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Processes and technologies for the recycling and recovery of spent lithium-ion batteries

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LiBs pose a very specific threat, given that they contain a high percentage of dangerous heavy metals. From the 4000 t of used lithium-ion batteries collected in 2005, 1100 t of heavy metals and more than 200 t of toxic electrolytes were generated. This is why a lot of attention has been paid to the development of the technology necessary to recover and recycle LiBs in order not only to protect the environment but also to conserve resources. The recovery of major spent cell components is beneficial both in terms of environmental protection and also for the provision of raw materials. The authors of this article carried out a state of the art on the technologies used in the recycling and regeneration of industrial lithium-ion batteries. The main objective of such technologies is to enable the recycling of valuable elements present in the batteries, such as cobalt, nickel and copper, in a way which is both profitable and environmentally friendly. All the technologies used in the manufacture of lithium-ion batteries are constantly changing makes subsequent changes to the research into recycling and recovery technologies necessary. This does not mean merely finding ways to recover the precious metals, but also to recover other materials which may harm the environment, in order to dispose of them appropriately. The discussion of this research clearly reflects that:

- There are very few studies on the recovery of metals such as graphite, the electrolyte in spent LIBs, and it is our belief that more research is needed in this area.
- The research into the application of microorganisms in the used lithium batteries is few and far between.
- It is important to find ways to recover the precious metals and to recover other materials which may harm the environment, in order to dispose of them appropriately.

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1. Introduction

The purpose of this paper is to review the current status of the recycling and recovering technologies of spent lithium-ion batteries. It introduces the structure and components of the lithium-ion batteries and summarizes all kinds of recycling and recovery processes from spent lithium-ion. Also, the problems and prospects arising from the studies of their recycling technologies have been put forward.

Lithium batteries (LiBs) are generally composed of a cathode, an anode, an organic electrolyte and a separator. Lamination of the cathode, anode and separator, achieved through compression, makes electrical contact possible. The anode is a copper plate coated with a mixture of graphite, a conductor, binder polyvinylidene fluoride (PVDF) and additives such as $LiPF_6$ [1].

Similarly, the cathode is an aluminum plate coated with a mixture of active cathode material, an electric conductor, a PVDF binder, and additives. $LiCoO_2$ is commonly used as the active cathode material for almost all LiBs on the market [1]. Reference names for Li-ion batteries are shown in Table 1.

Advantages of LiBs such as their lightweight components, inflated energy capacity, high voltage per cell, favorable discharge resistance, ability to work through a large number of regeneration cycles, and a wide range of temperatures, alongside the fact that they are less harmful to the environment than other batteries, have meant that, since their introduction onto the market in 1991 [3], LiBs have been widely used in mobile electronic applications like PCs, video cameras, and mobile telephones, and later as energy storing devices in electric vehicles and stationary storage of renewable energies such a solar and wind. The success of lithium ion technology for the latter applications will depend largely on the cost, safety, cycle life, energy, and power, which are in turn controlled by the component materials used. Accordingly, several authors provide reviews focusing on the challenges and prospects associated with the electrode materials [4–7].

Table 2 provides an overview of the major class of lithium insertion electrode materials. Each system in Table 2 has its own advantages and disadvantages, which often dictate their application areas.

Global consumption of LiBs between the years 2000 and 2004 stood at around 500–700 million cells, whilst, according to the International Telecommunications Union (ITU), the number of mobile telephone users exceeded 6.8 billion in 2013.

LiBs pose a very specific threat, given that they contain a high percentage of dangerous heavy metals. From the 4000 t of used lithium-ion batteries collected in 2005, 1100 t of heavy metals and more than 200 t of toxic electrolytes were generated [8,9,40].

Some of the components of these batteries are difficult to break down; meaning that discarding them after their end-of-life into municipal waste landfill sights may pollute the soil and underground water, while their incineration contaminates the air by releasing toxic gases [10].

Dorella and Mansur [11] ascertained the metal content of LiBs and found that valuable metals such as aluminum, cobalt, lead and lithium were the main components to be separated. They emphasized that irresponsible disposal of spent LiBs will result in environmental pollution.

This is why a lot of attention has been paid to the development of the technology necessary to recover and recycle LiBs in order not only to protect the environment but also to conserve resources. The recovery of major spent cell components is beneficial both in terms of environmental protection and also for the provision of raw materials [12–16].

2. Selection of research studies

This paper systematically reviews recent research on technologies used in the recycling and regeneration of industrial lithium-ion batteries. The main objective of such technologies is to enable the recycling of valuable elements present in the batteries, such as cobalt, nickel and copper, in a way which is both profitable and environmentally friendly. According to Dewulf et al. [17], the use of recycled cobalt and nickel in the production of the active cathode material present in LiBs leads to the following savings: 51.3% in natural resources, 45.3% in fossil fuels, and 57.2% in nuclear energy demand.

The methodology used for this systematic review is described in [18,19], and consists of the following steps:

Table 1
Reference names for Li-ion batteries [2].

Chemical name	Material	Short form	Characteristics
Lithium Cobalt Oxide[a]	$LiCoO_2$ (60% Co)	Li-cobalt	Its high capacity makes it ideal for mobile phones, laptops and cameras.
Lithium Manganese Oxide[a]	$LiMn_2O_4$	Li-manganese, or spinel	This is the safest kind of battery, with a lower capacity than Li-cobalt but a high specific power and long life. Used in power tools, e-bikes. EV, medical, hobbyist.
Lithium Iron Phosphate[a]	$LiFePO_4$	Li-phosphate	
Lithium Nickel Manganese Cobalt Oxide[a]	$LiNiMnCoO_2$ (10–20% Co)	NMC	
Lithium Nickel Cobalt Aluminum Oxide[a]	$LiNiCoAlO_2$ (9% Co)	NCA	
Lithium Titanate[b]	$Li_4Ti_5O_{12}$	Li-titanate	Gaining importance in electric powertrain and grid storage.

