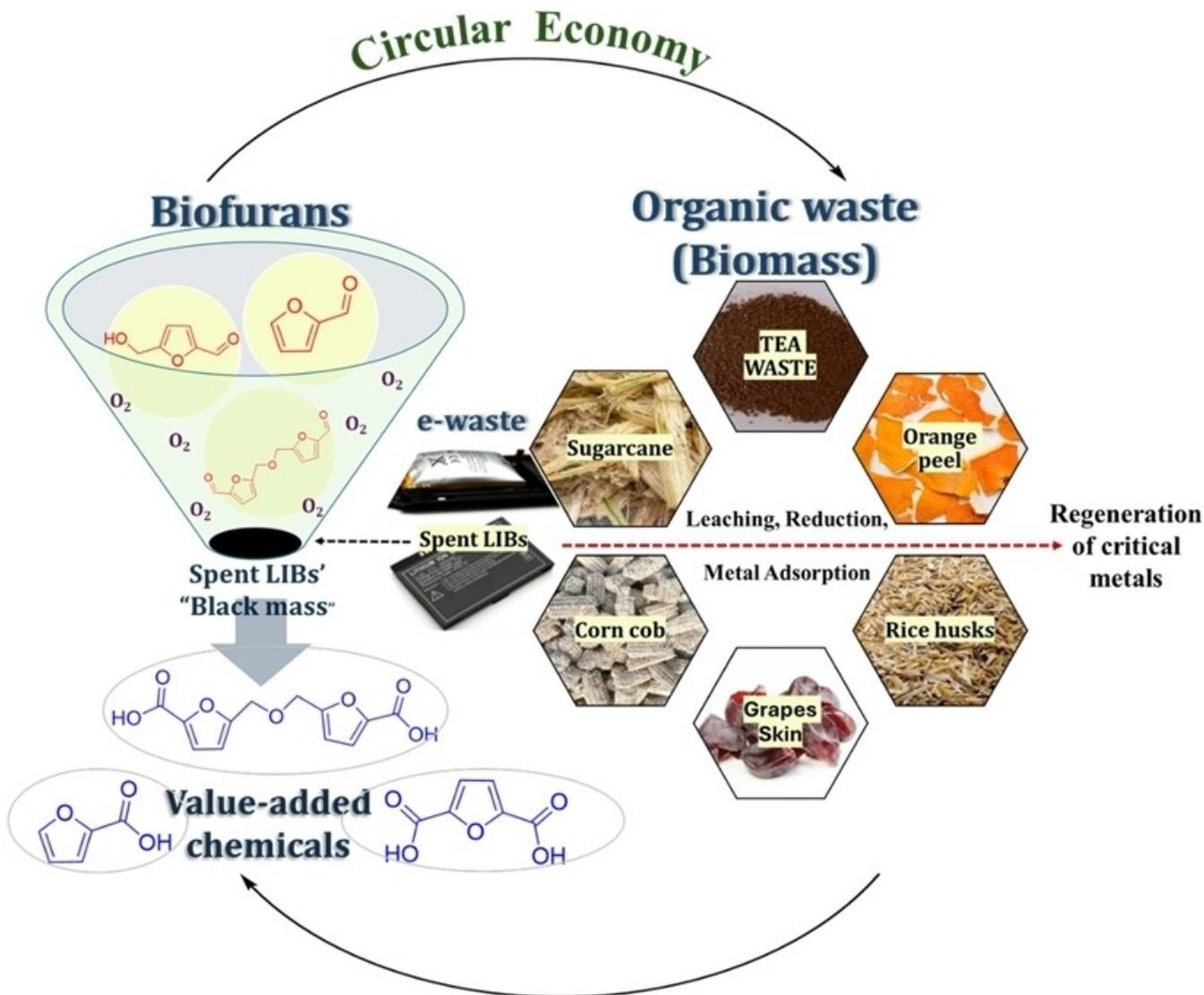


Sustainable Combination of Waste with Waste: Utilization of Biomass to Recover Critical Metals from Spent Lithium ion Batteries

Hiren Jungi,^[a, b] Asma A. Virani,^[a, b] Suman Podder,^[a, b] Harpal Girase,^[a] and Joyee Mitra^{*[a, b]}



The generation of e-waste from lithium ion batteries (LIBs) is rapidly increasing due to the rising utilization of LIBs in portable electronics, and electric vehicles, with an average life span of 3–5 years. The disposal of spent LIBs is a major environmental concern due to the presence of high percentages of toxic heavy metals and corrosive electrolytes. Efficient and sustainable recycling of spent LIBs has become immensely important, both environmentally and from a circular economy perspective, as LIBs serve as secondary sources of critical metals needed for renewable energy conversion and storage systems. We provide

a concise review of metal recovery from spent LIBs using waste biomass in a green and sustainable approach for resource generation, in addition to the valorization of waste biomass. Biomass is used to recover metals from spent LIBs, acting as lixiviant, reductant, and as absorbent. We have also discussed a reverse strategy utilizing ‘black mass’ from spent LIBs as catalyst for biomass conversion to value-added products. The concept of “circular economy” is highlighted in a “killing two birds with one stone” approach through the utilization of biomass for the recovery of metals from spent LIBs and vice versa.

1. Introduction

Changing lifestyle of humankind, consequent to the technological advancement and the aim to achieve ‘carbon neutrality’, has resulted in a significant reliance on lithium-ion batteries (LIBs). The escalating demand for electric vehicles (EVs), portable electronic devices, and renewable energy generation/storage systems has been a driver for LIBs with higher energy storage capacities, faster charging capabilities, and longer cycle life, and the global LIB demand is expected to reach \$95 billion by 2025 with a projected CAGR of ~16%.^[1–3] The World Economic Forum has forecasted that the global battery demand will reach 2,600 GWh by 2030. The projected global battery

demand from 2021 to 2040 across various Shared Socio-economic Pathway (SSP) scenarios, along with the predicted market shares of different battery types (Figure 1) depict a continued growth of LIBs irrespective of the battery chemistries involved.^[4] The rapid market growth in LIBs also raises concerns about the disposal of discarded LIBs, which are likely to exceed 4,64,000 tons by 2025, a significant rise of ~59% from 2012. On an average, most mobile phones are replaced within 12–18 months, regardless of their service condition.^[5,6] Currently, only about 6% of spent LIBs are recycled, while the majority end up in landfills. This poses a serious environmental threat due to toxic metal leaching into the groundwater and corrosive, flammable electrolytes that can contaminate groundwater and soil runoffs.^[7,8] Recycling LIBs is economically and environmentally beneficial, as it reduces the cost of mining from primary resources, and reduces the volume of waste generation. The recovery and reuse of lithium and valuable transition metals, i.e. cobalt, nickel etc. from waste LIBs would reduce the dependency on natural mineral reserves, diminish the geopolitical issues related to resource utilization, and at the same time preclude secondary waste generation from the mining of natural reserves. This promotes circular economy, maintaining the supply chain and supporting sustainable global development of the battery industry. Since the cathode accounts for more than 30% of the cost, it is the primary focus of the recycling processes.^[9,10]

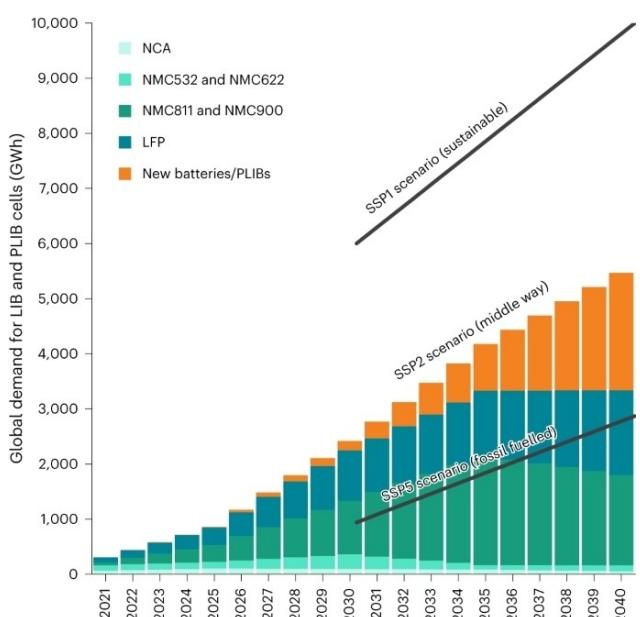


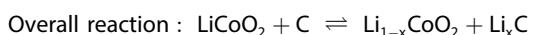
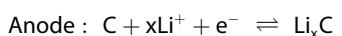
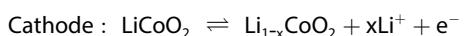
Figure 1. Projected global demand for LIB and PLIB cells from 2021 to 2040. Reproduced with permission from Reference^[4]. Copyright 2023, Springer Nature.

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1.1. Types of Lithium Ion Batteries

Primary LIB consisting of lithium metal as anode and metal oxides as cathode are non-rechargeable. Secondary batteries comprise of lithium transition metal oxides as cathode, graphite anode and an organic solvent with lithium salt as the electrolyte. LIBs can be classified into several types depending on the composition of their constituent electrodes and electrolytes, i.e. cathode (different types of materials with varying chemistries), anode, electrolyte, separators and casing. Graphite and lithium titanate (Li_2TiO_3) are commonly used anode material in most types of LIBs, while the electrolyte consists of lithium salts (including lithium hexafluorophosphate LiPF_6 , lithium tetrafluoroborate LiBF_4) dissolved in organic carbonates (e.g. ethylene carbonate, dimethyl carbonate etc.). The cathode materials in use are lithium cobalt oxide (LiCoO_2 , LCO), lithium manganese oxide (LiMn_2O_4 , LMO), lithium nickel cobalt manganese oxide (,

$\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2\text{NCM}$), lithium iron phosphate (LiFePO_4 , LFP) and lithium nickel cobalt aluminium oxide (LiNiCoAlO_2 , NCA). Aluminium foil acts as a current collector in cathodes whereas copper foil is the anodic current collector (Figure 2). Polymers like polyethylene (PE) or polypropylene (PP) are employed as separators. During charging, lithium ions removed from the cathode intercalate into the graphite anode, and while discharging, these lithium ions de-intercalate from the anode and the reverse reaction takes place (Figure 2). The cathodic and anodic reactions are presented in the following equations, employing the commonly used LCO as cathode and graphite (C) anode as representative examples:^[11]



Difference in cathode chemistries result in differences in their specific energy, operating range, voltages, cycle life and so on, and finds use in various applications (Table 1).^[1,13] The retirement of LIBs is often due to critical issues caused by defects such as temperature increase, voltage drop, state of charge loss (SOC), leakage current and capacity loss, which can be triggered by the intrusion of foreign bodies.^[14] Additionally,

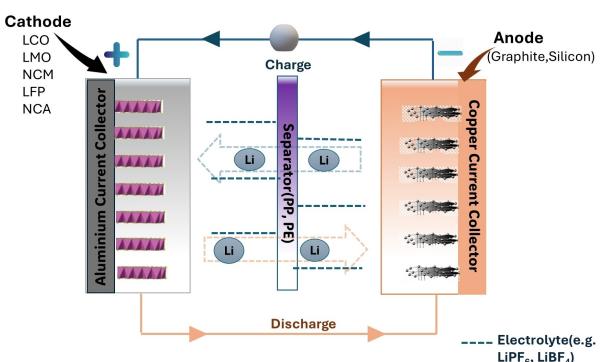


Figure 2. Schematic diagram of components of LIBs.^[12]

increasing cost of cobalt and its limited global reserves (approx. 145 million tons of Co) is also an important factor in a gradual shift towards batteries having lower amounts of cobalt, and the increasing popularity of batteries of other chemistries. Effective recycling processes needs to address '3R' i.e. recovery, recycling and reuse. Hence, the recycling processes being developed must be continually updated in order to facilitate the recovery of these newer materials efficiently.



