Pamukkale Univ Muh Bilim Derg, 29(4), 384-400, 2023

Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi

Pamukkale University Journal of Engineering Sciences

Recovery of lithium, cobalt and other metals from lithium-ion batteries

Lityum-iyon pillerden lityum, kobalt ve diğer metallerin kazanımı

Oktay CELEP[1*], *Ersin Y. YAZICI*[1], *Haci DEVECI*[1], *Christie DORFLING*[2]

[1]Department of Mining Engineering Division of Mineral and Coal Process, Faculty of Engineering, Karadeniz Technical University, Trabzon, Turkey.
ocelep@ktu.edu.tr, eyazici@ktu.edu.tr, hdeveci@ktu.edu.tr

[2]Department of Process Engineering, Faculty of Engineering, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa.
dorfling@sun.ac.za

Received/Geliş Tarihi: 31.01.2022
Revision/Düzeltme Tarihi: 18.07.2022
doi: 10.5505/pajes.2022.98793
Accepted/Kabul Tarihi: 08.09.2022
Review Article/Derleme Makalesi

Abstract

Wastes with high metal content are an important secondary source. Utilisation of these wastes is important offering environmental and economic advantages as well as the conservation of natural resources. Due to the widespread use of portable electrical and electronic devices (mobile phones, laptops, video cameras, etc.) and electric cars, the consumption of lithium and cobalt, which are used as main components in lithium-ion batteries/batteries (LIB), has increased. Because LIBs contain lithium (1.5-7%), cobalt (5-20%), manganese (15-20%), copper (8-10%), aluminium (5-8%), and nickel (5-10%), they are considered as an important secondary source. Industrially, mechanical pretreatment, pyrometallurgical and hydrometallurgical methods as alone or in combination are used to recover metals from waste LIBs. After mechanical pretreatment and physical separation processes, hydrometallurgical methods, including solution purification, precipitation and solvent extraction methods, are used after leaching with inorganic such as H_2SO_4*, HCl and* HNO_3 *or organic acids. In this study, processes for recovery of metals from LIBs are discussed with a critical review of studies carried out on this. In addition, flowsheets of industrial applications for lithium/cobalt recovery in the world are presented.*

Keywords: Li-ion battery, Recycling, Hydrometallurgy, Leaching, Lithium, Cobalt.

Öz

Yüksek metal içeriklerine sahip olan atıklar önemli bir ikincil kaynak konumundadırlar. Bu atıkların değerlendirilmesi, çevresel ve ekonomik avantajlarının yanı sıra doğal kaynakların korunması açısından da önemlidir. Taşınabilir elektrikli ve elektronik cihazların (cep telefonları, dizüstü bilgisayarlar, video kameralar vb.) ve elektrikli otomobillerin yaygınlaşmasına bağlı olarak bunların temel bileşeni olan lityum-iyon pillerde/bataryalarda (LIB) kullanılan lityum ve kobalt tüketimleri de artmıştır. LIB'ler, lityum (%1,5-7), kobalt (%5-20), manganez (%15-20), bakır (%8-10), alüminyum (%5-8) ve nikel (%5-10) gibi metalleri içermesinden dolayı önemli bir ikincil kaynak olarak değerlendirilmektedirler. Atık LIB'lerden metallerin geri kazanımında endüstriyel olarak mekanik ön-işlem, pirometalurjik, hidrometalurjik veya bunların birleşimden oluşan yöntemler kullanılmaktadır. Mekanik ön-işlem ve fiziksel ayırma işlemlerinden sonra H_2SO_4*, HCl ve* HNO_3 *gibi inorganik ya da organik asitlerle liç sonrası çözelti saflaştırma, çöktürme ve solvent ekstraksiyon yöntemlerini içeren hidrometalurjik yöntemler kullanılmaktadır. Bu çalışmada, LIB'lerden metallerin geri kazanım prosesleri ve yapılmış farklı çalışmalar tartışılmıştır. Ayrıca, Dünya'da lityum/kobalt kazanımının gerçekleştirildiği endüstriyel uygulamalardan akım şemaları sunulmuştur.*

Anahtar kelimeler: Lityum-iyon pil, Geri Kazanım, Hidrometalurji, Liç, Lityum, Kobalt.

1 Introduction

Due to the rapid depletion of natural resources to meet the ever-increasing demand, some metals/raw materials used in advanced technologies have become "critical metal/raw materials". Alternative sources need to be sought to provide sustainability in industrial development. Scraps with high content of metals are often regarded as an important secondary resource. In addition to its environmental and economic benefits, the exploitation of the resource potential of scraps is significant for the conservation of natural resources and the sustainable development of metals and related industries.

Due to the widespread use of portable electrical/electronic equipment (mobile phones, laptops, video cameras, etc.) and electric vehicles (EV, PHEV, HEV), the importance of lithium-ion batteries (LIBs), which are the essential components of these devices, have particularly increased in recent years [1],[2]. In effect, the growth in the automotive sector with the development of electric vehicles/automobiles has led to the widespread use of these batteries. This has concomitantly increased the demand and consumption of battery raw materials.

LIBs are widely used due to their high electrical density, high operating voltage and long cycle life. In 2017, 43% (19,870 tons) of lithium supplied in the world was used in battery production, and this value is estimated to increase to 65% (61,123 tons) in 2025 [3]. Similarly, about 43% of the cobalt produced in 2014 was used in battery production [4]. Cobalt prices soared by approximately 500% between 2016 and 2018 in concordance with the ever-increasing demand for lithium-ion batteries [5]. The EU predicts that 18 times more lithium and 5 times more cobalt by 2030, and almost 60 times more lithium and 15 times more cobalt by 2050 will be needed in electric vehicle batteries and energy storage systems [6].

LIBs that typically complete their economic life within ~3-8 years) harm the environment and human health since they contain heavy metals (Cu, Pb, Cd, Zn) in high quantities and toxic electrolytes. Therefore, proper management of end-of-life LIBs is of uttermost importance for the protection of the environment and the exploitation of its economic potential. In

---

[*] Corresponding author/Yazışılan Yazar

this regard, LIBs containing lithium (1.5-7%), cobalt (5-20%), manganese (15-20%), copper (8-10%), aluminium (5-8%), and nickel (5-10%) are considered as a ready secondary source.

In this study, an overview of LIBs is presented. The treatment of LIBs for the recovery of the contained metal values is comprehensively reviewed. Worldwide industrial processes developed for the recovery of metals from LIBs are also discussed.

2 Overview of lithium-ion batteries

LIBs are electrochemical cells that can reversibly convert chemical energy into electrical energy through a redox reaction. They are essentially energy storage systems developed for the highest energy density among rechargeable batteries (Figure 1).