[a] Cathode material.
[b] Anode material.

Table 2
Advantages and disadvantages of the electrode materials [4].

Electrode material	Cell voltage (V)	Capacity (mAh/g)	Specific energy (mWh/g)	Advantages	Disadvantages
Layered $LiCoO_2$ cathode (2-d structure)	~4	140	560	High electronic and Li^+ ion conductivity; Revolutionized the portable electronics market	Expensive and toxic Co; safety concerns; only 50% of the theoretical capacity can be utilized
Spinel $LiMn_2O_4$ cathode (3-d structure)	~4	120	480	Inexpensive and environmentally benign Mn; high electronic and Li^+ ion conductivity; excellent rate capability; good safety	Severe capacity fade at elevated temperatures (55 °C)
Olivine $LiFePO_4$ cathode (1-d structure)	~3.5	160	560	Inexpensive and environmentally benign Fe; covalently bonded PO_4 groups lead to excellent safety	Low electronic and Li^+ ion conductivity; needs small particle size and carbon coating to realize high rate capability; high processing cost
Graphite anode	~0.1	370	–	Inexpensive and environmentally benign C; low operating potential maximizes cell voltage	Solid-electrolyte interfacial layer formation and lithium plating lead to safety concerns; high processing cost

- An exhaustive literature search performed by applying predefined criteria for the identification of the most relevant articles in the field.
- A critical evaluation of the quality of the selected articles achieved by synthesizing their content and summarizing the results and conclusions.

For this research, the data were obtained by searching databases of different disciplines (e.g. power sources, electric and hybrid electric vehicles, renewable energy, energy conversion…). The search engines used were those on the Internet, on environmental and battery web pages. The key words for the searches were battery, battery and lithium, recycling and recovering. The inclusion criteria for articles were explicitly defined according to the characteristics of the study. Any article to be included in the review had to be an in-depth study of the battery, its characteristics, recycling and regeneration technologies, effects on the environment, etc.

The structure of this review reflects the inventory of recycling and regeneration technologies to be applied to lithium-ion batteries. These technologies were identified by analyzing the contents of the articles, presupposing that there is a clear overlap between them because, on the one hand, in the recovery and recycling of lithium-ion batteries, the different processes and technologies used tend to overlap and, on the other, many of the results used are based on the implementation of various processes and/or technologies for recovery and recycling of batteries.

The articles analyzed in the review were retrieved from the following data bases: Journal Citation Reports, Web of Knowledge, Web of Science, and Scopus. From each article, the research objectives, description of methodology applied or developed, geographical location of the study, theoretical premises, computer tools used, and above all, information in the conclusions regarding technologies for the recycling and regeneration of lithium-ion batteries were extracted.

3. Technologies for the recycling and regeneration of lithium-ion batteries

Lithium-ion batteries are made up of heavy metals, organic chemical products, and plastics, in a proportion of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemical products and 7% plastics. This composition may vary slightly depending on the manufacturer. When the waste generated by spent lithium-ion batteries is properly processed, the heavy metals such as cobalt or lithium can be recovered. The recovery of these metals is also very important and desirable for the conservation and the defense of the environment.

In recent years, countries have strengthened legislation regarding more flexible recycling processes, intended to ensure the availability of accessible collection points that allow end users to dispose of their spent batteries at no cost. For example, the EU requires each Member State to reach a minimum collection rate in 2015 of between 15–25% of spent batteries and accumulators with a recycling efficiency of at least 45–50% [10].

Existing methods of recycling and regeneration for LiBs comprise principally physical and chemical processes. Among the physical processes are:

- Mechanical separation processes
- Thermal treatment
- Mechanochemical processes
- Dissolution processes

The chemical processes include:

- Acid leaching
- Bioleaching
- Solvent extraction
- Chemical precipitation
- Electrochemical processes

It is worth noting that, as mentioned above, there is a clear overlap between the different processes and technologies applied, given their close correlation and also due to the fact that the results presented are based on the application of various processes and/or technologies for the recovery and recycling of batteries. Thus, Castillo et al. [36], propose the use of nitric acid for the leaching of the lithium. During their proposed process they also include a chemical treatment of the filtrate and a thermal treatment of the solid residue. Lee and Rhee [38] applied a recycling process which involves mechanical and hydrometallurgical treatment, as well as an amorphous citrate precursor process (ACP) to prepare $LiCoO_2$ from spent LiBs.

3.1. Physical processes

Among the physical processes for the recycling of spent LiBs, the function of the mechanical separation processes or techniques is to separate materials according to different properties such as density, conductivity, magnetism, etc. [20]. The thermal processes are generally associated with the production of steel, ferro alloys or other metal alloys. The mechanochemical process uses a grinding technique which turns the crystallized structure of $LiCoO_2$ (the positive electrode present in LiBs) into a disordered system, allowing easy extraction of useful substances such as Co and Li through acid leaching at room temperature using the scrap waste gained from LiBs. The dissolution process involves using specific organic reactors to dissolve the adhesive substance (polyvinylidene fluoride), which joins the anode and cathode electrodes. This process makes $LiCoO_2$ easily separable from its support substrate and allows for effective recovery.

3.1.1. *Mechanical separation processes*

Unlike other batteries, lithium-ion batteries often explode during the recycling process through radical oxidation when lithium metal produced from battery overcharge sustains a mechanical shock on exposure to air. Therefore, a preliminary mechanical separation, carried out before the heavy metals which make up the lithium-ion batteries are recovered, is necessary. Mechanical separation is also advantageous as it reduces the volume of waste and separates and enriches the components of the batteries [21].

Mechanical separation processes are usually applied as a pretreatment. Their function is to treat the outer cases and shells and to concentrate the metallic fraction, which will lead to a hydrometallurgical or a pyrometallurgical recycling process [22,39].