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Table 1. Types of secondary lithium ion batteries and their properties.^[1]

Types of LIBs	Anode	Cathode	Nominal voltages	Specific energy (capacity)	Typical operating range	Cycle life (related to depth of discharge, load and temperature)
Lithium cobalt oxide (LCO)	Graphite	LiCoO ₂	3.06 V	150–200 Wh Kg ⁻¹	3.0–4.2 V per cell	500–100
Lithium nickel cobalt oxide (NCM)	Graphite	LiNiCoMnO ₂	3.60–3.70 V	150–220 Wh Kg ⁻¹	3.0–4.2 V per cell	1000–2000
Lithium nickel cobalt aluminum oxide (NCA)	Graphite	LiNiAlO ₂	3.60 V	200–260 Wh Kg ⁻¹ 300 Wh Kg ⁻¹ predictable	3.0–4.2 V per cell	500
Lithium manganese oxide (LMO)	Graphite	LiMn ₂ O ₄	3.70–3.80 V	100–150 Wh Kg ⁻¹	3.0–4.2 V per cell	300–700
Lithium iron phosphate (LFP)	Graphite	LiFePO ₄	3.20–3.30 V	90–120 Wh Kg ⁻¹	2.5–3.65 V per cell	2000 and higher
Lithium titanate (LTO)	Li ₂ TiO ₃	LiNiCoMnO ₂ or LiMn ₂ O ₄	2.40 V	50–80 Wh Kg ⁻¹	1.85–2.85 V per cell	3000–7000

1.2. Pre-Treatment Processes and Common Recycling Methods

Pre-treatment serves as the initial stage in the processing of spent LIBs, with the goal of thoroughly sorting the various components of the battery to streamline the subsequent material recycling process, minimize the use of chemicals and enhance overall efficiency (Figure 3).^[15] Recycling of spent LIBs involves a series of pre-treatment steps including sorting,

discharging, dismantling, shredding, and mechanical and physical separation processes followed by the utilization of constituent metals. Spent LIBs consist of cathode, anode, separator, and metal casing. After collection, the spent batteries are manually segregated, and discharged in brine to avoid fire hazards and explosion risk during shredding. After discharging, the spent LIBs are dried in air or in a hot air oven. The physical dismantling process is followed by shredding, air classifier to remove plastic separator, sieving, magnetic separation, froth

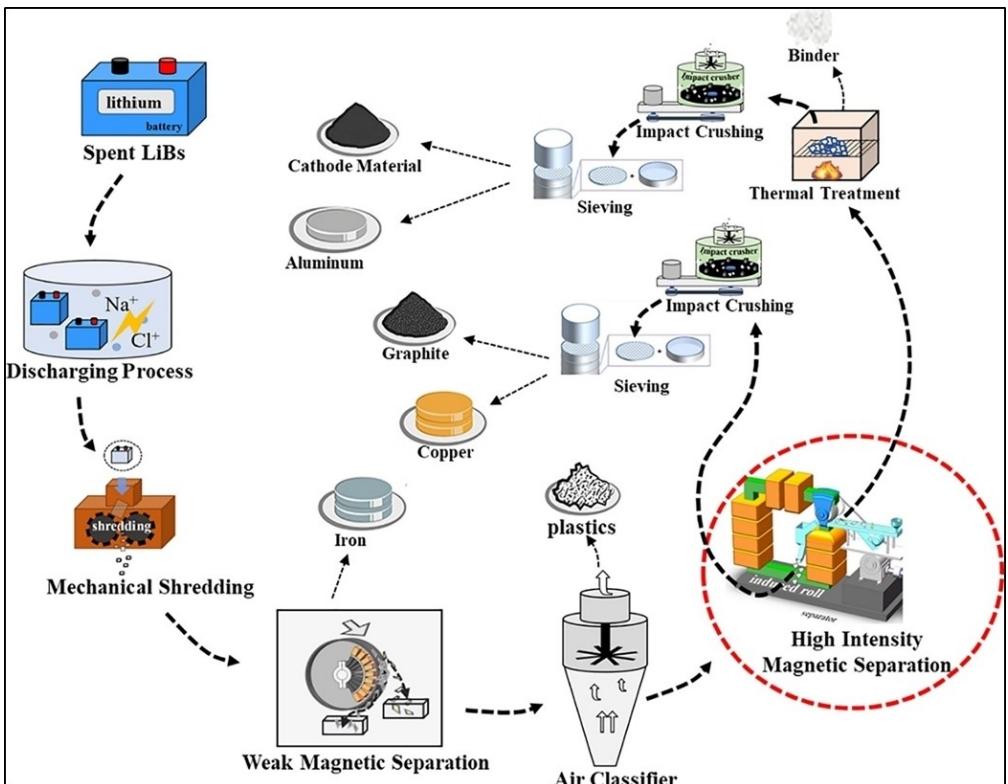


Figure 3. General pre-treatment strategies of spent LIBs. Reproduced with permission from Reference^[18] Copyright 2022, Elsevier.

floatation or their combinations. Pyrolysis is often necessary for the removal of toxic organic binder to obtain the black mass powder, to avoid any interference from the organic binders in the metal recovery processes.^[16] Pyrolysis is often followed by mechanical crushing and sieving to separate black mass and aluminium foil.^[17,18] Pre-treatment steps are important, as these steps often affect the quality of the recovered cathode black mass, which can alter the efficiencies of the metal recovery processes. Various recycling methods are reported in the literature, which discuss the recovery of metals from spent LIBs, but they are often detrimental to the environment.^[19]

The current mainstream industrial LIB-recycling processes can be subdivided into i) pyrometallurgy, ii) hydrometallurgy, iii) bio-hydrometallurgy and iv) direct recycling. Pyrometallurgical or thermal processing methods offer several advantages in a recycling system, including increased scalability and reduced reliance on chemicals. The primary approach to battery recycling using thermal treatment involves adding reducing agents to spent battery materials, which directly produces alloys and metal oxides.^[20] The hydrometallurgical process has been the subject of extensive research due to its ability to effectively leach desired metals from the spent LIBs with high selectivity and sensitivity.^[21] However, the use of corrosive acids and the complex nature of the operating procedure have hindered its extensive application.^[22] Each of these recycling processes has their own merits and demerits, including the requirement of very high temperature ($> 1000^{\circ}\text{C}$), emission of hazardous gases, complex treatment steps with the use of corrosive acids, reducing agents to dissolve battery materials, that are environmentally damaging. In view of this, extensive research efforts have been devoted towards finding suitable alternatives to the above processes, or to make them more environment friendly. Chemical-free leaching approaches employing ultrasonication, plasma-treatment approaches, etc. have also been explored as alternatives to conventional metal recovery routes.^[23-25] Recent reports discuss the direct use of materials from spent LIBs to design new cathode materials for sodium-ion batteries.^[26] Bioleaching or bio-hydrometallurgy is one such eco-friendly alternative to pyro- and hydro-metallurgy that employs naturally existing microbes as biocatalysts to produce organic or inorganic acids through their metabolic pathways.^[1,27] Microbial growth requires specific nutrients in desired dosages in order to produce specific metabolites essential to dissolve the metals from spent LIBs. However, high pulp density is often associated with decreased efficiency owing to a highly viscous solution that might result in reduced air penetration through it. Generation of solid residue, which can lead to influent or sludge, further reduces the applicability of the process.^[28] Bioleaching has been the subject of several excellent review articles^[29] and is not discussed here.

Aside from bioleaching, other studies have explored the use of weak organic acids including citric acid, tartaric acid and so on to replace strong mineral acids during leaching. However, these weak acids require the assistance of hydrogen peroxide (H_2O_2) as a reducing agent (0.5 to 15 vol %) in order to facilitate the extraction of $> 95\%$ of the metals from spent LIB mixtures. However, there are concerns owing to the chemical instability

and explosive nature of H_2O_2 , which has provided further impetus in the quest for greener alternatives to H_2O_2 in hydrometallurgical processes. Though reductants including sodium bisulfite (NaHSO_3) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) have been employed as reductants with some success,^[40] their utility have been limited owing to the requirement of additional product purification steps as a consequence of the introduction of Na^+ ions in the lixiviant solutions. The development of a concise, efficient, and eco-friendly method for direct cathode recycling under mild processing conditions is a promising improvement that requires further attention. However, concerns regarding the contamination of organic and metallic impurities, such as PVDF binder and Al particles, resulting from physical or chemical separation, pose a challenge to achieving optimal electrochemical performance.^[30]

Figure 4 shows the techno-economic and life-cycle analysis of pyrometallurgical, hydrometallurgical, and direct (biomass reduction) recycling methods. The energy consumption, costs, revenues and greenhouse gas (GHG) emissions are evaluated with hydrometallurgy as the benchmark, given its prevalence in the battery recycling industry.^[31] The cumulative effects of all these concerns have resulted in the search for alternative, bio-friendly reducing agents, especially from the large amount of biomass-waste that are available with us. This review provides a comprehensive account of the applicability of various sources of biomass for the recycling of metals from spent LIBs from a "Waste-for-Waste-to-Resources" perspective. We have also discussed a few examples where the 'black mass' obtained from spent LIBs can be used as sustainable catalysts for the valorization of lignocellulosic biomass to chemicals and fuel additives.

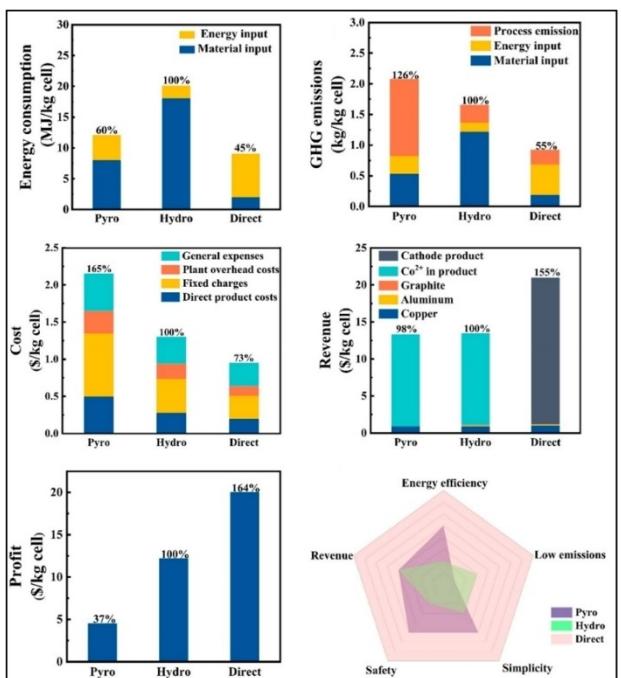


Figure 4. Impact assessment of pyrometallurgical, hydrometallurgical and direct recycling processes. Reproduced with permission from Reference^[31]. Copyright 2022, American Chemical Society.

2. Utilization of Biomass for Recycling Spent LIBs

Biomass i.e. lignocellulosic biomass is a sustainable source of chemicals, where the energy derived from photosynthesis is stored in the form of chemical bonds.^[32,33] The major components of lignocellulosic biomass are cellulose (40–50%), hemicellulose (15–30%) and lignin (15–35%) (Figure 5).^[34] Biomass waste including crop residues, especially food waste has increased rapidly in recent decades. The EU estimates an annual food wastage of ~123 Kg/person, ~60% of which is waste biomass from fruits and vegetables.^[35] Majority of the generated food waste are either incinerated or dumped in landfills, and pollute the environment. Considering the presence of reactive flavonoids, phenols etc in these lignocellulosic biomass waste, efforts are being undertaken to utilize these under-utilized waste biomass for inexpensive, sustainable recovery of critical metals from spent LIBs. Lignocellulosic biomass, especially cellulosic and hemicellulosic components are reported to be crucial for the extraction of metals from spent LIBs.^[36] Green reductants including reducing sugars like glucose, waste tea leaves, fruit peels etc., derived from waste food biomass are effective in the selective removal of metals from spent LIBs.^[37,38] Natural reductants present in waste biomass are a safer, cost-effective alternative to H₂O₂ for the sustainable recovery of critical metals from spent LIBs, providing a pathway for the better management of both spent LIBs and waste biomass in a “killing two birds with one stone strategy”.