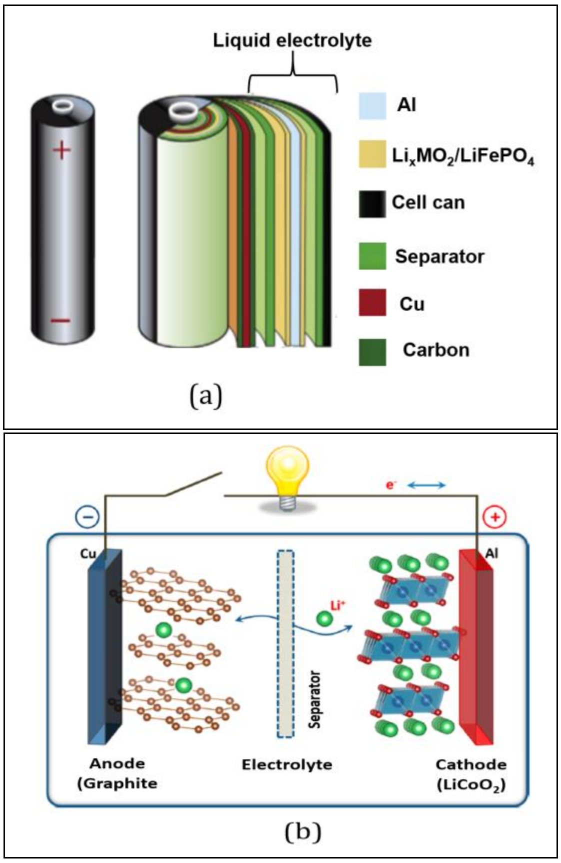

Figure 1. Schematic views of; (a): A cylindrical lithium-ion battery; (b): The operation of a lithium-ion battery ($LiCoO_2/Li^+$ electrolyte/graphite) [9].

As a result of the oxidation (electrode to electrolyte) and reduction (electrolyte to electrode) reactions, ion movement occurs between the anode and the cathode by the movement of electrons. Lithium ions move between the anode and the cathode in a rechargeable LIB. While the battery is charged by the movement of lithium ions from the cathode, which is commonly a lithium-metal-oxide material, towards the anode (mostly graphite), it is discharged in the opposite case. When using the battery, lithium ions (Li^+) move from the negative electrode to the positive electrode, while the current moves in the opposite direction Figure 1(b). The oxidation-reduction reactions taking place at the anode and cathode are given in Equations 1-3, [14],[19]-[21].

	Anode (oxidation)	Cathode (Reduction)	
Charge:	$LiMO_2 \rightarrow Li_{1-x}MO_2 + xLi^+ + xe^-$	$yC + xLi^+ + xe^- \rightarrow Li_xC_y$	(1)
Discharge:	$Li_xC_y \rightarrow yC + xLi^+ + xe^-$	$Li_{1-x}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$	(2)

$$LiMO_2 + yC \leftrightarrow Li_{1-x}MO_2 + Li_xC_y \quad (3)$$

Total: (M=Co, Ni, Mn)

LIBs consist of different components such as positive electrode (cathode), negative electrode (anode), electrolyte, and separator in addition to the iron or aluminium coating (Figure 1), (Table 1), [1]-[6].

Table 1. Lithium-ion battery components and metal contents [27],[33],[34],[37],[49],[53]-[61].

Component	Content	Content, %
Coating	Fe-Ni alloy Al	20-26 5-23
Cathode		25-33
Aluminium	Al (Current collector foil)	5-8
Binder	PVDF	1-2
Metal Oxide (80-85%, $LiMO_2$, M=Co, Ni, Mn)	Li	1.5-7
	Co LCO ($LiCoO_2$, 33.5%)	5-20
	Ni LNO ($LiNiO_2$)	1-15
	NCA ($LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$)	
	Mn LMO ($LiMnO_2$)	5-10
	NMC ($LiNi_xCo_yMn_zO_2$)	
$LiFePO_4$		
Polymeric separator	Micro-pores polyethylene or polypropylene	4-10
Electrolyte		10-15
Li salts	$LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiBF_4$	
Organic Solvents	DMC-EC, PC-DME, BL-THF, EMC, DEC(1)	
Anode		15-30
Copper	Cu (Current collector foil)	8-10
Binder	PVDF	1-2
Graphite		15-17

[1]: DMC-EC: dimethyl carbonate-ethylene carbonate; PC-DME: propylene carbonate-1,2-dimethoxyethane; BL-THF: butyrolactone (BL) tetrahydrofuran (THF), EMC=ethyl methyl carbonate; DEC=diethyl carbonate; PVDF: Polyvinylidene fluoride.

Materials such as $LiMO_2$ (lithium metal oxide, M: Co, Ni, Mn) and $LiFePO_4$ have been developed as cathode materials [7]-[10]. $LiCoO_2$ (LCO) cathode batteries with graphite anode, which were first developed in 1991 are the most widely used batteries. The production of 32,000 tons of LCO cathodes were reported in 2013 [11]. $Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$, $LiMn_2O_4$ and $LiFePO_4$ are also currently widely used cathode materials (Table 1) [11]-[13]. High voltage electrodes such as $LiNiPO_4$, $LiCoPO_4$, $LiNi_{0.5}Mn_{1and.5}O_4$, $LiCoMnO_4$ are proposed for use in batteries requiring high energy density [14]. Depending on the composition of the cathode, anode or electrolyte, the lithium content varies between 50-563 g/kWh (according to the specific battery capacity) [15]-[18].

Graphite is the most preferred anode material in LIB's due to its low cost and low-voltage reaction with lithium. Anodes such as silicon, tin and lithium titanate (Li_2TiO_3) could also be used in place of graphite [1],[22].

The electrolyte provides the transmission of lithium ions between the anode and the cathode. The electrolyte contains a lithium salt dissolved in an organic solvent mixture (e.g., ethylene carbonate and dimethyl carbonate) [23]. The most commonly used lithium salts are $LiClO_4$, $LiAsF_6$, $LiBF_4$ and $LiPF_6$ [24]. The separator is a microporous polymer membrane that allows lithium ions to pass through the pores and prevents short circuits between the cathode and the anode [25]-[27].