Shin et al. [23] propose a new procedure for the recovery of metals in spent lithium-ion batteries. It includes mechanical separation of the particles of oxide, cobalt and lithium and a hydrometallurgical process for the recovery of the lithium and the cobalt. The experimental results seem to indicate that a concentration of 15 vol% of hydrogen peroxide in sulfuric acid leaching is sufficient for total recovery of the lithium and cobalt through fast leaching.

Li et al. [40] applied a hydrometallurgical process based on leaching to recover cobalt and lithium from spent lithium-ion batteries (LiBs). The proposed procedure includes the mechanical separation of particles containing metal.

The disadvantage of applying mechanical separation processes is that not all the components of spent LiBs are completely separated since they are composed of several metals alongside organic and inorganic substances which penetrate into each other, whilst their small volume and accurate, fine, complicated structure make components difficult to separate [12].

Bertoul et al. [24], apply mechanical methods (grinding, sieving and elutriation) to separate the different materials that compose LIBs. Through the mechanical processing, it was possible to separate the following materials: 17.2 wt% of Cu/Al, 15.8 wt% of Al (external casing); 42.7 wt% of $LiCoO_2$ and graphite, 6.1 wt% of polymers and 2.3 wt% of a mixture that can be reprocessed.

3.1.2. *Thermal treatment*

Thermal processes usually consist of furnace heating in a controlled atmosphere to between 100–150 °C to separate out the insoluble organic additives and adhesives. This process is also used as an intermediary step after each bout of hot acid leaching. Heating time is not standardized but never exceeds two hours [12].

Bahgat et al. [25] successfully synthesized a microcrystalline Li/Co ferrite composite of about 0.14 μm crystallite size by treating a mixture of cathode material of spent lithium-ion batteries and iron oxide at temperatures ≥ 1000 °C and for ≥ 4 h firing times.

Castillo et al. [36], propose the use of nitric acid for the leaching of lithium. This process also includes thermal treatment of the solid residue. The solid residue (made up of iron, cobalt nickel hydroxide mixture and some traces of $Mn(OH)_3$) is introduced in a muffle furnace at 500 °C for 2 h in order to eliminate the carbon and the organic compounds.

Lee and Rhee [38], apply a recycling process using mechanical, thermal, hydrometallurgical and sol–gel steps to recover the cobalt and the lithium from the spent lithium batteries and to synthesize $LiCoO_2$ from leach liquor as cathode active materials.

Thermal treatment is advantageous in so far as the operations necessary are simple and convenient. However the process has been linked to high emissions of dioxins, chloride compounds and mercury, making it necessary to install special equipment to purify the gases and smoke caused by combustion.

3.1.3. *Mechanochemical process*

The common mechanochemical process is a special grinding technique for $LiCoO_2$ chemistries. It consists of exposing greater surface areas enabling a successful acid leaching for the recovery of cobalt and lithium. The dissolution process uses organic reactants to dissolve the adhesive substance, generally polyvinylidene fluoride (PVDF).

Zhang et al. [26] carried out extractions of valuable substances from scrap $LiCo_{0.2}Ni_{0.8}O_2$ metals containing polyvinylidene fluoride (PVDF) at room temperature by applying a 1 N HNO_3 solution after mechanochemical (MC) treatment had been executed using a planetary mill with and without Al_2O_3 powder. The results showed that using Al_2O_3 for mechanochemical treatment is very effective, enabling extraction of Co as well as Ni and Li at a high yield of more than 90% from the amorphous scrap sample.

Tanaka el al. [27] propose a mechanochemical method to synthesize spinel $Li_4Mn_5O_{12}$. This method involves grinding a mixture of $LiOH{\bullet}H_2O$ and γ-MnO_2 with a planetary ball mill, followed by thermal treatment, heating the substance to between 400 and 600 °C, causing the mixture to crystallize in magnesium oxide and lithium. The spinel structure type of compound synthesized by applying this method consists of agglomerates with fine cubic grains of about 100 nm.

Saeki et al. [28], developed a procedure to recover Co and Li from lithium-ion secondary (LIS) battery waste using the mechanochemical process. The process consists of co-grinding $LiCoO_2$ with PVC in air to form Li and Co-chlorides. The ground product is subsequently leached with water to extract Co and Li. During the grinding phase, a mechanochemical reaction which occurs between the $LiCoO_2$ and the PVC leads to the formation of chlorides which are soluble in water. According to these authors, the grinding phase is very important as it improves efficiency. Furthermore, the role of the PVC is important insofar as it provides a source of chlorides to be used during the mechanochemical process. For a proper, safe treatment of waste generated by PVC, Zhang et al. [29] and Saeki et al. [30] have developed a procedure which proposes the use of a grinding technique followed by leaching with water to dechlorinate the PVC.

Zhang and Saito [31] and Lee et al. [32], applied a mechanochemical process to extract useful substances from the lithium-ion secondary battery scrap waste. The method consists of a grinding technique which turns the crystal structure of the $LiCoO_2$ into a disordered system, allowing easy extraction of Co and Li through acid leaching at room temperature.

3.1.4. *Dissolution process*

The dissolution process offers a greater efficiency in the recovery of valuable components of spent batteries. The process weakens the adhesion of the PVDF which holds the electrode active materials (anode and cathode) to the current collectors. Therefore selecting the correct organic solvent able to dissolve either the polyvinylidene fluoride (PVDF) or the polytetrafluoroethylene (PTFE) is very important for a successful dissolution process. Among those solvents which have been successful at this stage are: N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO) [16].