Pre-treatment steps are necessary before the waste biomass including food waste can be utilized in the recovery of metals from LIBs, as it enables the collapse of recalcitrant lignocellulosic structure to release reductants useful for battery recycling process. Various strategies including physical, chemical and biological have evolved in the course of the past few years to pre-treat waste biomass. Physical pre-treatments (eg. grinding, ball milling, ultrasonication etc) help in reducing the size of the food waste, increases its effective surface area and consequently, enhances reactivity. Chemical and biochemical treatments help in depolymerisation of the biomass, reduces their crystallinity and pre-activates the biomass waste by generating reducing agents. Acids and alkalis are commonly used for depolymerisation and activation of waste biomass, though

these steps often require high temperature and pressure conditions. Recently, ionic liquids (ILs) have shown promise as relatively milder pre-treatment methods compared to the use of acids and alkalis, albeit at a higher cost.^[39] Biological pre-treatment strategies are the most benign, considering the requirement of lower temperature/pressure and less chemical usage. However, low process efficiency limit their practical utility.

In the subsequent sections, we have grouped the utilization of waste biomass based on the strategies employed for the recovery of metals from the spent LIBs.

3. Approaches for the Recovery of Metals from Spent LIBs using Waste Biomass

Waste biomass has been employed for both hydrometallurgical processes, as lixiviant and/or reducing agent, and cathode materials from spent LIBs have been co-pyrolyzed with biomass waste to selectively and sustainably recover metals from spent LIBs. In addition, biomass-based materials were found useful as adsorbent during the recovery of metals from spent LIBs. We will be elaborating the utilization of waste biomass for the processing of spent LIBs in the subsequent sections.

3.1. Hydrometallurgy

3.1.1. Biomass as Leaching Agent

Chen et al.^[40] discussed the synthesis of “natural biomass soup” (NBS) from reed waste as a promising natural alternative to ILs and deep eutectic solvents, and its utilization as green lixivients to recover metals from spent LIBs without requiring any prior treatment with acid or reducing agents. Leaching efficiency was contingent on several factors including time temperature, mass of spent battery materials and NBS, and so on. NBS efficiently leached ~35.1% of Li and 8.0% of Co at 120 °C in 24 h. Leaching efficiency for Li was reported to be higher compared to cobalt in all types of batteries in the order NCM > LCO > LFP, while the Co leaching efficiency varies in the order LCO > NCM.^[40] It was observed that Li in NCM has better leaching efficiency while the

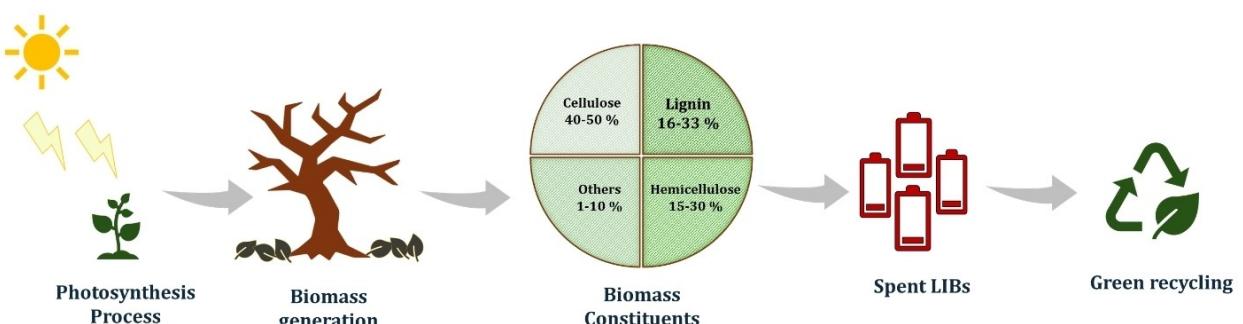


Figure 5. Overall recycling of spent LIBs from Biomass.

leaching of Co from LCO is higher using NBSs. Pant et al.^[41] tested Citrus fruit juice (CJ) from commonly known galgal or Hill lemon to remove the binder from cathode and anode and facilitate metal leaching, thereby precluding the use of toxic solvents including dimethylformamide, dimethylsulfoxide and so on, with a pulp density of 50 g/L at 90 °C for 20 min. After removing Cu and Al, the remaining solution was refluxed for 30 min and filtered to eliminate carbon and other impurities. The efficiency of metal leaching with CJ is ~100% of Li, 99% of Mn, 98% of Ni and 94% of Co. CJ consist of a mixture of various complexing agents such as citric and malic acids along with ascorbic acid and flavonoids, which act as reducing agents to reduce the heavy metal ions present in the black mass. The pH of the leachate was found to be 5.9 for the citrus juice, while it is 2.4 and 1.9 for individual citric and malic acids respectively. The presence of counter ions like Ca^{2+} , Na^+ , and K^+ , further improve the leaching efficiency of the organic acids present in CJ and prevents the formation of metal hydroxides (Figure 6). Selective precipitation of individual metals from the leached liquor was achieved using oxalic acid, followed by Na_2CO_3 .^[41] A similar lemon juice-assisted ultrasound method was reported by Esmaeili et al. who achieved a leaching efficiency of 100% of Li, 96% of Co and 96% of Ni in 35 min with an optimised condition of 57.8% (v/v) lemon juice, 8.07% (v/v) H_2O_2 and 0.98% (w/v) S/L ratio.^[42] The lemon juice was purified prior to utilization as leaching agent, and HPLC data suggested the presence of 90 mg/g of citric acid, 0.86 mg/g of malic acid and 1.24 mg/g of ascorbic acid, respectively. Ultrasound, utilizing the explosion of microbubbles to generate high-speed liquid jets, significantly impacts solid surfaces in hydrometallurgy and expedite leaching with low energy consumption.^[43]

Citrus fruit juice rich in citric acid and malic acid has been utilized as leaching agents to recover Li and FePO_4 from LiFePO_4 batteries along with associated metals like Al and Cu. Among the several juices explored by Kumar et al. including lemon, orange and apple juice, lemon juice proved to be the most effective as a lixiviant, owing to its suitable pH. The authors reported high leaching efficiency for Li (94.83%) and Cu (96.92%), while a moderate leaching efficiency of 47.24% was observed for Al. The system proved less effective for leaching Fe (4.05%) and P (0.84%) and FePO_4 remained as residue.^[44]

3.1.2. Biomass as Reducing Agent in Hydrometallurgical Process

Employing biomass as a reducing agent not only enhances the reaction efficiency, it also moderates the recovery cost and helps to mitigate an increase in the overall atmospheric CO_2 levels.^[45] Although, hydrometallurgy is a sustainable approach for leaching metals from spent LIBs, however the use of explosive reducing agents including H_2O_2 is a concern. Biomass-assisted hydrometallurgical processes offer a better alternative in a "waste-for-waste" approach. Some examples of biomass-assisted hydrometallurgical approaches are mentioned in Table 2.

Zhuoran et al. used orange peel waste (OP) as green reducing agent to recover metals in presence of citric acid as lixiviant.^[46] The reductive potential of OP is ascribed to the thermal conversion of cellulose into reducing sugars and the availability of natural antioxidants like flavonoids and phenolic acids, which were further validated by 3,5-dinitrosalicylic acid and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid assays. The addition of OP significantly enhanced the leaching ability of the citric acid lixiviant, achieving 100% extraction of Co and Li from pure LCO samples. Presence of OP resulted in ~80–99% recovery efficacy for Ni, Mn, Co and Li from spent NCM batteries.^[46] Cobalt was recovered as Co(OH)_2 , with minimal impurities of Al (6.76%) and Cu (1.42%). The recovered cobalt was subsequently combined with lithium carbonate in a 1:1.1 atomic ratio followed by thermal treatment at 850 °C for 5 hours. This material was used to fabricate new LiCoO_2 coin cells in a 'close the waste loop approach', which showed initial galvanostatic charge value of 120 and discharge value ~103 mAh g^{-1} respectively, which are comparable to commercial LCO cells (Figure 7a). X. Chen et al. reported a comparative analysis of three leaching systems i.e. tea waste (TW), *Phytolacca americana* (PA), and H_2O_2 as reducing agents for recycling LCO batteries using citric acid as the lixiviant. The results indicated that the metal recovery observed for citric acid/TW and citric acid/ H_2O_2 systems were comparable, with a leaching efficiency of 96–98% for Co and 98–99% for Li. In contrast, citric acid/PA resulted in inferior leaching of 83% for Co and 96% for Li, in a marked reduction in the leaching efficiency of cobalt.^[47] The reducing abilities of PA and TW arise from their high content of cellulose/hemicellulose and reducing substances, respectively. PA degrades into D-glucose, fructose, and other compounds under acidic conditions, which serve as

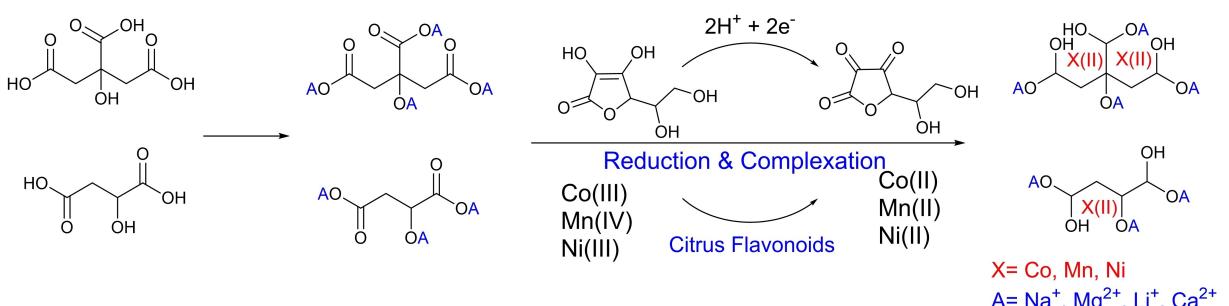


Figure 6. In situ reduction of metals using citrus juice.^[41]

Table 2. Biomass assisted hydrometallurgical process for recovery of metals from spent LIBs.

