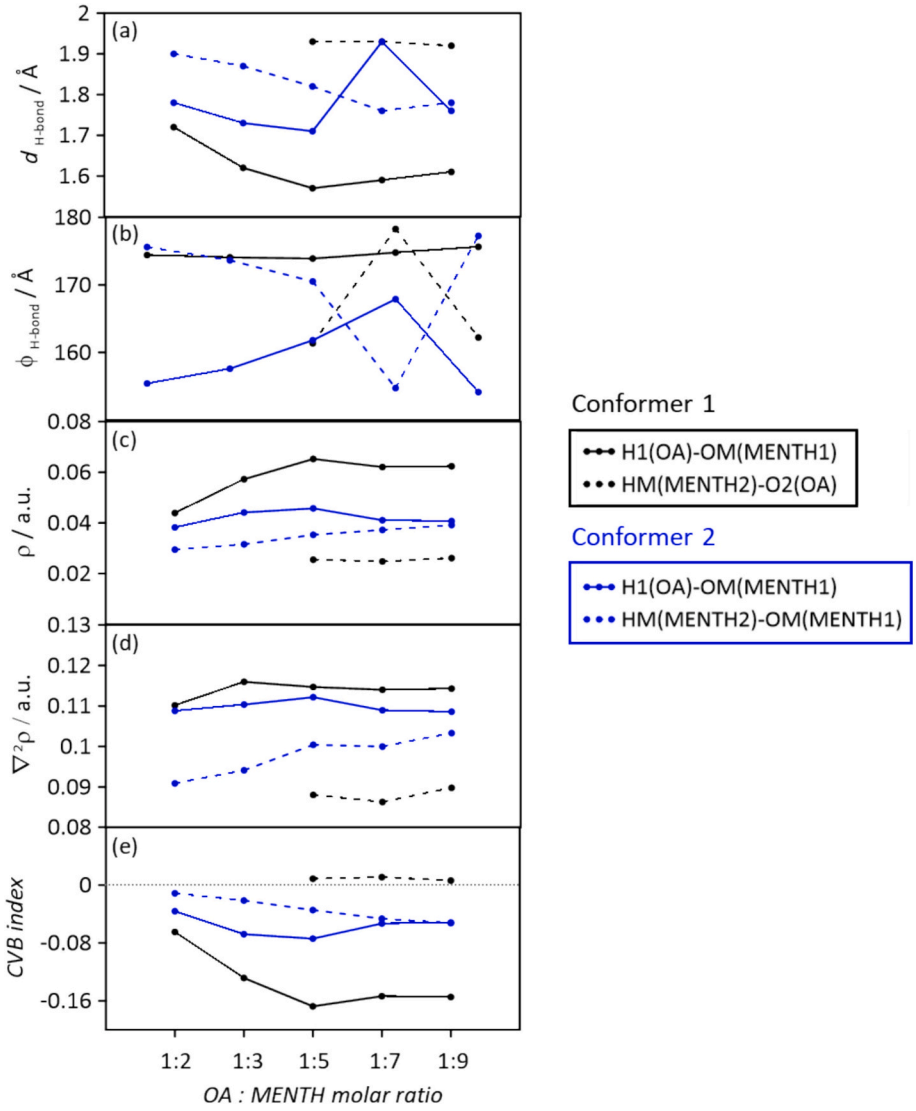

Fig. 5. H-bond distance, $d_{H\text{-}bond}$, (a) and angle, $f_{H\text{-}bond}$, (b), electron density, r, (c) and Laplacian of electron density, $\nabla^2 r$, (d) at the H-bond CP, and CVB index (e) of the studied H-bonds for all the considered oleic acid:Menthol minimal clusters from DFT calculations. Colour code: black lines correspond to H_1(OA)-O_M(MENTH1) bond, dashed black lines correspond to H_M(MENTH2)-O_2(OA) bond, blue lines correspond to H_1(OA)-O_M(MENTH1) bond, and dashed blue lines correspond to H_M(MENTH2)-O_M(MENTH1) bond. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

waste-derived eutectic mixture to its counterpart made with pure oleic acid further highlights the feasibility of upcycling waste feedstocks without compromising chemical functionality, thus reinforcing the circular economy approach adopted in this study. However, differences in leaching performances were detected when the mixture of FAs was replaced by pure oleic acid (especially for Li and Mn). These results suggest a possible variation in the leaching ability related to the nature of the FAs' chain which should be taken into account when waste cooking oil, which has a variable composition, is used as raw material.