Contestabile et al. [21], offer a recycling process for lithium batteries carried out under laboratory conditions without the separation of the anode and cathode electrodes. The batteries were treated with N-methylpyrrolidone (NMP) at 100 °C for one hour. The $LiCoO_2$ was separated and recovered efficiently. The authors therefore demonstrated that the recovery of $LiCoO_2$ is highly influenced by the adhesive agent used and by the rolling method of electrodes. However this process is impractical on an industrial scale, given the cost of the solvent used (NMP) to dissolve the polyvinylidene fluoride (PVDF).

Among all organic solvents tested, the use of DMSO at 60 °C for 85 min may be the most efficient due to its low cost, zero toxicity and environmental safety [33].

Bankole and Lei [34] extracted the electrolyte solution into organic solvents such as ethanol or isobutyl alcohol water after manually or mechanically dismantling LiBs, leading to a reduction in the environmental pollution caused by the hydrolysis of electrolyte salt, $LiPF_6$ and also the toxic electrolyte mixture. Interestingly, innovative conversion of $LiPF_6$ to a useful compound such as Li_2SiF_6 was achieved for the first time.

3.2. Chemical processes

The chemical processes are mainly hydrometallurgical methods involving acid or base leaching, solvent extraction, chemical precipitation, bioprocess and electrochemical process or a combination of these processes.

3.2.1. Acid leaching

Leaching is a process during which one or more solutes are extracted from a solid through the application of a liquid solvent. Both phases come into close contact and the solute or solutes employed can diffuse from the solid to the liquid phase, leading to a separation of the original components of the solid.

The lithium cobalt oxide ($LiCoO_2$) used as an active cathode is not easily dissolved using common chemical leaching products. The leaching of $LiCoO_2$ from spent LiBs is usually carried out using inorganic acids such as H_2SO_4 [35], HCl [21] and HNO_3 [36,38] as leaching agents. Zhang et al. [3] performed a study of various leachates to leach the lithium cobalt oxide such as sulfurous acid, hydroxylamine hydrochloride and hydrochloric acid. Hydrochloric acid gave the best performance among the three leachates examined. A leaching efficiency of more than 99% of cobalt and lithium could be achieved when 4 M HCI solution was used at a temperature of 80 °C and a reaction time of 1 h. Subsequently, hydrochloric acid was applied for the leaching of lithium and cobalt by other researchers such as Contestabile et al. [21]. Castillo et al. [36] used nitric acid instead of chlorhydric acid in the lithium leaching processes. A new procedure for the nitric acid leaching of lithium and cobalt from lithium-ion batteries was proposed by Lee and Rhee [37], and the procedure was extended to regenerate lithium cobalt oxide electrodes from the leachate and to examine the performance of the electrode [38].

Kim et al. [39] propose a leaching process using sulfuric acid to recover lithium and cobalt. The effects of the leaching agent, particle size and incineration during acid leaching were investigated in order to find the optimum condition for metal recovery. The procedure includes the mechanical separation of lithium cobalt oxide particles, which can be applicable in the commercial recycling of lithium-ion battery waste.

Li et al. [40] used citric acid and hydrogen peroxide ($C_6H_8O_7 \cdot H_2O$ and H_2O_2) to investigate reaction conditions. Co and Li were recovered from the leaching solutions as their respective citrates. Conditions for a recovery of more than 90% Co and nearly 100% Li were achieved experimentally by varying the concentrations of leachate, time and temperature of the reaction as well as the starting solid-to-liquid ratio.

Nayl et al. [41], established a procedure to dissolve and recover Al, Cu, Mn, Co, Ni and Li present in the powder made as a result of mixing and grinding different spent lithium-ion batteries. Here, 98.8% of Li was leached from the alkali residue of spent LiBs using 2.0 M H_2SO_4 with 4.0% H_2O_2 for 120 min with an L/S mass ratio of 10/1 at 70 °C.

Zou et al. [42], developed a methodology to recycle mixed cathode materials including $LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, and $LiFePO_4$. A method is adopted to separate Fe from Ni, Co and Mn in solution. The mixture of $Ni(OH)_2$, $Co(OH)_2$, and $Mn(OH)_2$ with recovered Li_2CO_3 is used to synthesize $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$. Analysis results show that almost 100% of Ni, Mn, Co are recovered, and experiments demonstrate that about 80% Li are recycled in the form of Li_2CO_3.

Li et al. [43], tested three acids for the leaching process: two inorganic acids (H_2SO_4 and HCl) and one organic acid (citric acid, $C_6H_8O_7.H_2O$). The results show that the leaching of Co and Li is more efficient with citric acid than with the two inorganic acids. More than 96% Co and nearly 100% Li were recovered from spent LIBs. The optimal leaching conditions were 0.5 M citric acid with 0.55 M H_2O_2, a solid-to-liquid ratio of 25 g L^{-1}, a temperature of 60 °C, leaching time of 5 h, and ultrasonic power of 90 W.

Zhang et al. [44], proved that compared with inorganic acids and alkalis, the acidic organic solvent could be reused in the subsequent separating and leaching steps. They applied a novel process in which an acidic organic solvent was employed to separate $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material and aluminum foil from spent lithium-ion batteries.

The leaching of lithium nickel cobalt aluminum oxide (NCA) cathodes has been investigated in sulfuric, nitric and hydrochloric acids. Joulie et al. [45] found the optimum leaching conditions, 4 mol L^{-1} hydrochloric acid, 90 °C, 18 h with 5% (w/v) solid to liquid ratio. Under these experimental conditions, all valuable metals of cathode material are leached out.

Zeng et al. [46], obtained results from theory and experiments showing that $LiCoO_2$ can be leached using oxalic acid without an assistance from hydrogen peroxide solution. The recovery rate of lithium and cobalt from spent LIBs can reach about 98% and 97%, respectively at 150 min retention time, 95 °C heating temperature, 15 g L^{-1} solid–liquid ratio, and 400 rpm rotation rate.