3 Recovery of metals from LIB's

World lithium-ion battery production increased 800% between 2000 and 2010 [28]. Spent LIBs are considered important secondary resources because they contain metals such as lithium, cobalt, manganese, copper, aluminium and nickel [3],[9]-[34]. Current industrial applications are mostly for the recovery of the contained metal values from lithium-cobalt-oxide (LCO) and nickel-manganese-cobalt oxide batteries (NMC) [35]-[44]. Mechanical pretreatment, pyrometallurgical processes, hydrometallurgical processes or their combination are used to recover metals from waste LIBs. The main steps applied for the hydrometallurgical recovery of metals from lithium-ion batteries are:

i. Disassembly of the battery after the cathode discharge,
ii. Extraction of the electrolyte and salt by vacuum distillation,
iii. Dissolution of the binder to separate the Cu and Al collectors from the electrodes,
iv. Grinding of the electrode material,
v. Physical separation,
vi. Leaching,
vii. Solution purification,
viii. Recovery of metals by precipitation, crystallisation or electro-winning methods (Figure 2), [12]. The crushing and physical separation steps are applied to obtain a material enriched in metals (Li, Co, Ni, Mn) [12],[34],[45]-[49].

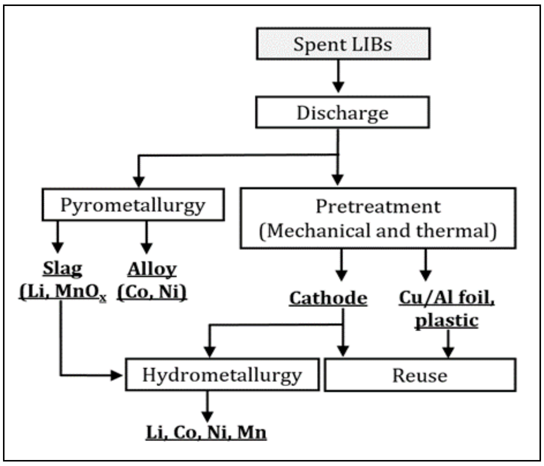

Figure 2. Recovery of metals from lithium-ion batteries [2],[4].

Pyrometallurgical processes often suffer from high energy consumption/cost, toxic gas and dust output. In these respects, hydrometallurgical processes offer some advantages, such as low toxic gas emissions and relatively low investment costs, with their suitability for small-scale applications. Metal recovery efficiencies of pyrometallurgical processes could be lower than hydrometallurgical ones. On the other hand, there is no need to separate batteries in pyrometallurgical processes. Although extensive research/development studies are directed for hydrometallurgical processes, most industrial recycling processes are based on pyrometallurgical processes [11, 50-52].

3.1 Pretreatment

Before the recovery of metals from lithium-ion batteries, the battery is discharged using saturated salt solutions such as NaCl and Na_2SO_4 to prevent risks such as spontaneous combustion/explosion and short-circuiting [22],[37],[62]-[65]. Thereafter, mechanical pretreatment and separation processes such as crushing, screening, magnetic separation, fine crushing and classification are applied to ensure the separation of certain parts and fragmentation/decomposition of batteries [49],[65], [66]. Flotation is also suggested for separation/recovery of graphite from the fine fraction (<75μm) [22]. After physical separation processes, the cathode can be leached with alkaline reagents such as either N-methyl-2-pyrrolidone or NaOH to separate the aluminium foil [34],[38],[64]-[68]. Since organic binders (such as PVDF) cause problems during the leaching and solid-liquid separation stages, thermal pretreatment is tested for the removal of these organic compounds and graphite [45],[50],[69],[70]. In addition, the presence of graphite is reported to cause low lithium recovery in leaching processes [37]. Batteries are heated at 300 °C and burned to evaporate solvents and electrolytes [63]. The battery electrolyte ($LiPF_6$) can be also dissolved in organic solvents, but it may react with water to form toxic gases such as pentafluorine arsenic, pentafluorophosphate and hydrogen fluoride (HF), causing lithium losses (Equation 4). Therefore, recovery of the electrolyte often incurs high costs with environmental risks [2].

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \tag{4}$$

3.2 Recovery of metal by hydrometallurgical methods

In the recovery of metals from the material obtained after mechanical pretreatment and physical separation processes, inorganic acids such as H_2SO_4 [56], HCI [71], and HNO_3 [72], organic acids [73] such as oxalic acid [74], formic acid and malic acid [75], and alkaline (NaOH) reagents are used in the development of leaching processes. In addition, ascorbic acid is also suggested as a reducing agent in leaching with glycine, which is an amino acid. Hydrometallurgical methods including solution purification, precipitation, solvent extraction and ion exchange can be utilised after leaching (Figure 3), [34],[37],[67],[75]-[81]. Inorganic acids are more advantageous than organic acids because they are comparatively cheaper.

Leaching of lithium-cobalt oxide is often difficult due to the strong chemical bond between cobalt and oxygen. Although Co^{3+} is more dominant in the cathode material, Co^{2+} dissolves more rapidly in leaching solutions at room temperature [4]. Therefore, Co^{3+} needs to be reduced to Co^{2+} to increase the leaching efficiency. For this purpose, a wide variety of reductants including H_2O_2 [56],[71],[82]-[85], $Na_2S_2O_3$ [28], $NaHSO_3$ [47],[86[-[88] and $Na_2S_2O_5$ [89] are used.

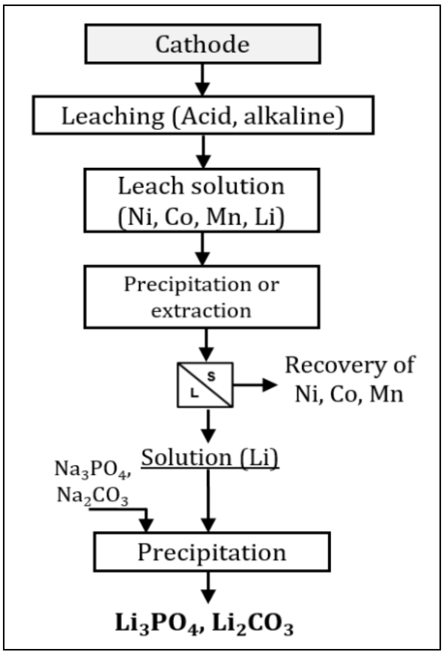

Figure 3. Recovery of metals from lithium-ion batteries by hydrometallurgical methods [2].

In recent years, D-glucose [90],[91], cellulose [92], Phytolacca Americana [92], grape seeds [93], orange peels [94], and waste tea [92] have been tested as alternative reducing agents [95].