Acid as leachate	Biomass as reducing agent	Reaction conditions	Leaching efficiency	Ref.
Citric acid	Orange peel (OP)	1.5 M citric acid, 200 mg OP, 25 g/LS/L ratio, 100 °C, 4 h	Li 80%, Co 91%, Mn 92% and Ni 90%	[46]
Citric acid	Tea Waste (TW)	1.5 M citric acid, 0.4 g/g TW, 30 g/LS/L ratio, 90 °C, 2 h	Li 98% and Co 96%	[47]
Citric acid	Phytolacca Americana	1.5 M citric acid, 0.4 g/g PA, 40 g/LS/L ratio, 80 °C, 2 h	Li 96% and Co 83%	[47]
Sulfuric acid	Tea waste (TW)	2 M H ₂ SO ₄ , 0.3 g/g TW, 50 g/LS/L ratio, 90 °C, 1.5 h	Li 93%, Co 67%, Mn 91% and Ni 91%	[48]
Malic acid	Grapes seed	1.5 M malic acid, 0.6 g/g biomass, 20 g/LS/L ratio, 80 °C, 3 h	99% Li and 92% Co	[49]
Acetic acid and ascorbic acid	Bagasse pith	0.5 M & 0.2 M acetic acid & ascorbic acid, 0.3 g/g bagasse pith, 20 g/LS/L ratio, 50 °C, ultrasound 450 W, 40 min	Li 99%, Co 98%, Mn 96% and Ni 97%	[50]
Sulfuric acid	Tea waste (TW)	1.25 M H ₂ SO ₄ , 50 g/LTW, 20:1 L/S ratio, 60 °C, 1 h	Li 99%, Co 99%, Mn 98% and Ni 98%	[51]
Methanesulfonic acid	Molasses	2 M methanesulfonic acid, 0.4 g/g molasses, 2.5 g/50 ml S/L ratio, 90 °C, 1 h	Li 98%, Co 88%, Mn 85% and Ni 88%	[52]
Methanesulfonic acid	Molasses	2 M methanesulfonic acid, 0.4 g/g molasses, 50 g/LS/L ratio, 90 °C, 1 h	Li 99%, Co 98%, Mn 99% and Ni 98%	[53]
Sulfuric acid	Ginkgo Biloba (GKB)	1.8 M H ₂ SO ₄ , 9 g/L GKB, 15 g/L S/L ratio, 40 °C, 40 min	Li 99%, Co 98%, Mn 98.2% and Ni 98.6%	[54]
Acetic acid	Molasses	2 M acetic acid, 75% w/v Molasses, 100 g/LS/L ratio, 90 °C, 30 min	Li 99%, Co 99%, Mn 96.4% and Ni 99.3%	[55]
Sulfuric acid	Glucose/Sucrose/cellulose	3 M H ₂ SO ₄ , 0.4 g/g glucose/sucrose/cellulose, 25 g/L S/L ratio, 95 °C, 2 h	Li 100% and Co 96%/Li 100% and Co 96%/Li 100% and Co 54%	[56]
Phosphoric acid	Glucose	1.5 M phosphoric acid, 0.02 mol/L glucose, 80 °C, 2 h	Li 100% and Co 98%	[57]
Citric acid	Grapes skin (GS)	0.15 M citric acid, 0.3 g _{GS} /g _{LCO} GS, 30 g/L S/L, mechanochemical, 400 rpm, 1 h	Li 99% and Co 98%	[58]
Citric acid	Litchi peel powder (LPP)	0.2 M citric acid, 0.15 g LPP, 25 g/L S/L, co-ball-milling, 400 rpm, 90 °C, 1.5 h	Li 99%, Co 96%, Mn 98% and Ni 95%	[59]
Sulfuric acid	Waste areca powder (WAP)	3 M H ₂ SO ₄ , 1:1 dosage of WAP:NCM, 20 ml/g L/S ratio, 90 °C, 120 min	Li 99%, Co 99%, Mn 99% and Ni 99%	[60]

potential reductants and are eventually oxidized into eco-friendly organic compounds. Similarly, TW contains high concentrations of polyphenols and four catechins: epicatechin gallate (ECG), epicatechin (EC), epigallocatechin (EGC) and epigallocatechin gallate (EGCG) which enhance leaching efficiency (Figure 7b). FTIR analysis of tea waste before and after leaching revealed a reduction in the –OH peak intensity, alongside an intensification of the C=C peak. This indicates the conversion of polyhydric groups to oxidized products, such as aldehyde and carboxylic acid groups. Addition of phosphoric acid and oxalic acid resulted in the precipitation of ~93% Li and 98% Co respectively. The recovered Li₃PO₄ and CoC₂O₄ had a purity of over 98%, and the citric acid was reusable up to five cycles with almost similar leaching efficiency as fresh acid, confirmed by circulatory leaching experiments.^[47] In another study, Y. Chen et al. demonstrated the dissolution of NCM cathode using green reductant TW, leaching agent H₂SO₄ and reported a leaching efficiency of ~90% Li, Mn, Ni and 67% of Co at 90 °C.^[48] Gu et al. also studied TW as reductant for the leaching and subsequent recovery of metals from NCM type spent LIBs (Figure 7c). The authors optimized the use of 1.25 M H₂SO₄ with 50 g/L TW at a pulp density 20:1 (L/S ratio) at 60 °C

for 1 h for effective leaching of 98% of Li, Co, Mn and Ni aided by the Box–Behnken experimental design.^[51] A co-precipitation method was employed to recover the metal precursors from the leachate and fabricating NCM batteries, closing the waste loop. The regenerated cathode material showed uniform elemental distribution, good crystallinity, and was devoid of any agglomeration or impurities. The specific discharge capacity remained stable at 150.4 mAh g⁻¹ with a Coulombic efficiency of 93.75% even after 100 cycles. The authors conducted a thorough investigation on the oxidation mechanism of tea leaves waste, revealing that catechins present in TW are the active reducing species capable of reducing the metals present in spent black mass, while TW is oxidized to contiguous quinonoid structures generating gallic acid derivatives. At higher temperatures, the decomposition of cellulose present in TW aids in its reducing ability.

Zhang et al. investigated a green, low-cost route to dissolve metals present in spent LCO batteries, followed by their recovery using grapes seed waste as reductant.^[49] The authors pre-treated the spent LIB waste using 6% NaOH as precipitating agent for Al to separate Al foil from cathode material. Treatment of 1.0 g NaOH-treated cathode material with 0.6 g grapes

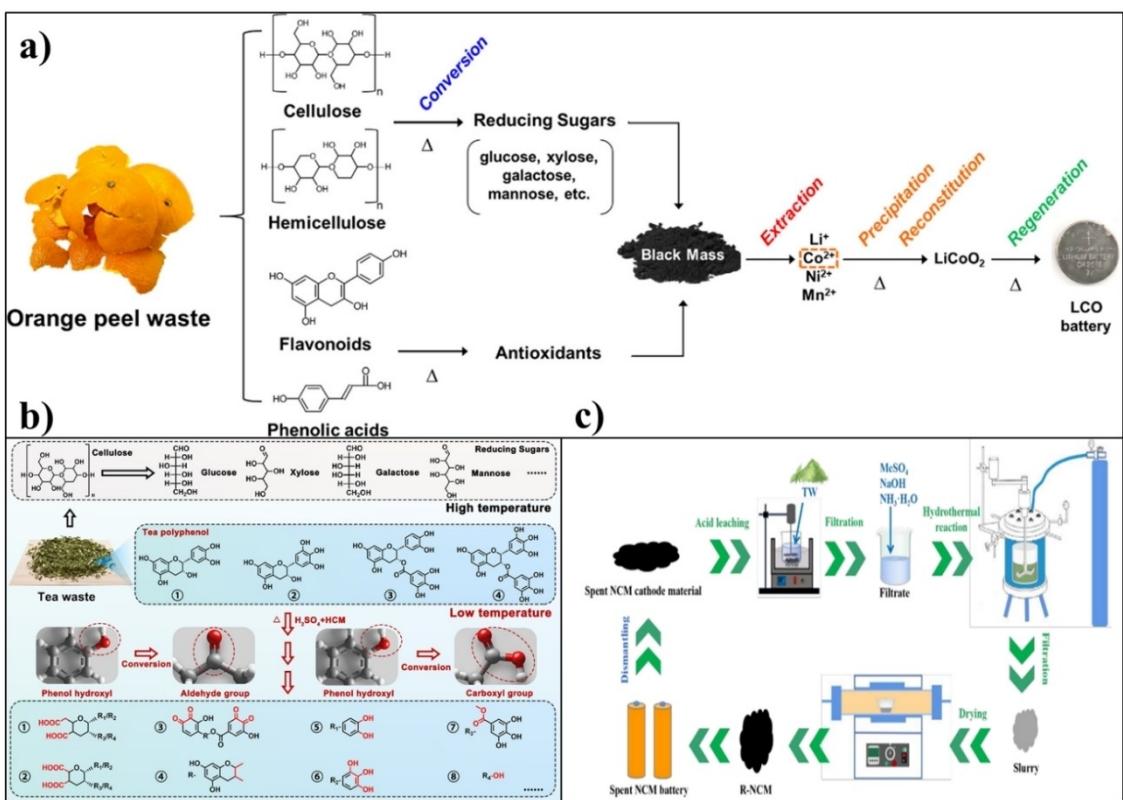


Figure 7. (a) Recycling of spent LIBs using orange peel waste. Reproduced with permission from Reference^[46] Copyright 2020, American Chemical Society. (b) Possible TW oxidation pathways and (c) Recycling procedure from TW. Reproduced with permission from Reference^[51] Copyright 2023, American Chemical Society.

seed as reductant with 1.5 M malic acid at 80 °C for 3 h with a pulp density of 20 g/L, resulted in a leaching efficiency of 99% of Li and 92% of Co. The presence of high content of polyphenols such as catechin, EC, epigallocatechin EGC, gallic acid, oligoprocyanidins enhances reducing ability of grapes seed. The superior leaching efficiency of grapes seed wastes originated due to surface chemical reactions and diffusion of reactive ions with an activation energy of ~11.96 kJ mol⁻¹, as estimated from kinetics studies. However, the recovery and reuse of grape seed waste and malic acid remained unexplored in this study. Interestingly, S. Zhang et al. proposed the recovery of metals from the cathode of spent LIBs by a single-step mechanochemical approach using grapes skin (GS) waste as reductant.^[58] The beneficial aspects of mechanochemical method in improving the leaching efficiency, including reduction of the particle size of LCO battery material (from 12.126 μm to 0.0928 μm), ~130 fold increase in the specific surface area, enhanced hydrophilicity, promoting mesoporosity, disrupting the crystal structure and so on, were also elaborated in this study. The GS waste consisting glucose, fructose, cellulose, hemicellulose along with phenolic substance such as resveratrol and proanthocyanidins exhibited antioxidant properties to promote the leaching of high valent metals from LCO. Synergism between citric acid and mechanochemical activation promotes the release of active ingredients from GS waste. The 0.15 M citric acid added as lixivient with GS waste successfully leached out ~99% of Li and 98.8% of Co at 30 g/L solid-to-

liquid ratio. Cobalt was precipitated out as cobalt oxalate from the leached liquor followed by the removal of Li as Li₂CO₃ after adjusting the pH to 14. In another report, litchi peel waste powder (LPP) containing similar types of reducing agent as in grapes seed waste and grape skin, was investigated for leaching critical metals from spent LIBs by J. Chen et. al.^[59] About 99 wt% Li, 96.5 wt% Co, 98 wt% Mn and 95 wt% Ni were reported to leach out using 0.15 g LPP, 0.2 M citric acid, 25 g/L pulp density at 90 °C in 1.5 h by ball milling. The authors report a pre-mixing step where they co-ball milled LPP and cathode material in presence of water followed by leaching experiments. The authors state that the pre-mixing process reduces particle agglomeration, increases dispersion, and ensures close contact between LPP and cathode material, which in turn increases the activation energy of the reaction to facilitate leaching.

Zhu et al. report the utilization of ginkgo biloba (GKB) as green reductant for the leaching of metals from spent NCM-type LIBs, along with a systematic exploration of the process kinetics. The leaching efficacy of Li, Co, Mn and Ni was reported to be 99%, 98%, 98% and 98% respectively under optimised condition employing a concoction of 1.8 M H₂SO₄, 9 g/L GKB, pulp density of 15 g/L at 80 °C for 40 min. The authors calculated the activation energies required for each individual metal leaching, and specified the role of surface chemical reactions in facilitating metal leaching from spent LIBs.^[54] The leached solution was treated with acetate salts of Ni, Co and Mn to adjust the metal ratio to 6:2:2, followed by filtration.