3.2.2. Bioleaching

Bioleaching is a low-cost technique used in the treatment of conventional waste which is highly efficient and has few industrial requirements [47]. Bioleaching is a process of mineral bio-oxidation, assisted using microorganisms, which transforms insoluble metal sulfates into water-soluble metal sulfates [48].

Mishra et al. [49] used a bioleaching method for the extraction of cobalt and lithium from spent lithium-ion secondary batteries. Results revealed that a culture of ferrooxidans can produce sulfuric acid to leach metals indirectly from the LiBs. Cobalt was leached faster than lithium. The aim of the use of Fe (II) ion in the leaching experiments was to proliferate the cell growth in the lixiviant: the higher the Fe (II) ion concentration, the slower the metal dissolution. The Fe (III) ion formed during the investigation was found to be precipitated with the metals in the leach residues. Higher solid/liquid ratios prevented bacterial activity in the process as higher metal concentrations are considered to be toxic for cells.

Xin et al. [50] investigated the mechanism of bioleaching Co and Li from spent lithium-ion batteries through a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria. The dissolution of Co and Li from the spent lithium-ion battery depended exclusively on the non-contact mechanism, not on the contact mechanism. Bioacidic dissolution was applied as the bioleaching mechanism of Li in three bioleaching systems; Li displayed the maximum extraction efficiency in the S system due to its having the lowest pH. However, the dissolution mechanisms of Co differed according to the energy materials. Acid dissolution was the sole mechanism for Co release in the S system, whilst a combined action of acid dissolution and Fe^{2+} mediated reduction accounted for Co release in the S+FeS_2 or FeS_2 system.

Yoo et al. [51] treated the wastewater produced during a lithium primary battery recycling process using A. ferrooxidans, re-circulating the treated water in the process. The results of this investigation seem to suggest that wastewater treated by the bacteria can be reused in the recycling process as, during the treatment of the simulated wastewater, bacteria was found to grow in solutions with high metal concentrations such as 8000 $g\ m^{-3}$ of Cr and 13,000 $g\ m^{-3}$ of Ni, but a Li concentration of 5000 $g\ m^{-3}$ in a pure 9 K medium significantly suppresses the Fe^{2+} oxidation activity of the bacteria. In the case of a 90 vol% real wastewater solution, although a low Fe oxidation ratio is observed, the pH and Fe concentration decreased to 1.8 and 21,633 $g\ m^{-3}$, respectively.

Due to the slow kinetics of bioleaching, commercial application of this method in metal extraction is relatively limited [49,50]. Thus different methods, such as improving bacterial cultivation, adhesion of metal-ions, and the addition of tensioactive agents, have been tested with the aim of improving bioleaching rates [52–55]. Various authors [56–59], have shown that the rate of metal dissolution during the bioleaching process can be improved by adding catalytic ions to the solution.

Authors such as Hu et al. [60] and Carranza et al. [61], used metals such as Ag, Bi, Ru and Hg, as catalysts. It is important, however, to use metal catalysts which are efficient while being cheap enough to enable application during the bioleaching process on an industrial scale.

Along these lines, Scott and Dyson [62], were the first to use Cu^{2+} as a catalyst in bioleaching. Dutrizac [63] investigated the effect of leaching by applying cupric chloride on sintered chalcopyrite in ferric chloride solution and found that the $CuCl_2$ substantially speeds up the leaching rate. Chen et al. [64] found that copper ion was effective in the catalysis of metal sulfates.

Along these lines, Zeng et al. [65], developed a process of copper-catalyzed bioleaching to recycle cobalt in spent lithium-ion batteries (mainly $LiCoO_2$). The authors studied the influence of copper ions on the bioleaching of $LiCoO_2$ using Acidithiobacillus ferrooxidans (A.f). They proved that almost all of the cobalt (99.9%) went into the solution after 6 days in the presence of 0.75 g/l of copper ions, whilst only 43.1% of cobalt dissolution was achieved after 10 days without the use of copper ions.

3.2.3. *Solvent extraction*

Solvent extraction has been widely used for the recovery and separation of metals from the leach liquor, effluents, and the waste. Recovery of metal from waste $LiCoO_2$ by leaching-solvent extraction is possible through different routes and using different extractants such as PC-88A [3], D2EHPA and PC-88A [66,67], and Cyanex 272 [35,68].

Swain et al. [69], developed a hydrometallurgical process (acid leaching, solvent extraction, scrubbing and stripping) for the recovery of a pure and marketable form of cobalt sulfate solution/salt from the waste generated by the LiB industry. The results can be summed up as follows:

- The best condition for leaching cobalt from the waste $LiCoO_2$ was found to be 2 M H_2SO_4 at a leaching temperature of 75 °C, pulp density of 100 $g\ L^{-1}$, and 5 vol% of H_2O_2 for 30 min. Under these conditions, the leaching efficiencies of cobalt and lithium were 93 and 94%, respectively.
- The quantitative recovery of cobalt with a minimum lithium co-extraction was achieved using a Cyanex 272 concentration of 1.5 M, an initial pH of 5 and an O/A ratio of 1.6 in a single stage. Subsequently, the rest of the cobalt was extracted at a Cyanex 272 concentration of 0.5 M, an initial pH of 5.35 and an O/A ratio of 1 in a single stage.

Lupi et al. [70], carried out a hydrometallurgical process to recycle Li-ion and Li-polymer batteries containing both $LiCoO_2$ and Li-Cox$Ni_{(1-x)}O_2$ as cathode materials. The operations involved in the process were: cathodic paste leaching, cobalt–nickel separation by solvent extraction with modified Cyanex 272 in kerosene, Co and Ni metal recovery by galvanostatic electrowinning and Co and Ni recovery by potentiostatic electrolysis carried out on partially depleted electrolytes. The results obtained were: Electrowinning of the metallic Ni is achieved at 250 A/m^2, pH 3–3.2 and 50 °C, with 87% current efficiency and 2.96 kWh/kg specific energy consumption. Potentiostatic electrolysis produces a very poor Ni powder in about 1 h with current efficiency changing from 70% to 45% depending on Ni concentration in the electrolyte. Current efficiency of 96% and specific energy consumption of 2.8 kWh/kg were obtained for Co at 250 A/m^2, pH 4–4.2 and 50 °C, by using a solution containing manganese and $(NH_4)_2SO_4$. The Co powder, produced in potentiostatic conditions (-0.9 V vs. SCE, pH 4, room temperature) appears particularly suitable for recycling Co as cobaltite in new batteries.