Leaching solutions containing metals such as Li, Co, and Ni are subjected to purification and metal recovery steps. Dissolved cobalt is recovered by precipitation with NaOH (4M NaOH, pH: 11-12) as cobalt hydroxide $Co(OH)_2$ (Equation 5) and lithium remaining in the solution is recovered as lithium carbonate [96],[97].

$$M^{2+} + 2OH^- \rightarrow M(OH)_2 \quad (M: Co, Ni, Mn) \tag{5}$$

3.2.1 Alkaline leach

The electrodes are first treated with N-methyl-2-pyrrolidone (NPM) to separate the active material from the Al and Cu foils and dissolve the binder [98]. After this stage, metals such as aluminium and copper are recovered before leaching lithium and cobalt. Alkaline (NaOH) leaching can be exploited for selective recovery of aluminium from cathode material (Equation 6) [20],[99]. The dissolved aluminium is then recovered by precipitation with NH_4OH (pH: 5), [36]. Nayl et al. [100] obtained 98% Al and 65% Cu recovery with ammonia (NH_4OH) solution (4 M NH_4OH, 80 °C, 66.6 g/L, 60 min.) with Co and Li remaining in the solids. After selective leaching of Cu and Al, the solids are further leached using various acids for the extraction of Li, Co and other metal values present.

$$2Al^0 + 2NaOH + 6H_2O \rightarrow 2Na\,[Al(OH)_4SO_4] + 3H_2 \tag{6}$$

3.2.2 Inorganic acids for leaching

Inorganic acids such as sulphuric acid (H_2SO_4) [20],[36],[49],[62],[101]-[104], hydrochloric acid (HCI) [14,[96],[105], nitric acid (HNO_3) [45],[106]-[108], and phosphoric acid (H_3PO_4) [64],[65] are extensively studied for the recovery of metals from lithium-ion batteries. This can be attributed to their relatively low cost, effectiveness as leaching reagents, well-known chemistry of reactions and ready availability of downstream treatments for solution purification and metal recovery processes.

3.2.2.1 Sulfuric acid leaching

As the cheapest inorganic acid, sulphuric acid (H_2SO_4) is widely used in the leaching of metals such as copper, cobalt and nickel from primary or secondary sources. It is also the most widely studied reagent for the leaching of metals from the cathode material of lithium-ion batteries (Table 2). High acid concentrations (2-4 M H_2SO_4) are often required to achieve high metal extractions and concomitantly, pregnant leach solutions obtained contain high levels of sulphate [4],[109]. In addition, due to the high acidity, a high amount of neutralising reagent is often warranted for the neutralisation of leach solution prior to the downstream recovery of metals. Inorganic reducing reagents such as H_2O_2 (1-15%), $NaHSO_3$ and $Na_2S_2O_5$ are added as reductants in sulphuric acid leaching to achieve a high rate and extent of metal (e.g. cobalt) extractions [20],[89],[102],[103],[110],[111]. The dissolution reactions of lithium and cobalt with sulphuric acid leaching from $LiCoO_2$ are given in Equations 7 and 8 [62]. Figure 4 illustrates a typical flowsheet for treatment of LIBs based on sulphuric acid leaching.

$$4LiCoO_2 + 6H_2SO_4 \rightarrow 2Li_2SO_4 + 4CoSO_4 + 6H_2O + O_2 \tag{7}$$

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow Li_2SO_4 + 2CoSO_4 + 4H_2O + O_2 \tag{8}$$

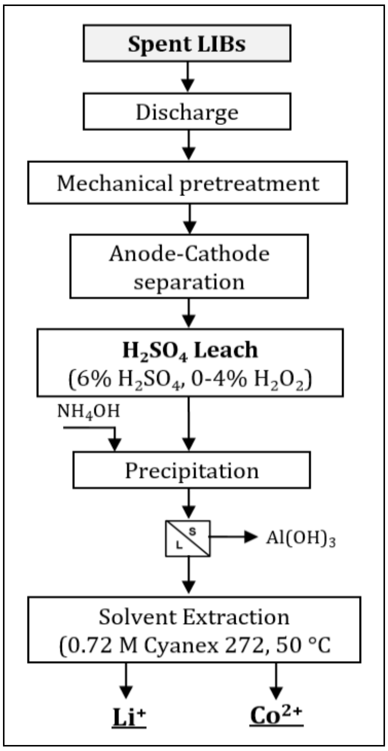

Figure 4. Recovery of metals from lithium-ion batteries by H_2SO_4 leaching [67].

The leaching characteristics and conditions can be predicted by the Eh-pH diagrams. Figures 5 illustrates the stability diagram of an individual metal ion in the presence of other constituents at 298 K and 50 g/L solids for the sodium bisulfide.

Table 2. Parameters and results of studies on sulfuric acid leaching.

Leach condition	Metal Recovery (Precipitation/SX)	Recovery	Ref.
3 M H_2SO_4, 70 °C, 4 h, 200 g/L	Prec. + SX (Acorga M5640, Cyanex 272)	Prec.: %90 Co; SX: 97% Cu (Acorga M5640), %97 Co (Cyanex 272)	[62]
1 M H_2SO_4 + 5% H_2O_2, 65 °C, 1 h, 33 g/L	Prec. (NH_3, pH 5) Co/ Li SX (0.72 M Cyanex	80% Co, 95% Li, 55% Al; SX: 85% Co (Cyanex 272)	[36]
2 M H_2SO_4 + 5% H_2O_2, 75 °C, 40 min., 100 g/L	SX (0.5 M Cyanex 272, pH 5.35)	93% Co, 94% Li	[30], [101]
4 M H_2SO_4 + H_2O_2, 80 °C, 4 h	Prec.: ethanol (3:1), 15 min.	92% Co ($CoSO_4$); 8% Co ($Co(OH)_2$, with $Li(OH)_2$, pH 10)	[101]
2 M H_2SO_4 + 6% H_2O_2, 60 °C, 1 h., 100 g/L	Prec.: Cu, Fe, Al (pH 6,5) SX: 0.4 M Cyanex 272, pH 6, O/L=2	>99% Co, SX: 99,9% Co, pH 6 Co/Ni	[102]
1 M H_2SO_4 + 30% H_2O_2, 80°C, 2 h, 714 g/L	Prec.: 1 M citric acid, 2 h, 65 °C, 450°C calcination, 4 h.	88,3% Co, $LiCoO_2$	[120]
4 M H_2SO_4 + 10% H_2O_2, 85 °C, 3 h, 100 g/L	SX: 25% P507; Prec.: Ammonium oxalate, pH 1.5	SX: 98% Co, 97% Ni and Li	[99]
0,4 M H_2SO_4, 5% H_2O_2, 1 h, 75 °C, 100g/L	Prec.: Oxalic acid; Na_2CO_3	86% Li, Li_2CO_3 and 90% Co, CoC_2O_4	[117]
2 M H_2SO_4 + 15% H_2O_2, 75 °C, 20 min., 50 g/L	-	%95 Co, %100 Li	[49]
3 M H_2SO_4, H_2O_2,	-	99% Co and Li	[121]
3 M H_2SO_4, 1.5 M H_2O_2, 70 °C, 1 h	-	99.4% Co, 99% Li	[46]
2 M H_2SO_4 + 0.25 M H_2O_2, 90 °C, 3 h, 67 g/L	-	>99	[88]
H_2SO_4, glucose, 90 °C, 3 h	-	98% Co and Li	[91]
2 M H_2SO_4 + %% H_2O_2, 75 °C, 1 h, 100 g/L	-	99.1% Li, 70% Co	[122]
2 M H_2SO_4 + 2% H_2O_2, 60 °C, 2 h, %3,3 solid ratio	-	87.5% Li, 96.3% Co	[4]
1 M H_2SO_4, 5% H_2O_2, 95 °C, 4 h, 5% solid ratio	-	93.1% Li, 66.2% Co, 96.3% Ni, 50.2% Mn	[47]
2 M H_2SO_4, 4% H_2O_2, 70 °C, 2 h, 100 g/L	-	98.8% Li, 99.6% Co, 99.4% Ni, 97.8% Mn	[100]