$\text{LiOH}\cdot\text{H}_2\text{O}$ was added to the resultant precursor solution in 1:1.03 molar ratio, preheated to 450°C for 5 h, followed by calcination at 850°C for 12 h to obtain regenerated NCM type battery material ($\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$). The regenerated cathode material shows initial discharge capacity 159.9 mAh g^{-1} , stable Coulombic efficiency ~98% with a capacity retention rate of 92.58% after 50 cycles, demonstrating its excellent electrochemical performance. Su et al. reported the leaching of valuable metals from the black mass of spent NCM batteries using waste areca powder (WAP) as reducing agent and sulfuric acid as lixiviant.^[60] Authors report ~99.9% leaching efficiency for Li, Co, Mn and Ni under optimised condition of 3 M sulfuric acid, 1:1 mixture of WAP/NCM, liquid-to-solid ratio 20 ml/g at 90°C and a leaching time of 2 hr. The shrinking core model revealed that the leaching procedure is restricted by chemical reactions with an activation energy $>40 \text{ kJ mol}^{-1}$, while the reducing ability of WAP was reported to emerge from the presence of reducing sugars. Co, Mn and Ni were precipitated and recovered from the leachate as nickel cobalt manganese oxalate. In order to ascertain the environmental impact of the residue after leaching, the toxicity of the material was examined. The waste residue was carbonized to obtain anode materials having good recyclable performance. The recycled anode displayed a Coulombic efficiency of 92% and the reversible charge-discharge capacity of the battery remained stable at $\sim 240 \text{ mAh g}^{-1}$ during 200 cycles at 0.2 C, though there was a reduction in the reversible capacity to $\sim 160 \text{ mAh g}^{-1}$ at a higher current of 2 C.^[60]

Abundantly available sugarcane bagasse pith, a waste material produced from sugar manufacturing industries is often used in paper mills, and as a boiler fuel, but its use is limited

due to its high moisture content and low calorific values with significant environmental concerns due to CO_2 production.^[61] Yan et al.^[50] reported an alternative use of waste bagasse pith as reducing agent in a binary mixture of acetic acid and ascorbic acid for efficient dissolution of spent NCM batteries through ultrasonication (Figure 8a). The leaching efficiency of metals is ~96% under optimized condition. i.e., 0.5 M acetic acid, 0.2 M ascorbic acid, bagasse pith 0.3 g/g of spent cathode powder, pulp density 20 g/L at 50°C for 40 min and 450 W power of ultra-sonicator. In this process, ascorbic acid reacts with bagasse under acidic conditions, degrading cellulose, hemicellulose, and lignin in the bagasse pith into small molecules like glucose, furfural and other degradable redox-active products that help in the reduction of Co^{3+} and Mn^{4+} to Co^{2+} and Mn^{2+} respectively. Co, Ni and Mn were recovered as mixed metal oxalate using oxalic acid as precipitating agent and Li was recovered as Li_3PO_4 . The synergism between mixed acids helps in reducing the overall acid concentration in the process, and improves the process sustainability. Meng et al. recovered around 100% of Li and 98% of Co using 1.5 M phosphoric acid and 0.02 mol L⁻¹ glucose instead of the conventionally used H_2O_2 as reducing agent at 80°C for 2 h. The authors report the oxidation of glucose to monocarboxylic acid concomitant to the reduction of Co^{3+} to Co^{2+} .^[57] X. Chen et al. explored the use of glucose, sucrose and cellulose as reductant with sulphuric acid as leaching agent, and achieved a maximum recovery of 96–100% of Li and 96–98% of cobalt under optimised condition 3 M sulfuric acid, 0.4 g/g glucose or sucrose, solid:liquid ratio 25 g/L at 95°C for 2 h.^[56] However, in case of cellulose, the metal recovery process was less efficient as only ~54% Co was dissolved in the cellulose/ H_2SO_4 leaching

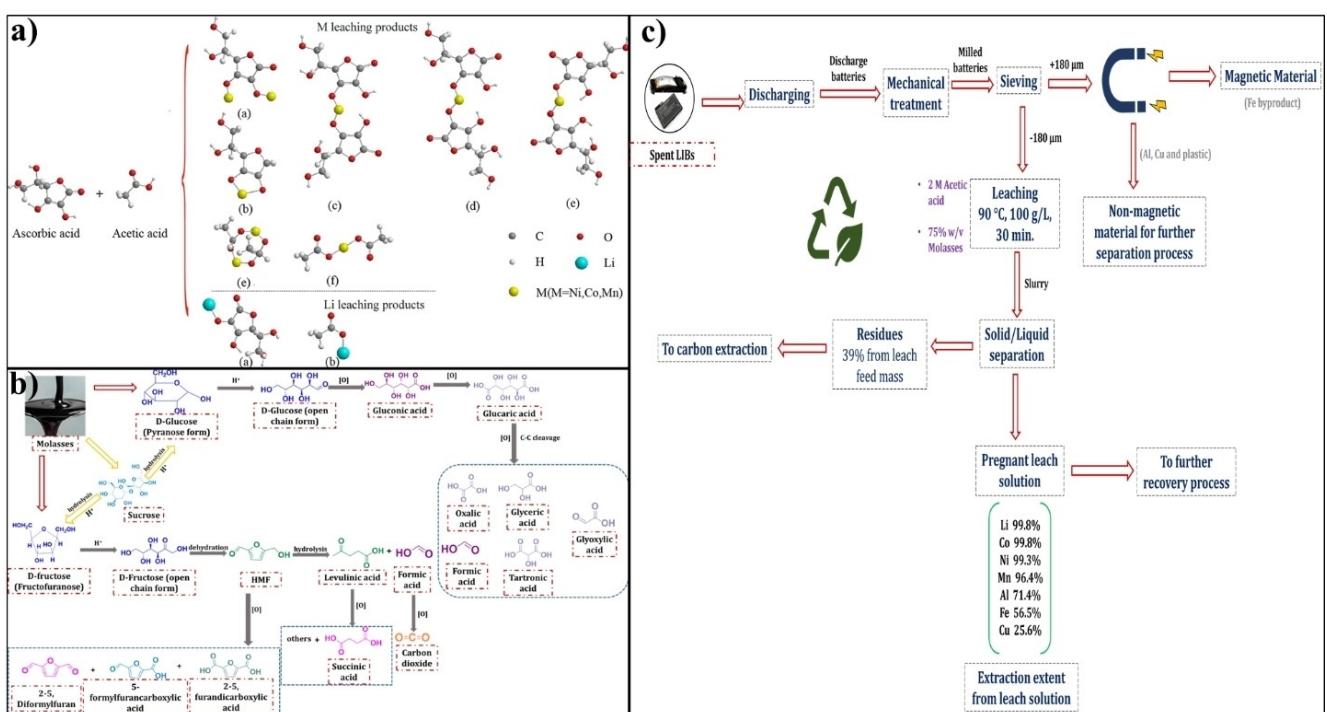


Figure 8. (a) Possible leaching mechanism. Reproduced with permission from Reference^[50]. Copyright 2020, Elsevier. (b) Plausible pathway of molasses oxidation during the reductive leaching of metals from spent LIBs.^[52] (c) Flow chart of recovery of metals from black mass using molasses.^[55]

solution. The authors inferred that cellulose requires further degradation to organics prior to use as reductant, while glucose and sucrose can be used directly.^[56] Figure 8c show a 96% leaching efficiency of metals from black mass using 2 M acetic acid and 10 mL of 75% w/v molasses as the reductant, with a high pulp density of 100 g/L at 90 °C for 30 minutes. However, 3 M acetic acid alone as the lixiviant, results in only 20–30% metal leaching. When molasses is used as a reductant with acetic acid, there is a 60–70% increase in leaching efficiency.^[55] Okonkwo et al.^[52,53] reported a comparative analysis of sugar-based reductants such as molasses, glucose, fructose and sucrose, using methanesulfonic acid as the lixiviant, without any significant changes in metal leaching efficiency. The possible pathway of molasses and sugar as reductant is shown in Figure 8b. Non-sugar organic compounds (impurities) in molasses did not hamper the reducing ability of these sugar-based molecules. On the contrary, they might have acted as performance enhancers, particularly at lower temperatures.

3.2. Co-pyrolysis of Spent LIBs with Waste Biomass

In recent years, reductive roasting methods such as gas-thermal,^[70] carbothermal,^[71] and biomass-based thermal reduction^[72] have garnered significant attention. These techniques are valued for their ability to reduce cathode materials at relatively low temperatures, thereby enabling the efficient separation of lithium and other valuable metals. However, most of these processes are energy demanding and release a significant amount of CO₂. Researchers are actively seeking mild, environmentally benign reductants in order to improve the process economics and reduce the environmental footprint of these processes. Biomass is a highly promising option for reductive roasting due to its cost-effectiveness, availability, renewability and carbon neutrality. Aside from the use of waste biomass as lixivient and reducing agents in hydrometallurgical processes for the dissolution and recovery of critical metals from spent LIBs (discussed in previous sections), waste biomass has also been employed in co-pyrolysis with spent LIBs for pyrometallurgical processes of metal recovery. Using waste

biomass as a reducing agent boosts reaction efficiency, lowers recovery costs, and prevents additional CO₂ emissions.

Commonly explored pyrolytic recycling of metals using biomass as reducing agent recovered Li as Li₂CO₃ in water followed by the isolation of other metals as low valent oxides or pristine metals, as mentioned in Table 3. Zhou et al. studied the pyrolysis behaviour of various sources of biomass such as corn stalk, sawdust, rice husk, kraft paper, and corncob meal powder, revealing the relationship between biomass constituents (cellulose, hemicellulose, lignin, and sawdust) and pyrolysis gas compositions.^[38] Different compositions of pyrolysis gases are discussed for the reduction of LCO below 500 °C (Figure 9). Different stages of biomass pyrolysis i.e. dehydration, gas production and reduction was explored, with gas production efficiency much higher >250 °C in the order of cellulose > hemicelluloses > lignin. Figure 9b depicts that the increase in gas generation was attributed to the catalytic effect of transition metals in the waste biomass, which enhanced the gas output. The relevant equations for the production of hydrogen and other gases in presence of spent LIB materials are the following:



LCO reacted with CO, CH₄, and H₂ produced from the pyrolysis of biomass, consuming CO₂ to produce Li₂CO₃ and Co as CoO.^[38] Notably, cellulose, hemicellulose, and lignin achieve over 93% lithium recovery with 98% purity of Li₂CO₃, and five types of biomass (i.e. sawdust, corn stalk, corncob meal, rice husk, kraft paper powder) achieved a recovery of >93% of Li at 500 °C. Authors proved that biomass with cellulose and low lignin content tended to generate pyrolysis gas with a high volume of CO due to the breakdown of carboxyl, carbonyl, ether and ester linkages shown in Figure 10.

Table 3. Comparative analysis of waste biomass used for co-pyrolysis with spent LIBs.