Nayl et al. [71], extracted and separated Mn(II), Co(II), Ni(II) and Li(I) from the leach liquor spent LIBs. Precipitates of Mn(II), Co(II), Ni(II) and Li(I) with purity $>99\%$ could be obtained under the investigated conditions (20% Acorga M5640 in kerosene with agitation for 5 min at 30 °C at equal phase ratio of unity).

Chen et al. [72], proposed a combined hydrometallurgical process to recover metal values from the leaching liquor of spent LIBs by selective precipitation and solvent extraction. First, nickel was precipitated using dimethylglyoxime reagent after purification operation. Recycled dimethylglyoxime could be re-used as precipitant for nickel and revealed similar precipitation performance compared with fresh dimethylglyoxime. Then the separation of manganese and cobalt was conducted by solvent extraction method using cobalt loaded D2EHPA. Finally, cobalt and lithium were sequentially precipitated and recovered as $CoC_2O_4 \cdot 2H_2O$ and Li_2CO_3 using ammonium oxalate solution and saturated sodium carbonate solution, respectively. Recovery efficiencies could be attained as follows: 98.7% for Ni; 97.1% for Mn, 98.2% for Co and 81.0% for Li under optimized experimental conditions.

3.2.4. *Chemical precipitation*

The chemical precipitation method, applied during recovery and recycling of spent lithium-ion batteries, applies precipitation agents in order to precipitate precious metals present in the batteries, such as cobalt.

According to Ou et al. [73], the key to the success of this process lies in the selection of adequate chemical precipitation agents.

Contestabile et al. [21], developed a process under laboratory conditions for the treatment and recycling of spent lithium-ion batteries. The process involved the following stages: classification, trituration and sieving, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. The cobalt, dissolved in a chlorhydric solution, was recovered as cobalt hydroxide $Co(OH)_2$ when equivalent volume of a 4 M NaOH solution was added.

Precipitation of cobalt hydroxide starts at pH 6 and is considered complete when pH 8 is reached. Ideally, Co precipitation

Table 3
Summary of research on processes and technologies for the recycling and recovery of spent lithium-ion batteries.

Reference	Process/technology	Battery type	Objective	Major findings/limitations
[9]	- Calcination at 500 °C (5 h). - Fusion with KHSO4 (500 °C, 5 h).	Li/MnO_2 and Li-ion	To develop new hydrometallurgical processes applicable to both Li/MnO2 and Li-ion batteries, with emphasis on recovery of the metals present and low waste generation.	Previous separation of the battery components allowed selective processing of the "active mass" (cathode + anode + electrolyte), thus saving chemicals and energy compared to the processing of the full battery.
[24]	In the first step, batteries of different brands and models were characterized regarding to the quantity of each material and its chemical composition. The second step comprised the application of mechanical methods (grinding, sieving and elutriation) to separate the different materials that make up LIBs.	Li-ion	A sample of LIBs is shredded and the different materials present are separated by spouted bed elutriation.	The results show that spouted bed elutriation is a simple and inexpensive way to obtain the separation of the different materials (polymers, metals, active electrode materials) present in spent LIBs.
[40]	Citric acid and hydrogen peroxide are introduced as leaching reagents and the leaching of cobalt and lithium with a solution containing $C_6H_8O_7{\bullet}H_2O$.	$LiCoO_2$	To develop a new hydrometallurgical process that uses an environmentally friendly acid for leaching to recover lithium and cobalt from spent LIBs.	Nearly 100% Li and more than 90% Co were extracted from the spent LIBs using 1.25 M citric acid, 1.0 vol% hydrogen peroxide, a leaching temperature of 90 °C, a S:L ratio of 20 g L^{-1} and a time interval of 30 min.
[11]	- Manual dismantling, acid leaching. - Precipitation with NH_4OH. - Liquid–liquid extraction using Cyanex 272 as the extractant agent.	Li-ion	To modify the route proposed by Mantuano et al. [31] through the introduction of a selective precipitation step after the leaching step aimed at reducing the concentration of aluminum in the leach liquor to be sent to the liquid–liquid extraction step.	Around 50% of cobalt was recovered from the battery dust.
[13]	Electrochemistry quartz crystal microbalance technique.	Li-ion	To clarify the cobalt electrodeposition mechanism as a function of pH.	Electro dissolution of cobalt occurs directly to Co^{2+} in pH 2.7 through the intermediary Co^{+} that is oxidized to Co^{2+} in pH.5.4.
[16]	Mechanical pulverization and sieving process.	Li-ion	To recycle all valuable components from spent Li-ion batteries by first dismantling then separating the components of anode and cathode.	95.9% of copper was recovered after shredding and sieving to the size range above 0.30 mm after 3 min pulverization. The selected organic solvent N, N-dimethylformamide (DMF) could be successfully applied to dissolve the polyvinylidene fluoride (PVDF) adhesive allowing the cathode active materials $LiCoO_2$ to be effectively separated from the aluminum current collector.
[25]	Separation of the main cathode electrode material ($LiCoO_2$) from the anode materials for use in the synthesis process. Chemical grade iron oxide (Fe_2O_3 99%, Adwic) was added for synthesis of ferrite.	Li-ion	To synthesize Li/Co ferrite composite from spent Li-ion batteries. To test structural and magnetic properties under different reaction conditions.	$LiCoO_2$ cathode material could be separated by thermal treatment of spent Li-ion batteries at a relatively low temperature (150–500 °C). $Li_{0.5}Fe_{2.5}O_4/CoFe_2O_4$ microcrystalline (0.14 μm) composite was successfully synthesized in pure form through firing of $LiCoO_2$ as a separated cathode material with Fe_2O_3 at 1000 °C for 4 h. Microstructure investigation revealed the formation of a homogeneous structure with non-uniform size and shape of two ferrite phases ($Li_{0.5}Fe_{2.5}O_4/CoFe_2O_4$). The coercivity (Hc) and saturation magnetization (Ms) values of synthesized Li/Co ferrite composite increased with increasing the firing time and temperature from 153.6 to 177 Oe and from 58.7 to 76.3 emu/g, respectively.
[41]	Acid leaching for different types of mixed spent Li-ion mobile batteries carried out after alkali decomposition using NH_4OH followed by $H_2SO_4+H_2O_2$ leaching.	Li-ion	To establish a procedure for dissolving and recovering Al, Cu, Mn, Co, Ni, and Li present in the powder obtained from crushing, and mixing different types of spent LIBs.	97.8% Al and 64.7% Cu leached by using 4.0 M NH_4OH with an L/S mass ratio of 15/1 at 60 °C for 60 min. About 97.8% Mn, 99.4% Ni, 99.6% Co, and 98.8% Li leached from the alkali residue of spent LIBs using 2.0 M H_2SO_4 with 4.0% H_2O_2 for 120 min with a L/S mass ratio of 10/1 at 70 °C. Data fit with chemical reaction control mechanism and the activation energies for the investigated metals are 30.1 kJ/mol for Mn, 36.7 kJ/mol for Ni, 41.4 kJ/mol for Co, and 37.4 kJ/mol for Li.
[49]	Elemental sulfur and ferrous ion used as energy source to create leaching medium made up of metabolites. Application of chemolithotrophic and acidophilic bacteria Acidithiobacillus ferrooxidans.	$LiCoO_2$	To attempt bioleaching of spent lithium-ion secondary batteries, containing $LiCoO_2$.	Acidophilioc bacteria can be used to dissolve metals from spent cathode material. A culture of A. ferrooxidans can produce sulfuric acid to leach metals indirectly from the LIBs. Cobalt was leached faster than lithium.
[46]	$LiCoO_2$ can be leached using oxalic acid without an assistance from hydrogen peroxide solution.	Li-ion	To develop a novel recovery process, only combined with oxalic acid leaching and filtering.	The recovery rate of lithium and cobalt from spent LIBs can reach about 98% and 97%, respectively at 150 min retention time, 95 °C heating temperature, 15 g L^{-1} solid–liquid ratio, and 400 rpm rotation rate.
[50]	The bioleaching mechanism of Co and Li from spent lithium-ion batteries by sulfur-oxidizing and iron-oxidizing bacteria.	Li-ion		The highest release of Li occurred at the lowest pH of 1.54 with elemental sulfur as an energy source, the lowest occurred at the highest