Taken together, these findings validate the dual strategy of resource recovery and waste valorisation. They also establish a solid foundation for further optimization and scaling of these green leaching media, potentially paving the way for sustainable, low-impact alternatives to traditional hydrometallurgical processes.

When compared with traditional hydrometallurgical approaches, which typically involve concentrated mineral acids (e.g., H_2SO_4 or HCl) and strong oxidants (e.g., H_2O_2) under controlled pH and elevated temperatures, the leaching systems presented here demonstrate several notable advantages. While industrial hydrometallurgy can achieve lithium recoveries exceeding 90–95 %, this is often at the cost of high reagent consumption, corrosion issues, complex effluent treatment, and significant greenhouse gas (GHG) emissions. In contrast, the GLY:H_2O (1:3) system achieved a lithium recovery comparable to or exceeding that of moderate-strength hydrometallurgical systems, but under milder conditions (80 °C, no added acid or oxidant) and using waste-derived, biodegradable solvents. Furthermore, the environmental footprint is drastically reduced: glycerol is non-toxic and fully biodegradable, and the process generates no hazardous fumes or acidic wastewater. From a cost perspective, glycerol sourced from waste cooking oil represents an essentially zero-cost solvent, avoiding the expense of purified reagents and neutralization steps. This positions the system as particularly attractive for decentralized or low-impact recovery operations. Although the transition metal recovery is currently limited in the GLY:H_2O system, the selectivity for lithium and the circular origin of the solvent together provide a promising green alternative to conventional processes, especially when recovery goals are lithium-focused.