Spent LIBs	Biomass as reducing agent	Pyrolysis condition	Biomass dosage	Products	Ref.
LCO	Various Lignocellulose biomass	500 °C for 1 h under Vacuum	1:1	Li ₂ CO ₃ & CoO	[38]
LCO	Bean dregs (BD)	600 °C for 20 min under Ar	12.5%	Li ₂ CO ₃ , CoO, NiO & MnO	[62]
NCM	Wood chips	500 °C for 120 min under Ar	1:1	Li ₂ CO ₃ , CoO, NiO & MnO	[63]
LCO	Pine sawdust (PS)	600 °C for 120 min under Vacuum	1:1	Li ₂ CO ₃ & Co/CoO	[31]
LCO	Urea	550 °C for 20 min under Ar	1:2	Li ₂ CO ₃ & CoO	[64]
NCM	Bean dregs (BDs)	700 °C for 40 min under Ar	1:0.3	Li ₂ CO ₃ , Co, Ni & MnO	[65]
NCM	macadamia nuts	750 °C for 25 min under Ar	24%	Li ₃ PO ₄	[66]
NCM	Crofton weed	800 °C for 30 min under N ₂	50%	Li ₂ CO ₃ , Co, Ni & MnO	[67]
NCM	Cornstalk	700 °C for 15 min under N ₂	1:0.3	Li ₂ CO ₃ , Co, Ni & MnO	[68]
NCM	Bidens pilosa	700 °C for 30 min under N ₂	50%	Li ₂ CO ₃ , Co, Ni & MnO	[69]

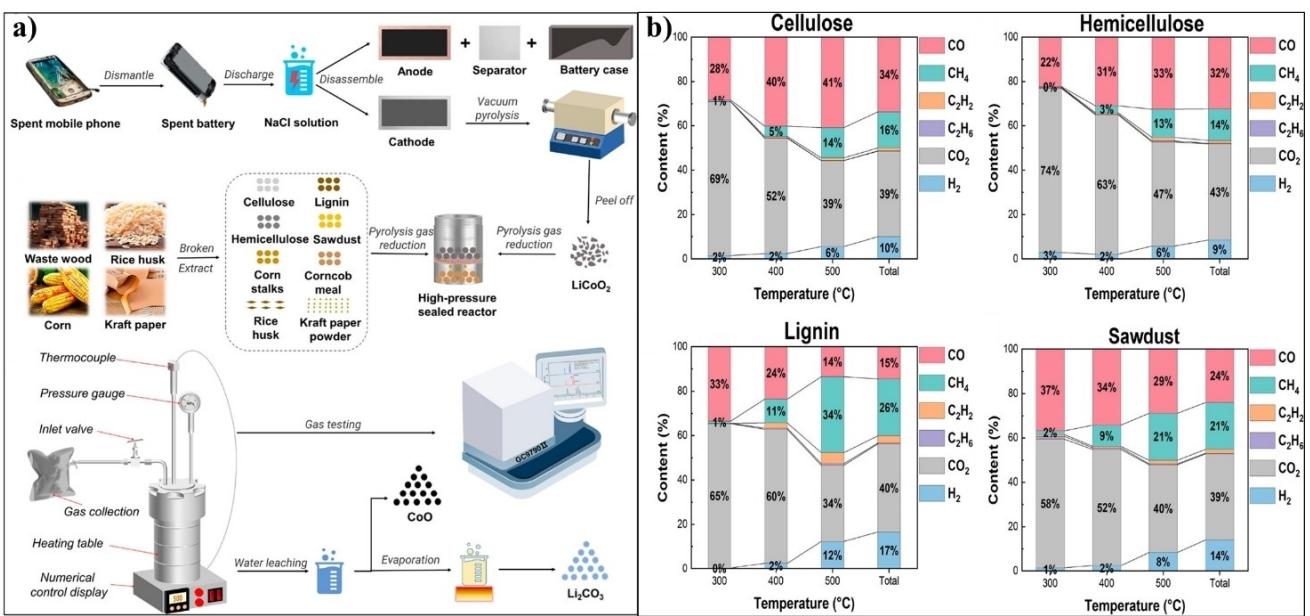


Figure 9. (a) Pyrolysis method for recovery of metals from spent LIBs. (b) Gases produced by cellulose, hemicellulose, lignin and sawdust. Reproduced with permission from Reference^[38] Copyright 2024, American Chemical Society.

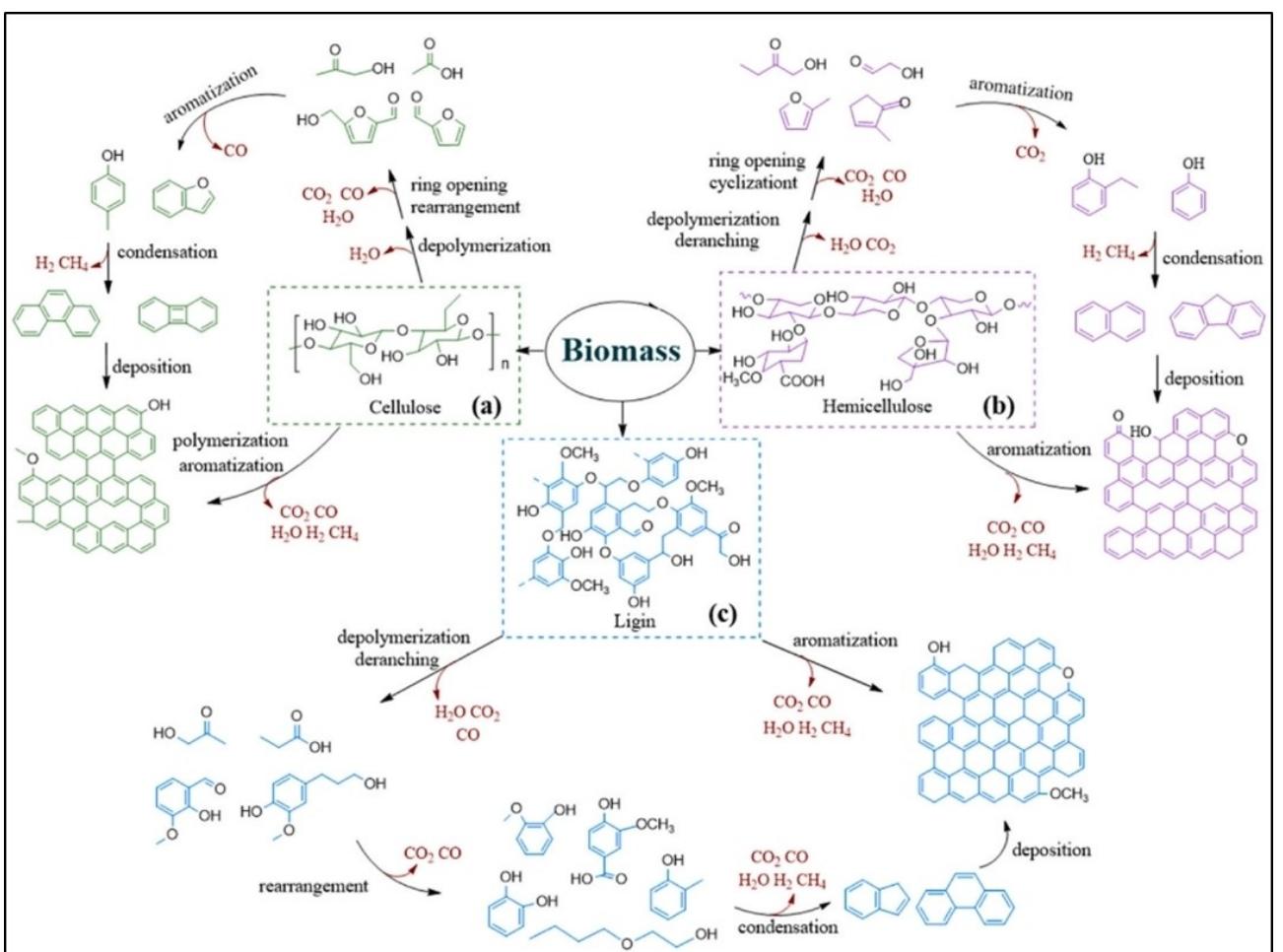
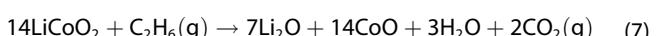


Figure 10. Biomass pyrolysis mechanism for: (a) cellulose; (b) hemicellulose; (c) lignin. Reproduced with permission from Reference^[67] Copyright 2023, Elsevier.

Zhou et al. additionally devised a win-win strategy for the recycling of metals from different cathode materials using wood chips as reducing agent at low temperature.^[63] Thermodynamics analysis confirmed the reduction of LCO with biomass-derived gases (presented in equations 5–8) and generated Li₂O reacted with CO₂ to form Li₂CO₃ (Equation 9). DFT calculations explained that the reduction of spent LIBs occurred due to the collapse of the oxygen skeleton of NCM material to form Li₂CO₃ and metal oxides, consequent to the thermochemical reaction during biomass pyrolysis which impacted the decomposition of NCM-type spent LIBs. By comparing the collapse mechanism of various lithium transition metal oxides, a collapse mechanism was proposed under the pyrolysis atmosphere that further validated the formation of Li₂CO₃ by combining Li–O with CO₂ and transition metal oxides from spent LIBs.^[63]



Lin^[65] and Lu^[67] groups optimized the process for reducing metals from spent NCM using bean dregs (BDs) and Crofton weed as the source of waste biomass respectively. Their process involved roasting at >700 °C, followed by leaching with carbonated water resulting in 93.7% recovery of Li as Li₂CO₃, metallic Ni, Co and MnO. Transition metals present in the spent cathode are reduced to lower valent oxides (Mn⁴⁺ to Mn²⁺ in MnO) or zero valent metals (Ni²⁺ to Ni⁰, Co³⁺ to Co⁰ via Co²⁺) after roasting, which was ascertained from XPS analysis (Figure 11). Another work by Lin et al. established that mechano-

chemical pre-treatment of BDs and spent NCM batteries prior to roasting resulted in a lower roasting temperature, shorter roasting time and a substantially reduced requirement of biomass (almost half) compared to the process without pre-activation.^[62]

Urea, a commonly used crop fertilizer was reported to be useful as a reductant for recycling of metals from LCO batteries. The generation of NH₃ by the thermal decomposition of urea helped in the reduction of LiCoO₂, yielding 99.96% Li as Li₂CO₃ in water leaching along with water insoluble metallic cobalt. The authors introduced a concept of 'oxygen elements removal' to justify the facile metal extraction from spent LCO based on the mechanism of O-cage digestion.^[64] Zhao et al. developed a microwave-assisted pyrolysis route to recover metals from spent cathode of NCM batteries utilizing macadamia nut shells as reducing agent.^[66] The authors reported the leaching of 93.4% of Li under their optimal working condition: 24% biomass, microwave-assisted pyrolysis temperature 500 °C, followed by roasting at 750 °C for 25 min. The authors disclose that the cathode powder starts to decompose around 300 °C, as evidenced from the disappearance of PXRD peaks compared to the spent NCM battery material. The discrepancy between the PXRD and TGA results (decomposition temperature 337 °C) was ascribed to thermal runaway triggered by "hot spots" and arcing during microwave irradiation. Biomass-derived H₂ and CO further enable the decomposition of NCM powder.^[66]

There is an urgent requirement for a cost-effective and closed-loop process for regeneration of fresh electrodes from spent LIBs. Zhuo et al. developed a '3 R' strategy for LCO employing Pine sawdust as reducing agent via vacuum pyrolysis at 600 °C for 120 min. Pine dust was introduced as a source for reducing gas and carbon to facilitate the metal recovery process to convert LiCoO₂ to Li₂CO₃ (~94% recovery) and Co/CoO (~97% recovery).^[31] The process benefitted from lower pyrolysis temperature owing to the synergy between reducing gases and carbon, as compared to carbothermic reactions commonly reported in the literature. The recovered

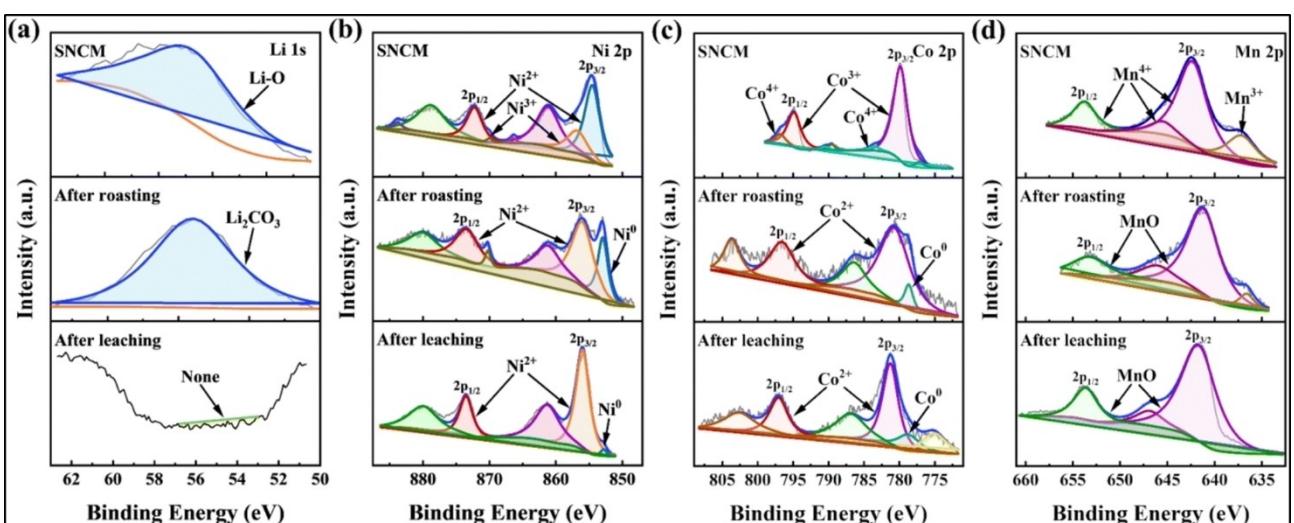


Figure 11. High-resolution XPS spectra of Spent NCM, roasted products and leaching residues. Reproduced with permission from Reference.^[65] Copyright 2022, Royal Society of Chemistry.