Table 3 (*continued*)

Reference	Process/technology	Battery type	Objective	Major findings/limitations
			To investigate the bioleaching mechanism of Co and Li from spent lithium-ion batteries applying a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria.	pH of 1.69 with FeS_2. In contrast, the highest release of Co occurred at higher pH and varied ORP with $S+FeS_2$, the lowest occurred at almost unchanged ORP with S. Apart from acid dissolution, Fe^{2+} catalyzed reduction takes part in the bioleaching process as well. Co^{2+} was released by acid dissolution after insoluble Co^{3+} was reduced into soluble Co^{2+} by Fe^{2+} in both FeS_2 and FeS_2+S systems.
[51]	The oxidation ratio of Fe^{2+} ions when the ions were oxidized by A. ferrooxidans in a 9 K medium containing Cr, Ni, and Li was determined to examine the effect of metal ions on the bacterial activity. Wastewater from a pilot plant was treated by A. ferrooxidans, and the stabilization test was performed using the treated wastewater.	Lithium primary battery	To biologically treat wastewater produced during recycling of spent lithium primary battery.	Bacteria can grow in solutions with high metal concentrations such as 8000 g m^{-3} of Cr and 13,000 g m^{-3} of Ni, but a Li concentration of 5000 g m^{-3} in a pure 9 K medium significantly suppresses the Fe^{2+} oxidation activity of the bacteria. In 90 vol% real wastewater solution the pH and Fe concentration decrease to 1.8 and 21,633 g m^{-3}, respectively. Wastewater treated by the bacteria can be reused in the recycling process.
[71]	Liquid–liquid extraction using Acorga M5640 (to remove some impurities) and CYANEX272 in kerosene is carried out.	Li-ion	To extract and separate Mn(II), Co(II), Ni(II) and Li(I) from the leach liquor spent LIBs.	The obtained results indicate that the extraction behavior of the investigated metal ions depends on the pH value, where 91.2% Mn(II), 89.3% Co(II) and 95.6% Ni(II) were extracted at pH 3.5, 5.0 and 8.0, respectively, while the extraction of Li(I) was almost constant regardless of the pH value. Mn(II), Co(II) and Ni(II) were extracted in the organic phase as $(MA_2 \cdot 3HA)$(org) while Li(I) was extracted as $(MA \cdot 2HA)_{(org)}$.
[72]	● Nickel was precipitated using dimethylglyoxime reagent after purification operation. ● The precipitate was then dissolved in 1 mol L^{-1} hydrochloric acid solution. ● After filtration, white powders of dimethylglyoxime regenerated could be re-used as precipitant and nickel ions were left in the filtrate. Subsequently, manganese was extracted using Co-D2EHPA. ● Cobalt and lithium were selectively precipitated using ammonium oxalate and hot saturated sodium carbonate, respectively.	Li-ion	To recover metal values from the leaching liquor of spent LIBs by selective precipitation and solvent extraction	About 98.2% and 81.0% of cobalt and lithium were recovered as $CoC_2O_4 \cdot 2H_2O$ and Li_2CO_3.

can be obtained using an ammoniac solution, a weak base, which forms a buffer solution at pH 9. However, the ammoniac, when mixed with the cobalt, creates a stable complex, causing partial dissolution of the hydroxide, which prevents a quantitative recovery. Therefore NaOH is still the best option [12,23].