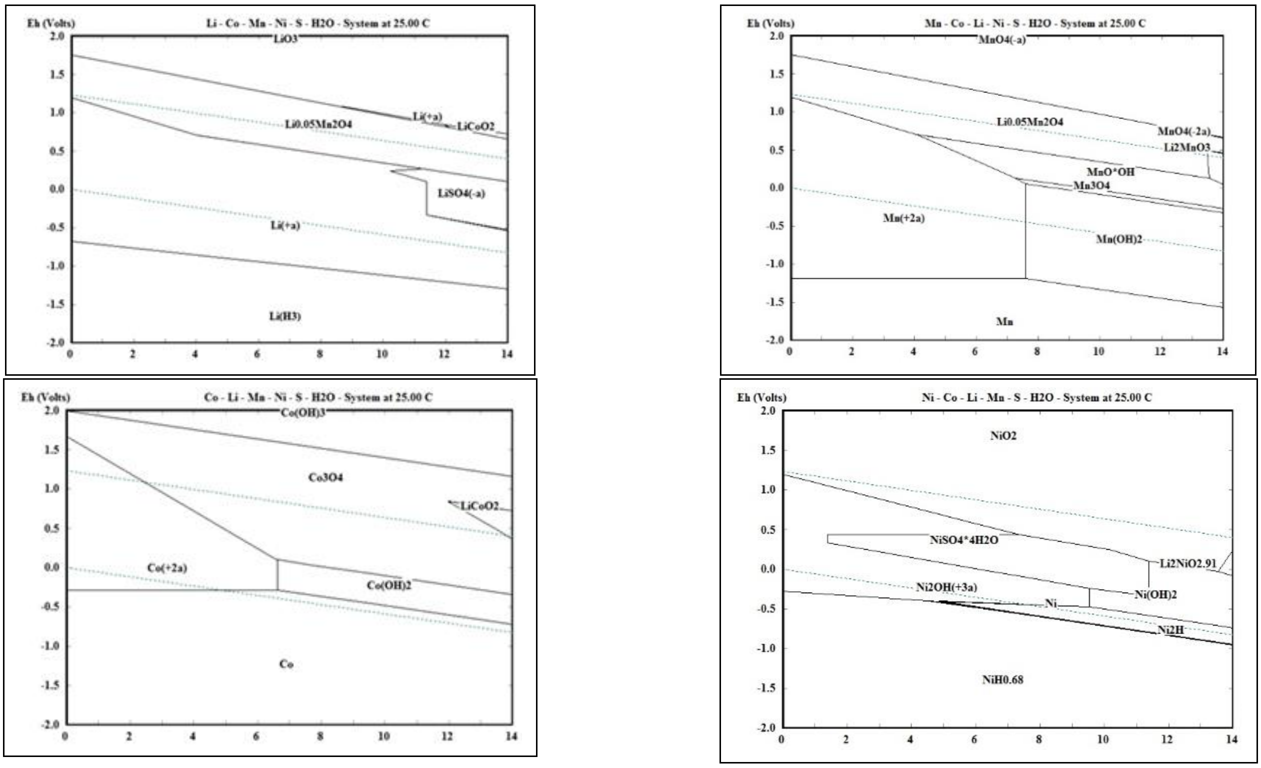

Figure 5. Eh-pH diagrams (25 °C) for $NaHSO_3$ system. (a): Li-SO_3-SO_4, (b): Co-SO_3-SO_4, (c): Mn-SO_3-SO_4, (d): Ni-SO_3-SO_4, in the presence of other elements [112].

In a recent study, Zhao et al. (2020) [95] utilised ethanol to reduce Co^{3+} to Co^{2+} in sulphuric acid leaching. When 3 M H_2SO_4 and 5% ethanol (by volume) are used (S/L= 20 g/L, 90 °C, 160 min.), >99% Li and Co recoveries were apparently obtained by these researchers. Yang et al. [113] (2020) found 97% Li, 96% Ni, 95% Co and 86%Mn extractions using hydrazine sulphate ($N_2H_6SO_4$, 30 g/L) as a reductant in sulphuric acid leaching (2 M, 50 g/L, 80 °C, 1 h). There are also studies in which various organic compounds are suggested as reducing agents. D-glucose ($C_6H_{12}O_6$) as the reducing reagent instead of H_2O_2 (Equation 9) was preferred by various researchers [87],[91],[114].

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow Li_2SO_4 + 2CoSO_4 + 4H_2O + O_2 \qquad (9)$$

Chen et al. [115] (2018) achieved 54%, 96%, 98% Co and 100%, 100% and 96% Li recoveries using cellulose, sucrose and glucose (0.4 g/g), respectively as reducing agents in sulphuric acid leaching (3 M, 95 °C, 25 g/L, 2 h). Glucose and sucrose were shown to have better reducing properties than cellulose (Glucose>sucrose>cellulose). Chen et al. (2019) [116] recovered 90% Co and all of Li, Ni and Mn using waste tea (0.3 g/g) as a reductant in sulphuric acid leaching (2 M, 90 °C, 50 g/L, 2 h). They stated that the polyphenols in tea have reducing properties. Various downstream treatment options appear to be available for purification and metal recovery from pregnant acid leach solutions. Cobalt can be precipitated as $CoC_2O_4.2H_2O$ (Equation 10) by ammonium oxalate from sulphuric acid leach solutions [4],[117].

$$CoSO_{4(l)} + (H_4)_2C_2O_{4(l)} \rightarrow CoC_2O_{4(s)} + (NH_4)_2SO_{4(s)} \quad (10)$$

Chen et al. [99] investigated the recovery of lithium and cobalt from waste lithium-ion batteries by alkali and acid leaching processes. First, after burning the carbon and binder at 700-800 °C, they leached the material with NaOH to recover Al prior to the leaching of Co and Li. In the presence of H_2O_2, they obtained 95% Co and 96% Li by H_2SO_4 leaching (4M H_2SO_4, 10% H_2O_2, L/S=10:1, 2 h, 85 °C).