3.4. Preliminary economic considerations and feasibility assessment

The treatment of waste cooking oil (WCO) through alkaline

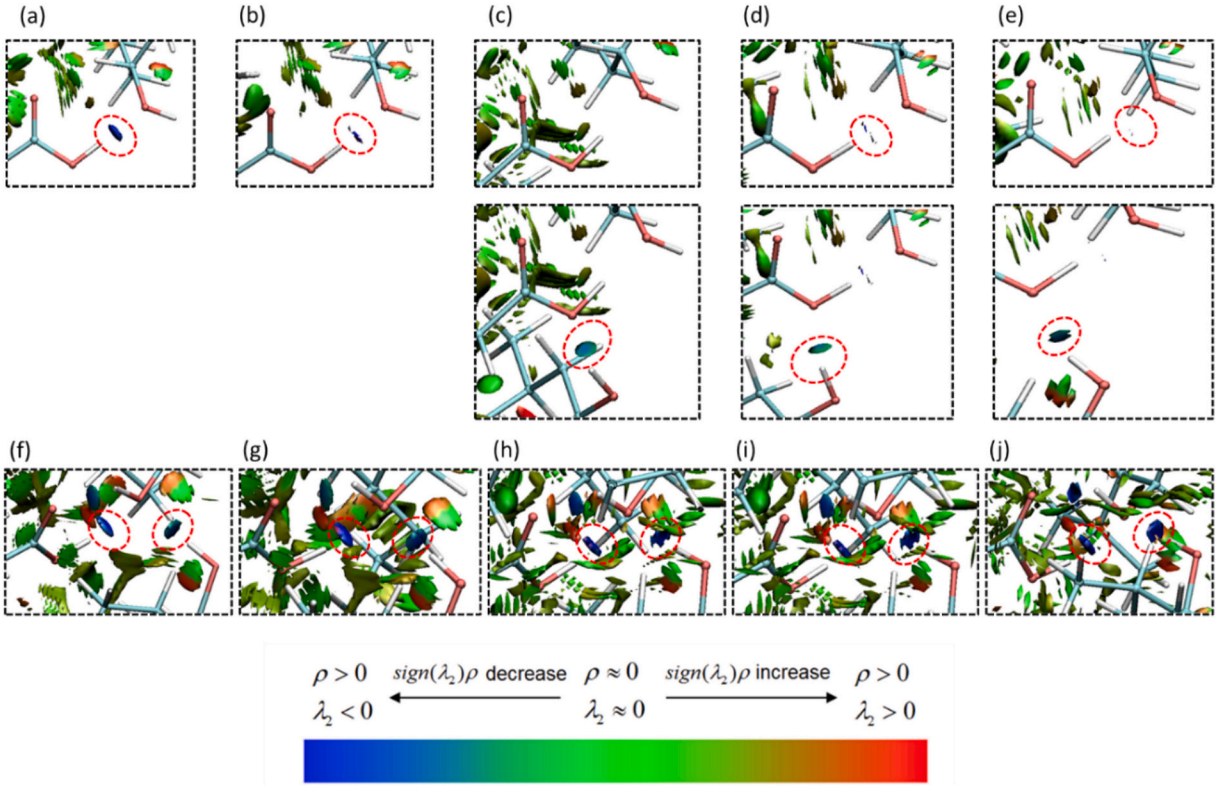

Fig. 6. Non-Covalent Interactions (NCI) analysis of H_1(OA)-O_M(MENTH) H-bond of the considered minimal clusters with molar ratios 1:2 (a), 1:3 (b), 1:5 (c), 1:7 (d) and 1:9 (e) for conformer 1, and ratios 1:2 (f), 1:3 (g), 1:5 (h), 1:7 (i) and 1:9 (j) for conformer 2. Red circles indicate blue spots corresponding to H-bond. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

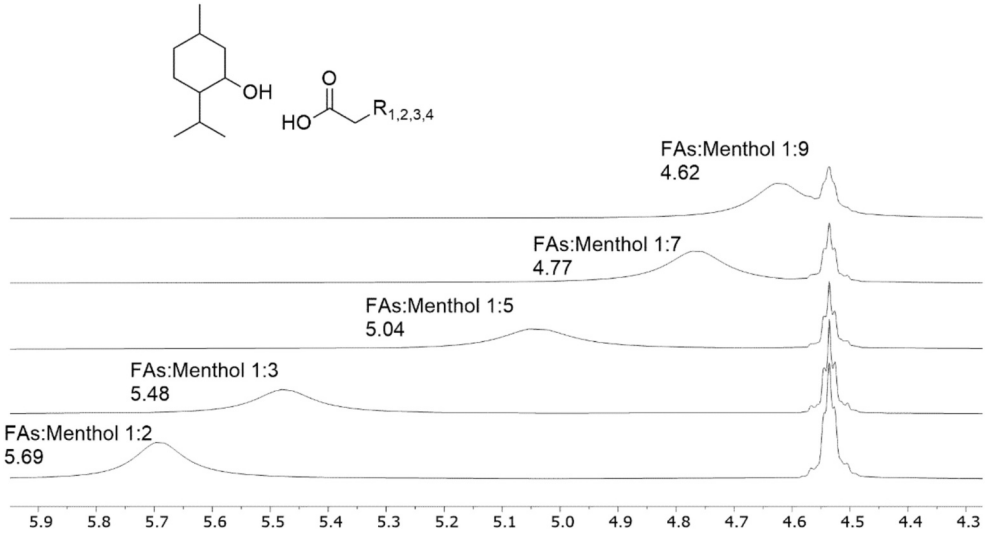

Fig. 7. Selected region of ^{1}H NMR spectra of FFAs:Menthol low melting mixtures, corresponding to the exchangeable OH signal.

Table 3
Amount of Li, Al, Co, Mn, and Ni (g/g) in starting black mass (BMTQ), in residual BM after leaching (BM_FFAs:Menthol, BMGLY:H_2O), determined by ICP-MS.

Element	BMTQ[1]	RES_GLY:H_2O[1]	RES_FFAs:Menthol[1]
Li	28 ± 0.08	1.6 ± 0.05	0.5 ± 0.02
Co	16.2 ± 0.5	12.5 ± 0.4	15.9 ± 0.5
Ni	5.7 ± 0.2	3.3 ± 0.1	4.1 ± 0.1
Mn	3.5 ± 0.1	3.3 ± 0.1	4.5 ± 0.1

[1] Results expressed as mass percentages.