3.2.5. Electrochemical process

Myoung et al. [74] applied an electrochemical deposition and appropriate thermal treatment to prepare cobalt oxide from Co (III) of waste $LiCoO_2$ cathodes. Under appropriate pH conditions, island-shaped cobalt hydroxide is precipitated on the titanium substrate and heat treatment of the cobalt hydroxide results in the formation of cobalt oxide.

Shen [75] investigated the recovery of cobalt from spent LiBs through sulfuric acid leaching and electrowinning. At 70 °C, with a sulfuric acid concentration of 10 mol L^{-1} and a retention time of one hour, almost 100% of the cobalt is dissolved. Hydrolyzed deposition purifies the leach liquor within the interval of pH 2.0–3.0 and 90 °C.

The cathode cobalt is produced through electrowinning in current density 235 A m^{-2}. The quality of cathode cobalt is in accordance with China's 1 A# cobalt standard GB6517-86. The net recovery of the cobalt is over 93%.

Compared to other hydrometallurgical processes used to recycle the metals present in spent LiBs, electrolysis can obtain a very pure cobalt compound given that no other substances need be introduced, avoiding impurities [76]. However, this process tends to use large amounts of electricity.

Table 3 presents a summary of research on recycling and recovery of spent lithium-ion batteries.

4. Conclusions

4.1. Major survey findings

Spent lithium-ion batteries are classified as dangerous waste. If they are not properly treated, they will damage the environment and cause harm to animals and human health. Coupled with this, the fact that the batteries contain precious metals such as Co, Li and Mn mean that, from an economical as well as an environmental point of view, the recycling and recuperation of these batteries is highly advantageous.

Through a thorough analysis of the research carried out in this area, it is clear that all processes and techniques applied in the recycling of lithium-ion batteries guarantee the recovery of the metals to a greater or lesser extent, whilst reducing the negative effect these batteries may have on the environment

Here is a summary of the main advantages and disadvantages of the processes analyzed:

- It is necessary to carry out a preliminary mechanical separation before heavy metals which make up lithium-ion batteries can be recovered. Mechanical separation also reduces the volume of waste and separates and enriches the components of the batteries.
- Furthermore, mechanical separation prior to leaching improves recovery efficiency of the target metals and makes purifying the leachates unnecessary.
- The spouted bed elutriation can be successfully employed as a viable and easy alternative to separate the materials that compose the spent LIBs.
- The advantages of thermal treatment are the simplicity and convenience of the operations. However the process has been linked to high emissions of dioxins, chloride compounds and mercury, making it necessary to install special equipment to purify the gases and smoke caused by combustion.
- The addition of Al_2O_3 is very effective for mechanochemical treatment enabling a high yield (more than 90%) of Co as well as Ni and Li to be extracted from an amorphous scrap sample. For a successful dissolution process, the choice of the appropriate organic solvent, able to dissolve the polyvinylidene fluoride (PVDF) or the politetrafluoroetileno (PTFE) used as adhesives, is key. The downside to this process is the high cost of the solvent used (NMP) to dissolve the polyvinylidene fluoride (PVDF). This makes it inappropriate for use on an industrial scale. Due to its low cost, zero toxicity and environmental safety, DMSO at 60 °C for 85 min could be the most adequate solvent.
- Almost all the experimental results indicated that the leaching efficiency of Co is highest in hydrochloric acid.
- The main advantages of bioleaching processes are: their low cost, few industrial requirements, and that they are relatively environmentally friendly. Due to the slow kinetics of bioleaching, however, commercial application of this method in metal extraction is relatively limited.
- The extraction method using Cyanex 272 (bis-2, 4, 4-trimethylpentyl phosphinic acid) is technically viable to separate base metals from NiCd, NiMH and Li-ion Batteries.
- Acorga M5640 can be effectively used as extractant for the extraction and separation of some ions such as Fe(III), Cu(II) and Al(III) which are found as impurities in the leach liquor of mixed types of spent LIBs. At a pH close to 1.0, 99.2% Cu was extracted; at pH 2.0–2.2 about 94% Fe(III) and 95.6% Al(III) were also extracted. The extraction of Mn(II), Co(II), Ni(II) and Li(I) was negligible.
- For successful chemical precipitation, the key lies in selecting adequate chemical precipitation agents. NaOH is still the best option.
- The electrolysis process can obtain a very pure cobalt compound given that no other substances need be introduced, avoiding impurities. However this process uses a lot of electricity.

4.2. Future perspectives

Currently, most of the research carried out in the area of recuperation and recycling of spent LiBs concentrates on recovering or recycling precious metals such as cobalt, nickel or lithium. The interest in recovering cobalt lies in the fact that it is a rare and precious metal. Nickel and lithium are expensive. There are however very few studies on the recovery of other metals such as graphite, the electrolyte in spent LIBs, and it is our belief that more research is needed in this area.

Technologies based on the use of microorganisms (bioleaching) are gaining prominence and maturity in the field of mineral processing. However, research into the application of this process in the recovery and recycling of used lithium batteries is few and far between.

The fact that the technology used in the manufacture of lithium-ion batteries is constantly changing makes subsequent changes to the research into recycling and recovery technologies necessary. This does not mean merely finding ways to recover the precious metals, but also to recover other materials which may harm the environment, in order to dispose of them appropriately.

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