CoO was converted to Co_3O_4 by calcining at 750°C , which was subsequently used to regenerate LiCoO_2 via a solid phase reaction with Li_2CO_3 for 13 hrs at 950°C . A Li/Co ratio was fixed at 1.15:1 to offset the evaporation of Li_2CO_3 during the high-temperature process. Electrochemical performance of the regenerated LCO button cell for 130 cycles at 150 mAh g^{-1} showed a specific capacity of 160 mAh g^{-1} and a retention of ~95% of its initial capacity after 130 cycles.^[31] Recently, Yang et al. synthesized a high performance carbon anode material from spent NCM via bagasse pyrolysis and hydrometallurgical leaching.^[73] Bagasse as the reducing agent is reported to disrupt the layered structure of NCM-type cathode material, improve the leaching efficiency of Li^+ ions (~96.6%) and facilitating the formation of water soluble Li_2CO_3 . The carbon generated by the catalytic action of the metals from the NCM-type cathode material was effective as high-performance anode material with a high specific surface area ($242.85 \text{ m}^2/\text{g}$). The regenerated anode exhibits commendable cycling performance, retaining a capacity of 486.5 mAh g^{-1} even after 500 cycles at a 1 C.

In general, the financial inputs required in case of the biomass-based recovery of valuable metals and the environmental footprints are much less compared to the conventional recycling strategies. A comparative analysis of the different conventional recycling methods for spent LIBs, and the biomass-based recycling, in terms of efficiency, financial inputs associated, environmental impact etc has been presented in Table 4.

3.3. Biomass as Metals Adsorption Agent

The adsorption of heavy metals and their incorporation from waste materials is an active area of interest owing to the possibility of both physisorption and chemisorption of desired metals in various adsorbents including inorganic materials, polymeric materials, carbon based materials, biological adsorption and so on.^[74] The adsorption capacity of these materials varies depending on the specific surface area, presence of various functional groups and pore structure.^[75] The sustainable advancement in recovery of metals from spent LIBs has resulted

in the exploration of several purpose-tuned adsorbents, including biomass-derived materials, which are perhaps one of the best choices from the cost and environmental standpoint. Cunha et al.^[76] studied the adsorption of cobalt from spent LIBs with polysaccharide and fibrous material including chitin and rice husk which are abundantly available biomass waste. The screening of chitin and rice husk was accomplished with leached solution containing CoSO_4 and Li_2SO_4 with metal concentration of 98 mg/L and 12 mg/L respectively. The optimised condition for Co^{2+} recovery was $\text{pH}=6$, adsorbent: 10 g/L , volume of solution: 50 ml at 45°C for 4 h, which resulted in the recovery of 95% and 40% recovery of Co^{2+} with chitin and rice husk respectively. The higher adsorption capacity of chitin was attributed to the presence of N-acetyl groups, which interacted with Co^{2+} as confirmed from FTIR analysis. However, in case of rice husk there was no significant change in FTIR data, indicating a weak interaction between rice husk and Co^{2+} . Purnomo et al. recovered Li from spent NCM using coconut shell-derived activated carbon (AC). The authors utilized various physical and chemical activation processes to improve the surface area and pore volume of the AC including thermal activation.^[77] The highest surface area ($365 \text{ m}^2/\text{g}$ with $0.148 \text{ cm}^3/\text{g}$ total pore volume) was observed for AC after a physical activation at 800°C . Chemical activation with 10% KOH at 800°C under N_2 atmosphere resulted in a higher proportion of micropores. The authors tested the adsorption efficiency of the AC samples using a mixture of metal sulfate solutions, depicting low adsorption of Li in all cases. Chemically activated AC samples provided a better separation of Li, compared to physically activated sample, owing to the porosity generated by KOH activation that is more suited towards the adsorption of transition metals from the mixed liquor. Enrichment of Li in the filtrate was further facilitated by the faster elution through the column due to the lower atomic weight of Li compared to the transition metals which were retained in AC. The filtrate was treated with Na_2CO_3 for the ensuing precipitation of Li_2CO_3 .

In the previous sections, we have discussed the use of waste biomass to leach and recover valuable metals from spent LIBs. In the subsequent sections, we switch gears and discuss the application of spent LIBs as catalyst for the valorization of waste

Table 4. Comparative analysis of conventional and biomass-based recycling of spent LIBs.^[78]

	Metal recycling methods	Recycling efficiency	Temperature	Potential pollutant	Financial/chemical inputs
Conventional Method	Hydrometallurgy (without reductant)	76–99 %	50–100 °C	Organic/inorganic acid waste	Acid, reagents and energy
	Hydrometallurgy (with reductant)	99 %	40–70 °C	Organic/inorganic acid waste with corrosive H_2O_2	Acid, reductant, reagents and energy
	Pyrometallurgy	80–98 %	650–1700 °C	Volatile organic compounds	Carrier gas (N_2 or Ar) and energy
	Hydrometallurgy (without reductant)	35–99 %	90–120 °C	–	Energy
Biomass-based methods	Hydrometallurgy (with reductant)	80–99 %	40–100 °C	Organic/inorganic acid waste	Acid, reagents and energy
	Pyrometallurgy	90–99 %	500–800 °C	Volatile organic compounds	Carrier gas (N_2 or Ar) and energy

biomass to produce hydrogen or valuable chemicals in a further exploration of “killing two birds with one stone” concept towards resource generation.

4. Production of Hydrogen from Waste Biomass Catalysed by Spent LIBs

Hydrogen is regarded as the most promising “clean” fuel towards a sustainable carbon-neutral energy generation, since the combustion of hydrogen produces water as the only by-product.^[79] Hydrogen from the pyrolysis of biomass can effectively cater to sustainable global expansion of renewable energy.^[80] Currently, most researchers employ precious metal containing catalysts (Rh, Ru, Pd and Pt) for the reforming of tar into H₂-rich syngas with low carbon deposition at elevated temperatures.^[81] Unfortunately, low abundance and expensive nature of these metals preclude their deployment in industrial applications. The precious metals are slowly being substituted by earth abundant transition metals i.e. Ni and Co. However, the applicability of these metal-containing systems are limited by carbon deposition on the catalyst surface, that result in catalyst deactivation and blocking of the reactive sites.^[82,83]

In order to circumvent this issue, Yu et al. resorted to an innovative strategy by exploring the potential of the cathode of spent LCO-type LIBs, which are inexpensive and has substantial amounts of Li and Co, as catalysts for the pyrolytic reforming of sawdust biomass to produce hydrogen. The authors disclosed the generation of 11.31 mmol/g of H₂ and 91.8% pure synthetic gas by this novel approach.^[84] The authors further revealed an enhancement of reaction due to the presence of Al foil in the spent electrode, which facilitated the in-situ generation of LiAlO₂@CoO nanoporous network and Co nanoflowers with ~95% oxygen vacancy content, multiple hydrogen evolution sites and functional similarity to Li-CO₂ battery system. These factors culminated in achieving the unprecedented purity of synthetic gas with spent LCO cathode.^[84] Yu et al. utilized the Co recovered from the spent cathode of LCO type batteries as a catalyst in biomass pyrolysis and in-line steam reforming to produce hydrogen (the setup is shown in Figure 12).^[85] Co was recovered from spent LCO battery using coconut shell carbon via carbothermal reduction method at elevated temperatures. Catalyst designed from spent cathode material and coconut shell charcoal at mass ratio 5:1 was used for producing hydrogen from wheat straw at 800 °C. The catalytic reforming performance is notable, achieving 24.9 mmol/g hydrogen yield and 54.9% hydrogen concentration. A consistent performance was observed for five cycles without an appreciable loss in hydrogen yield. The highest yield of hydrogen i.e. 28.3 mmol/g⁻¹ was obtained with a 10:3 mass ratio of spent cathode material and activated carbon at 800 °C owing to an improved pore structure of straw pyrolytic carbon, that ascertained a better Co dispersion.^[85] These reports validate the efficacy of spent LIBs as useful sources of catalyst for the production of hydrogen through biomass pyrolysis. Table 5sum-

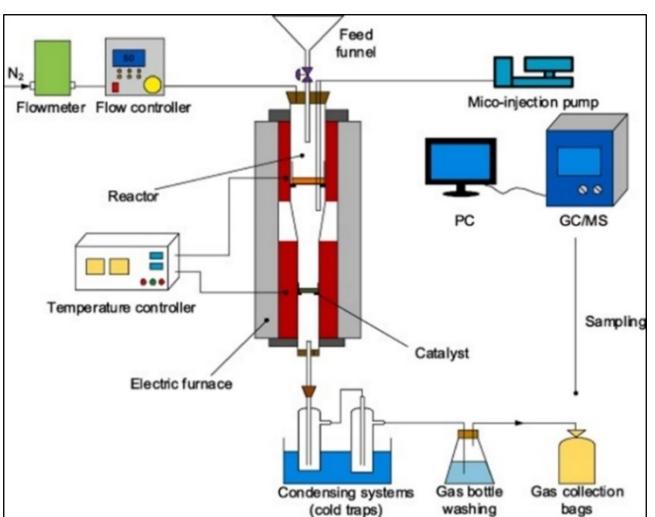


Figure 12. Two-stage fixed-bed reactor for biomass pyrolysis and in-line steam reforming for hydrogen production. Reproduced with permission from Reference^[85] Copyright 2023, Elsevier.

marizes the available literature discussing hydrogen production by biomass pyrolysis assisted by spent LIB/derived materials.

5. Biomass Valorisation using Spent LIBs as Catalyst

The effective conversion of biomass into platform chemicals and high-energy-density fuels/fuel additives is crucial for a sustainable economy and a carbon-neutral society.^[90] Heterogeneous catalysis is suitable for the valorization of bio-renewable substrates into desired products, offering controlled reactivity, easy separability, recyclability and reduced environmental impact.^[91] Heterogeneous catalysts including metal oxides, carbon supported metal species, metal-organic framework and other functionalized porous materials etc. have gained popularity for the transformation of biomass to value added products.^[90,91] However, the catalyst synthesis is often cumbersome requiring multi-step synthesis/post-synthetic steps for functionalization, poor recyclability that increases the overall cost and reduces the applicability of the material. Spent LIBs are being explored in the recent years as promising alternatives to these heterogeneous catalysts owing to the presence of transition and non-transition metals (Li, Co, Mn, Ni, Al and Cu) along with carbon support in a further exploration of the waste-to-wealth approach. Only a handful of articles have been reported in the literature, which discuss the organic transformations and valorization of lignocellulosic biomass utilizing spent LIB-derived catalysts.