3.2.2.2 Hydrochloric acid leaching

Another common leaching reagent used in the extraction of metals from LIB's is hydrochloric (HCl) acid (Table 3) [98]. Main disadvantages of this reagent system are the release of toxic Cl_2 gas during leaching and its highly corrosive nature, which requires the use of corrosion-resistant equipment with increased operating and investment costs. Although the sulphuric acid system is preferred in most cases [118] hydrochloric acid is stronger than sulphuric acid since hydrogen ions have much higher activity due to chloride in this system [119]. The dissolution reactions of lithium and cobalt from $LiCoO_2$ in HCl solutions are given in Equations 11 and 12.

$$2LiCoO_2 + 6HCl \rightarrow 2LiCl + 2CoCl_2 + 3H_2O + 0.5O_2 \quad (11)$$

$$2LiCoO_2 + 6HCl + H_2O_2 \rightarrow 2CoCl_2 + 2LiCl + 4H_2O + O_2 \quad (12)$$

In a previous study, Zhang et al. [14] achieved >99% Co and Li recovery by HCl leaching (4 M HCl, 80 °C, 1 h) from the spent lithium-ion battery cathode material. Wang et al. [105] also reported high extractions of metals, i.e. >99% Co, Mn, Ni and Li from lithium-ion battery cathode material by HCl leaching (4M HCl, 80 °C). The flowsheet showing the recovery of metals by HCl leaching from lithium-ion batteries is presented in Figure 6 [96].

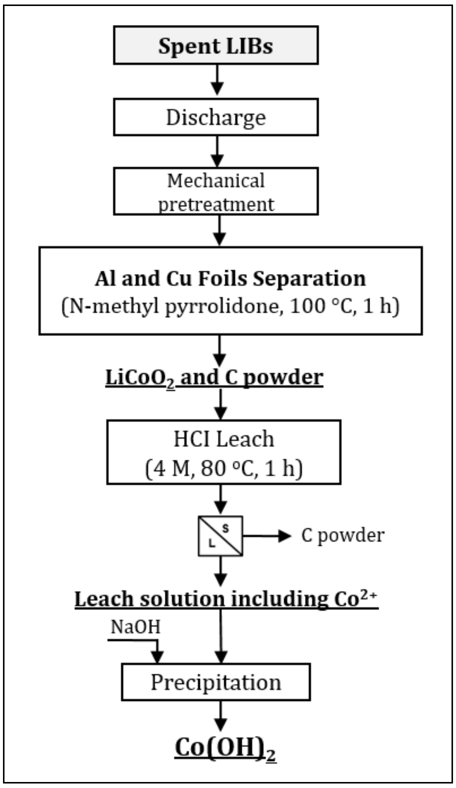

Figure 6. Recovery of metals from lithium-ion batteries by HCl leaching [96].

3.2.2.3 Nitric acid leaching

Nitric acid (HNO_3) with its high oxidising potential (E^0 = +0.96 V) can be exploited as oxidising lixiviant [125]. But, it is more expensive than other mineral acids. It can also be used as an oxidiser in sulphuric acid leaching [119]. The dissolution of Li and Co by leaching HNO_3 from $LiCoO_2$ is given in Equations 13 and 14. Zhang et al. [14] obtained 40% Co and 75% Li recovery in HNO_3 leaching but obtained 99% Co and Li recovery with the addition of 1.7% H_2O_2. Dorella and Mansur [36] also reported an increase in the cobalt recovery from 50% to 100% with the addition of H_2O_2. Castillo et al. [98] showed 100% lithium and 95% Mn recovery in the nitric acid leaching (1 M HNO_3, 80 °C, 2 h) (Table 4). It was separated from lithium by precipitating $Mn(OH)_2$ with NaOH at pH 10 (Figure 7).

$$2LiCoO_2 + 6HNO_3 \rightarrow 2Co(NO_3)_2 + 2LiNO_3 + 0.5O_2 + 3H_2O \quad (13)$$

$$2LiCoO_2 + 6HNO_3 + H_2O_2 \rightarrow 2Co(NO_3)_2 + 2LiNO_3 + 4H_2O + O_2 \quad (14)$$

Table 3. Parameters and results of studies on hydrochloric acid leaching (DMG: Dimethylglyoxime).

Leach conditions	Metal Recovery (Precipitation/SX)	Recovery	Reference
4 M HCl, 80 °C, 1 h, 100 g/L	Prec: $NaCO_3$; SX: 0.29 M D2EHPA and 0.9 M PC-88A	Leach: >99% Co and Li; SX: 0.9 M PC-88A, >99.9% Co and 12.6% Li; Prec.: 80% Li	[14]
4 M HCl, 80 °C, 1 h., 100 g/L	Prec.: 4 M NaOH, pH 6-8	$Co(OH)_2$	[96]
4 M HCl, 80 °C, 1 h., 20 g/L	Prec.: Mn ($KMnO_4$, pH 2, 40 °C); Ni (DMG, pH 9); Co (NaOH, pH 11); Li prec. ($NaCO_3$, 100 °C)	Leach: >99% Co, Mn, Ni, Li; Prec.: 97% Li ($LiCO_3$; 98% Mn, 97% Co and 97% Ni	[105]
3 M HCl + 3.5% H_2O_2, 80 °C, 1 h, 50 g/L	Prec.: NaOH for Co, pH 11-12; Na_2CO_3 for Li, 100 °C	95% Co and 93% Li	[97]
4 M HCl, 90 °C, 18 h, 50 g/L	Prec.: pH 3 and pH 11 with NaClO	100% Co and 99,99% Ni	[123]
4 M HCl, 90 °C, 2 h,	-	97% Li, 99% Co	[124]

Table 4. Parameters and results of studies on HNO_3 leaching.

Leach condition	Recovery	Reference
1 M HNO_3 + 1.7% H_2O_2, 75 °C, 1 h, 20 g/L	95% Co, Li	[45]
1 M HNO_3 + 1% H_2O_2, 80 °C, 1 h, 20 g/L	100% Co, Li	[106]
2 M HNO_3, 80 °C, 2 h	100% Li	[98]

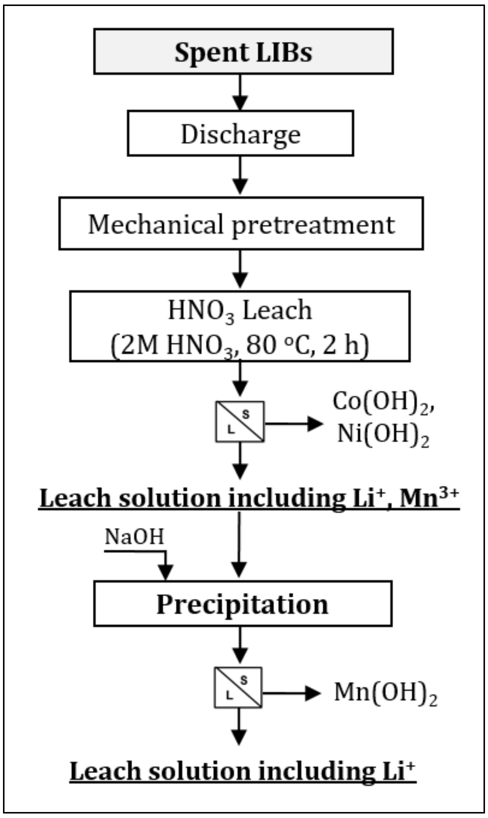

Figure 7. Recovery of metals from lithium-ion batteries by HNO_3 leaching [98].