Table 4
Amount of Li, Al, Co, Mn, and Ni (mg/kg) in the leachates (GLY:H_2O, FFAs:Menthol) determined by ICP-MS.

Element	GLY:H_2O[1]	FFAs:Menthol[1]	oleic:Menthol[1]
Li	588.2 ± 17	140.8 ± 2.3	336.0 ± 4.3
Co	0.4 ± 0.01	32.0 ± 0.5	40.5 ± 0.6
Ni	< 0.13 ± 0.01	12.3 ± 0.2	8.6 ± 0.2
Mn	1.2 ± 0.01	28.3 ± 0.5	17.9 ± 0.2

[1] Results expressed as mg of analyte per kg of leaching solution.

hydrolysis is a low-cost and well-established process, typically conducted at ~70 °C using NaOH or KOH. This yields glycerol and free fatty acids (FFAs), both usable as green solvents. WCO is often acquired at zero or negative cost due to disposal regulations, making it a highly economical feedstock [46]. The additional cost of menthol in the FFAs:Menthol system is moderate and partially offset by its potential for recovery and reuse. Overall, the reagent costs are significantly lower than conventional hydrometallurgical inputs like H_2SO_4 or HCl, which also incur costs for neutralization and effluent treatment [47]. From a scalability standpoint, both leaching systems operate under mild conditions (80 °C, atmospheric pressure) and require no specialized equipment, making them compatible with standard industrial setups. Glycerol is non-toxic and biodegradable, and menthol-based eutectic solvents have been successfully used in other green chemistry processes, suggesting strong potential for industrial application [48].

In sum, the process combines circular feedstocks with mild, scalable conditions, offering a potentially cost-effective and environmentally favourable route for selective metal recovery.

4. Conclusions

This study presents an innovative and sustainable approach to metal recovery from black mass (BM) derived from spent lithium-ion batteries, through the formulation and application of two novel liquid-phase leaching systems: a glycerol-water mixture and a low-melting eutectic composed of fatty acids and menthol, both derived from recycled waste cooking oils. The GLY:H_2O (1:3) system demonstrated remarkable selectivity and efficiency in lithium extraction, achieving yields (588.2 ± 17 mg/kg) comparable to advanced hydrometallurgical methods, but under much milder, low-energy conditions. This highlights the effectiveness of hydrogen-bonded solvent systems in facilitating targeted metal solubilization while maintaining environmental and operational advantages. The FFAs:Menthol eutectic system, while exhibiting lower overall lithium leaching efficiency, showed promising extraction capabilities, particularly for cobalt and manganese. Notably, its performance was consistent regardless of whether the fatty acids were sourced from pure oleic acid or recycled oils, confirming the viability of using circular feedstocks for functional eutectic solvent design. Complemented by Density Functional Theory (DFT) calculations and NMR spectroscopy, the study provides deep insight into the structural organization and hydrogen bonding dynamics that underpin the eutectic behaviour of the FFAs:Menthol system. This molecular-level understanding guided the selection of optimal molar ratios and supports broader applications of such solvents in liquid-phase separation science. In summary, this work delivers both practical and theoretical advancements in the design of eco-friendly liquid systems for critical metal recovery. It opens new avenues for the development of task-specific, waste-derived solvents, contributing to the growing field of sustainable molecular liquids. Future efforts will focus on optimizing process parameters, improving metal selectivity, and evaluating the scalability and environmental footprint of these systems for real-world applications in circular economy frameworks.

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CRediT authorship contribution statement

Alberto Mannu: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria Enrica Di Pietro:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Chiara Carotti:** Validation, Investigation. **Gabriele Magugliani:** Validation, Investigation, Formal analysis. **Eros Mossini:** Supervision, Methodology, Data curation. **Elena Macerata:** Validation, Supervision, Funding acquisition. **Sara Rozas:** Writing – original draft, Investigation, Formal analysis. **Santiago Aparicio:** Writing – original draft, Supervision, Resources, Methodology. **Andrea Mele:** Writing – review & editing, Writing – original draft, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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