Paone et al. transformed biomass derived furfural (FUR) to furfural alcohol (FAL) by using the black mass from spent NCM battery as the catalyst (Figure 13a).^[92] The material was activated prior to its use as a catalyst for hydrogenation reaction employing a series of techniques including filtration, ball milling, calcination and reduction with H₂ at 500 °C,

Table 5. Literature survey of spent LIBs and derived materials as catalysts for producing hydrogen from waste biomass.^[86]

Catalyst/Ab-sorber	Raw mate-rial	Technology	Reaction condition	H ₂ content (vol%)	Syngas purity (vol%)	H ₂ production effi-ciency	Ref.
Co/LiAlO ₂ @-CoO	sawdust	Pyrolysis conventional heating	800 °C in-situ	65.79	91.82%	11.31 mmol/g	[84]
Cat-CC-800	wheat straw	Pyrolysis and steam re-forming conventional heating	Pyrolysis: 500 °C steam reforming: 600 °C ex-situ	55.94	64.71	26.8 mmol/g	[85]
sNCMHC-C	Rice straw	Pyrolysis Microwave-assisted heating	360 W < 350 °C in-situ	50.22	84.66	5.11%	[86]
char1	Rice husk	Pyrolysis conventional heating	700 °C in-situ	38.80	60.20	12.02%	[87]
PyNCM	Wheat straw	Pyrolysis conventional heating	550 °C ex-situ	18.20	54.10	47.26%	[88]
PyNCM	Wheat straw	Pyrolysis conventional heating	550 °C in-situ	26.02	42.95	43.72%	[89]

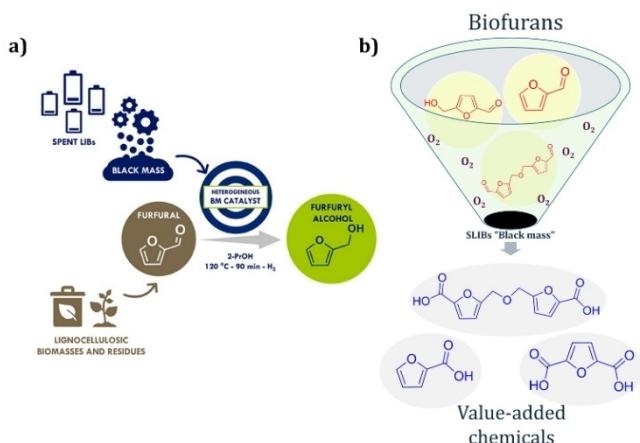


Figure 13. Organic transformation with spent LIBs-derived catalyst a) FUR to FAL. Reproduced with permission from Reference^[92] Copyright 2022, American Chemical Society. b) FA, HMF and OBFMF to FCA, FDCA and OBFCA.

followed by EDX analysis to confirm the metal composition (39.5% Co, 9.7% Ni, and 7.8% Mn). The authors report a near-quantitative hydrogenation of FUR to FAL under optimised condition of 40 ml solution of FUR (0.1 M), 0.25 g catalyst, H₂ gas pressure 10 bar or under transfer hydrogenation conditions with 2-propanol as solvent/hydrogen donor at 120 °C for 90 min. The essential role of the metals in the catalyst and the pre-treatment of spent LIBs were highlighted in the observed catalytic efficiency of the material. The catalytic transfer hydrogenation followed the Meerwein – Ponndorf – Verley (MPV) mechanism. Similarly, Amarasekara et al.^[93] studied spent NCM black mass catalyst for transformation of biofurans to value-added products. The catalyst activated at 600 °C for 30 min to remove the organic binders, was found to contain 6.14% Li and Ni:Co:Mn in 0.45:0.99:0.35 ratio. This material was subsequently employed for three organic transformation of biofurans i.e. the oxidations of furan-2-aldehyde (FUR), 5-hydroxymethyl furfural (HMF) and 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (OBMF) to higher carboxylic acid FCA, FDCA and OBFCA

respectively. The corresponding reported yields were 97%, 87% and 82% for FCA, FDCA and OBFCA respectively with 100% conversion (Figure 13b). The catalyst was reusable upto four cycles with minimum reduction in yield. Therefore, synthesizing platform chemicals from biomass using cost-effective, stable, and recyclable catalysts derived from spent LIBs is an excellent option for industrial applications, paving the way towards a circular economy.

6. Summary, Challenges and Future Prospects

The co-processing of waste biomass with spent LIBs, specifically their cathode materials, are receiving increased attention in the last two decades for an environmentally-friendly treatment of spent LIBs, to recover valuable metals. The waste biomass acts as green reducing agents and lixivients, including reducing sugars, phenolic compounds that are effective for hydrometallurgical processes to recover metals from the 'black mass' of spent LIBs, and can also generate reducing agents including H₂, CO, carbon materials etc, that facilitate the reduction of metals under pyrometallurgical conditions. This strategy of treating a waste with another abundant waste reduces the process cost, precludes the necessity of hazardous, explosive chemicals, and diminishes the environmental CO₂ footprint. In a reverse strategy, the spent LIB waste can be utilized for the depolymerisation and valorization of lignocellulosic biomass to various platform chemicals, polymer precursors and fuel intermediates. Figure 14 presents an overview of this two-way utilization of waste biomass and spent LIBs for resource generation in an illustration of 'killing two birds with one stone' strategy. The waste biomass is employed for the leaching, reduction or adsorption of valuable metals from spent LIBs, followed by their regeneration as water soluble Li₂CO₃, metal oxides (CoO, NiO), or as low-valent metals. Compared to the traditional processes i.e. hydrometallurgy, which depends on the reductants including H₂O₂, NaHSO₃ etc., and pyrometallurgy

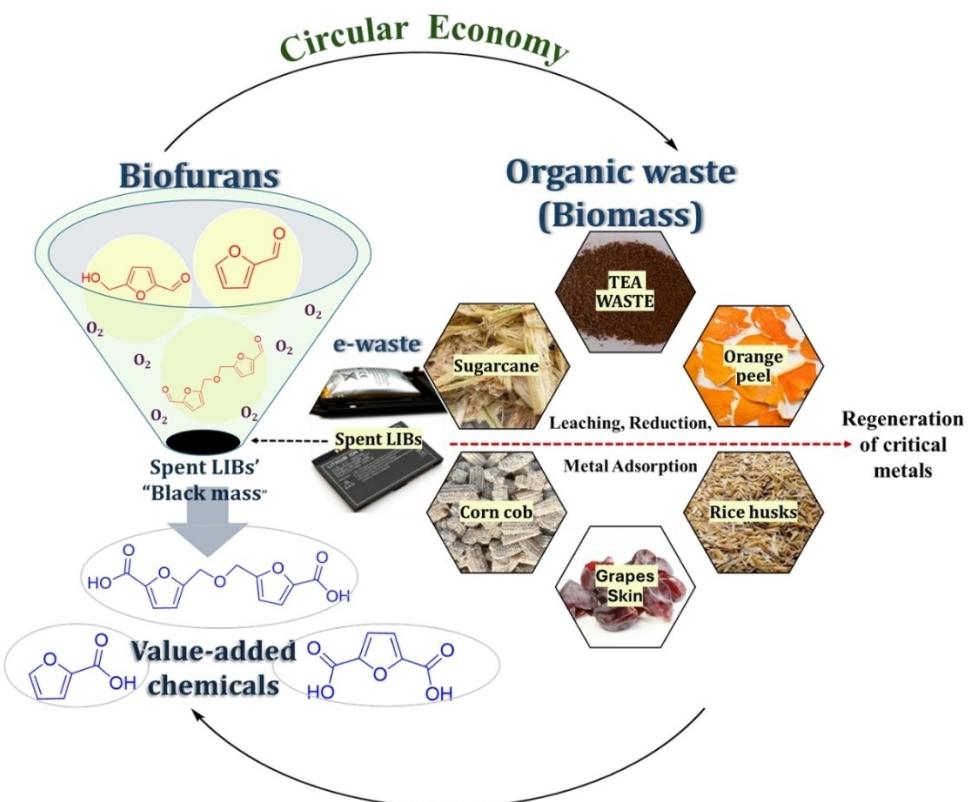


Figure 14. Overview of the utilization of waste biomass for the recovery of metals from spent LIBs, and the use of cathode 'black mass' from spent LIBs for the valorization of biomass to chemicals.

which require reductant gases and high temperature, the processes employing waste biomass provides a safer and less-expensive route to recover valuable metals from spent LIBs with high efficiency (80–99%). These recovered materials can be used as precursors/sources for the production of new battery materials, having charge-discharge capacity comparable to pristine LIBs. Thus, these processes can be promising alternatives to replace the conventional routes to recover metals from spent LIBs. Additionally, the cathode 'black mass' from spent LIB is useful as catalyst for the valorization of lignocellulosic biomass to obtain organic platform chemicals.

However, there are significant challenges associated with the recovery of metals from spent LIBs via the discussed biomass-based green recycling processes. These challenges need to be addressed for the large-scale implementation of this technology.

- Most of the reports that discuss the utility of waste biomass to recover valuable metals from spent LIBs present results obtained from small laboratory-scale experiments. The scale-up of such processes, considering the requirement of LIB recycling to treat tons of spent LIBs is an urgent necessity to gauge the potential for commercial application.
- The possible variation of the composition of lignocellulosic biomass depending on the speciation is another issue that needs consideration. Thus, more research is required to optimize the process conditions (i.e. time, temperature etc)

for large-scale experiments. While researchers worldwide have explored various sources of biomass for recovering valuable metals from spent LIBs, marine algal biomass remains significantly underexplored.^[94] Effect of metals present in the waste biomass (including Na^+ , Ca^{2+} , Mg^{2+} etc.) on the efficiency of metal recovery from spent LIBs need to be explored further.

- Treatment of post-processed waste biomass after metal leaching is a concern, especially as various species of biomass waste are increasingly being explored for recovering valuable metals from spent LIBs in recent years. Some of these biomass resources are rich in nitrogen-containing organics and other heteroatoms, carbon materials, metals that can be recovered and have various potential applications. Similarly, post-processed biomass waste dumped in landfills, leads to significant losses of valuable products and can potentially cause environmental pollution due to the presence of heavy metals from the treatment with spent LIBs.^[95] Although efforts are being made to recover and utilize nitrogen-containing organic compounds via microbial culture for soil conditioning, the recovery of carbon and metal salts from biomass waste has received little attention. The carbon from post-processed biomass has been utilized to synthesize anode materials in recent literature reports.
- Considering the rapid increase in the volume of both electronic waste, including spent LIBs, and waste biomass,

- such as food waste, exploring the combination of spent battery with other waste materials to synthesize functional materials is of immense importance.
- (v) Last, but not the least, an extensive techno-economic feasibility and life cycle and environmental impact analyses of the waste-for-waste processes needs to be analysed before these can be considered for industrial deployment.

The utilization of biomass to recover valuable resources from spent LIBs is a promising step towards sustainability, but the technological advancement is still in its infancy. Hence, detailed and systematic analysis of biomass-based metal recovery strategies need to be undertaken to validate its potency in the future.

Author Contributions

The manuscript was written through the contribution of all the authors. HJ: Conceptualization, Methodology, Writing of original draft; VAA: Writing of original draft; SP and HG: Writing, review and editing; JM: Conceptualization, Writing, review and editing, Supervision, Project administration, Funding acquisition.

Acknowledgements

Funding from CSIR Mission mode project (HCP 0028) and SERB-POWER Grant (SPG/2021/004430). CSIR-CSMCRI PRIS No. 132/2024.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: Spent Lithium ion battery • Biomass waste • Circular economy • Green recycling • Valuable metals

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Manuscript received: July 31, 2024

Revised manuscript received: November 8, 2024

Accepted manuscript online: November 16, 2024

Version of record online: November 27, 2024