3.2.3 Organic acid leaching

Due to the harmful nature of inorganic acids, many organic acids (Lactic acid-$C_3H_6O_3$, ascorbic acid-$C_6H_8O_6$, malic acid-$C_4H_6O_5$, citric acid-$C_6H_8O_7$, tartaric acid-$C_4H_6O_6$, aspartic acid-$C_4H_7NO_4$, oxalic acid-$H_2C_2O_4$, succinic acid-$C_4H_6O_4$, etc.) have been tested for the treatment of lithium-ion batteries (Table 5) [3],[34],[38,[51],[64],[72],[73],[126]-[30]. H_2O_2 is often used as a reductant for converting Co^{3+} to Co^{2+} in organic acid leaching. Compared to citric and malic acid, ascorbic acid was reported to have advantages such as low temperature and short leaching time under the same leaching conditions [126]. Oxalic acid leaching is more advantageous than other organic acids due to the selective precipitation of cobalt as oxalate salt (CoC_2O_4) [72],[74]. Because organic acids have relatively slow leaching kinetics, high acid concentrations are often required to obtain high metal extractions.

Organic acids such as methanosulfonic acid (MSA; CH_3SO_3H) and p-toluenesulfonic acid (TSA) have also been proposed in the leaching of Li and Co from lithium-ion batteries [131],[132]. Wang et al. [131] achieved 100% Li and Co recoveries from waste $LiCoO_2$ cathode material by MSA leaching (1 M MSA, 0.9% H_2O_2, 70 °C, 1 h, solid ratio: 20 g/L) in the presence of H_2O_2 as the reductant.

Table 5. Parameters and results of studies with organic acids.

Leach Condition	Recovery	Reference
1.5 M aspartic acid, 4% H_2O_2, 90 °C, 2 h, 10 g/L	60% Li and Co	[67]
1.5 M DL-Malic acid + 2% H_2O_2, 90 °C, 40 min., 20 g/L	90% Co and 100% Li	[34]
1.25 M citric acid + 1% H_2O_2, 90 °C, 30 min., 20 g/L	90% Co, 100% Li	[38]
1.25 M ascorbic acid, 70 °C, 20 min., 25 g/L	94,8% Co, 98,5% Li	[126]
1 M oxalic acid, 80 °C, 2 h, 50 g/L	98% Li and Co%	[74]
100 mM citric acid+ 20mM ascorbic acid, 80 °C, 6 h, 2 g/L	100% Li and Co	[42]
1.5 M succinic acid, 4% H_2O_2, 70 °C, 40 min., 15 g/L	100% Co, 96% Li	[82]
1 M oxalic acid, 95 °C, 2.5 h, 1.5%	98% Li, 97% Co	[72]
1 M MSA, 0.9% H_2O_2, 70 °C, 1 h, 20 g/L	100% Li and Co	[131]
0.6 M tartaric acid, 3% H_2O_2, 30 mL/g, 80 °C, 30 min.	98% Li and 97% Co	[116]

The reactions in the leaching of methanesulfonic acid, oxalic acid, citric acid, malic acid, succinic and ascorbic acid are given in Equations 15 to 20.

$$2LiCoO_2 + 6CH_4O_3S + H_2O_2 \rightarrow 2LiCH_3O_3S + 2(CH_3O_3S)_2Co + 4H_2O + O_2 \tag{15}$$

$$2LiCoO_2 + 7H_2C_2O_4 \rightarrow 2LiHC_2O_4 + 2Co(HC_2O_4)_2 + 4H_2O + 2CO_2 \tag{16}$$

$$LiCoO_2 + 6H_3Cit + H_2O_2 \rightarrow Co_3(Cit)_2 + Co(HCit) + Co(H_2Cit)_2 + Li_3Cit + Li_2(HCit) + Li(H_2Cit) + H_2O + O_2 \tag{17}$$

$$2LiCoO_2 + 6C_4H_6O_5 + H_2O_2 \rightarrow 2LiC_4H_5O_5 + 2Co(C_4H_5O_5)_2 + 4H_2O + O_2 \tag{18}$$

$$LiCoO_2 + 3C_4H_6O_4 + H^+ \rightarrow LiC_4H_5O_4 + Co(C_4H_5O_4)_2 + 2H_2O \tag{19}$$

$$2LiCoO_2 + 4C_6H_8O_6 \rightarrow Li_2C_6H_6O_6 + 2CoC_6H_6O_6 + C_6H_6O_6 + 4H_2O \tag{20}$$

Tartaric acid ($C_4H_6O_6$) has a lower cost and higher acidity than most organic acids [85]. It was used as a leaching and precipitating reagent in the selective separation and recovery of Co [85],[133]. In 2 M tartaric acid solution (4% H_2O_2, 17 g/L solids ratio, 70 °C, 30 min.), 99.07% Li, 98.64% Co, 99.31% Ni and 99.31% Mn extractions were reported [133]. The citric acid ($C_6H_8O_7$-H_3Cit), which is widely used as an organic lixiviant, ionises to H^+, H_2Cit^-, $HCit^{2-}$ and Cit^{3-} in leaching solutions and forms complexes such as $Co_3(Cit)_2$ and Li_3Cit [38],[90].

A variety of organic products/wastes such as Phytolacca Americana [92], waste tea [92], grape seed [93], and orange peels [94] have also been used as reducing agents in citric acid solutions. Chen et al. [92] found 98% Co and 99% Li, 83% Co and 98% Li, 96% Co and 98% Li using H_2O_2 (70 °C, 2 M, 0.6 g/g H_2O_2, solids ratio 50 g/L, 80 min.), Phytolacca Americana (80 °C, 1.5 M, 0.4 g/g PA, solids content 40 g/L, 120 min.) and waste tea (90 °C, 1.5 M, 0.4 g/g, solids content 30 g/L, 120 min.) respectively in citric acid leaching.

In a recent study, Wu et al. [94] used orange peels (200 mg) as a reductant in citric acid leaching (1 M, 90 °C, 25 g/mL, 24 h) and achieved complete extraction of metals (Co, Li, Ni and Mn). The authors mooted that the cellulose in orange peels turns into sugars such as glucose, which have reducing properties when heated under acidic conditions. Firstly, $Mn(OH)_2$ and $Ni(OH)_2$ were recovered at pH 12 using NaOH. In the second step, cobalt was recovered as $Co(OH)_2$ using ethanol (ethanol/solution = 1/10).

Using D-glucose ($C_6H_{12}O_6$) (0.5 g/g) as a reductant, Chen et al. [90] obtained high extractions of metals i.e. 99% Li, 92% Co, 91% Ni and 94% Mn in citric acid leaching (1.5 M, 80 °C, 20 g/L, 120 min.). D-glucose is easily oxidised and converted to gluconic acid, glyceric acid and CO_2, increasing the leaching efficiency [87],[91]. In the presence of D-glucose, high-valent transition metals such as Co^{3+} and Mn^{4+} are reduced to Co^{2+} and Mn^{2+}, respectively and hence, readily dissolved during leaching [134].

$$\begin{aligned} 18\,\mathrm{LiNi_{\frac{1}{3}}Co_{\frac{1}{3}}Mn_{\frac{1}{3}}O_2} + 18\mathrm{H_3Cit} + \mathrm{C_6H_{12}O_6} \\ \rightarrow 6\mathrm{Li_3Cit} + 2\mathrm{Co_3(Cit)_2} + 2\mathrm{Co_3(Cit)_2} \\ + 2\mathrm{Mn_3(Cit)_2} + 33\mathrm{H_2O} \end{aligned} \tag{21}$$

In the malic acid leaching of lithium-ion batteries, various waste products have been utilised as reducing reagents. Zhang et al. [93] used grape seeds as a reducing agent obtaining 92% Co and 99% Li extractions (0.6 g/g) in malic acid leaching (1.5 M, 80 °C, 180 min. 20 g/L). These researchers attributed the reducing properties of grape seed to its content of catechin, gallic acid and oligoprocyanidin as active substances.

3.3 Solution purification and metal recovery

Since the leaching solutions of lithium-ion batteries are highly acidic and contain many metals, solution purification and metal recovery stages may involve complex processes for the selective recovery of metals of interest [11]. Depending on the mechanical pretreatment applied, the cathode material contains varying amounts of Fe, Cu and Al from foil. It would be good practice to avoid Cu and Al leaching so as to ease the downstream processing for efficient and selective recovery of metals [118],[135]. Metals such as Cu, Fe, Mn and Al are often removed from Li, Co and Ni. These can then be recovered from clean solutions by precipitation or solvent extraction methods [3],[91],[136].

3.3.1 Precipitation

Pregnant leach solutions are treated to reject impurities such as Cu, Fe, Al and Mn through precipitation by using NaOH or $CaCO_3$ [36],[56]. Precipitation of metals from leaching solutions is a relatively easy and simple process. The required pH for precipitation of some metals as hydroxide is given in Table 6. Also, Figure 8 shows the precipitation curves of some metals from saturated NaCl solutions as a function of pH [137]. pH is one of the most important parameters controlling the precipitation of metals, allowing their selective recovery/removal under suitable conditions (Table 7). In this regard, from pregnant leach solutions, Co and Li can be recovered selectively by precipitation exploiting the difference in pH for the formation of their respective hydroxides.

Table 6. Precipitation pH of some metals as hydroxide (25 °C) [138].

Metal	pH
Ag	8.0
Zn	7.0
Co(II)	6.8
Ni	6.7
Fe(II)	5.5
Cu(II)	5.3
Co(III)	3.0
Fe(III)	2.0

Table 7. Studies to remove metals from leaching solutions.

Reagent	Metal	pH	Efficiency, %	Ref.
10% NaOH	Al, Fe	5,5	98% Al	[62]
4 M NaOH, Ca_2CO_3	Al, Cu, Fe	6,5	99%	[102]
NH_4OH	Al	5	80 %	[36]
NaOH	Al, Cu, Fe	5	100% Al, 100% Fe, 60% Cu	[91]
Na_2S	Cu		99,9% Cu	[103]

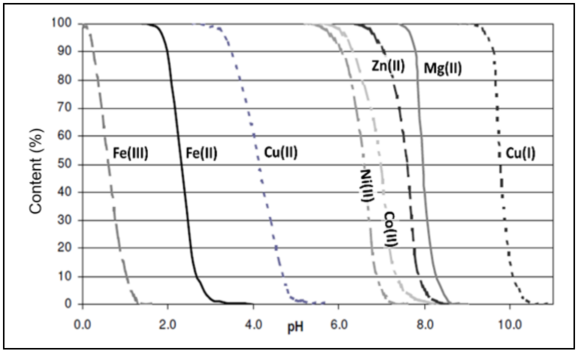

Figure 8. pH-dependent precipitation curves of some metals from saturated NaCl solutions [138].

Iron is removed as jarosite from leach solution (pH 3-3.5; 95 °C) (Equation 22), [99].

$$\begin{aligned} 3\mathrm{Fe_2(SO_4)_3} + 12\mathrm{H_2O} + \mathrm{Na_2SO_4} \\ \rightarrow \mathrm{Na_2Fe_6(SO_4)_4(OH)_{12}} \\ + 6\mathrm{H_2SO_4} \end{aligned} \tag{22}$$

Cobalt is recovered as $CoC_2O_4{\cdot}2H_2O$ (99.3% purity) by oxalic acid [93] and Li is recovered as Li_3PO_4 (98.5% purity) by phosphoric acid (H_3PO_4, 0.5 M) (60 °C, 30 min. 300 rpm) (Equations 23-24), [139]. It has been stated that the citric acid obtained after the metal recovery stage is reusable.

$$\mathrm{Co_3(Cit)_2} + 3\mathrm{H_2C_2O_4} \rightarrow 4\mathrm{CoC_2O_4}\downarrow + 2\mathrm{H_3Cit} \tag{23}$$

$$\mathrm{Li_3Cit} + \mathrm{H_3PO_4} \rightarrow \mathrm{Li_3PO_4}\downarrow + \mathrm{H_3Cit} \tag{24}$$

Joulie et al. [123] demonstrated that Co^{2+} could be oxidised to Co^{3+} with NaClO at pH 3 to selectively precipitate cobalt in the form of $Co_2O_3.3H_2O$ (Equations 25 and 26). Then, nickel is precipitated as nickel hydroxide at pH 11.

$$2\mathrm{Co^{2+}} + \mathrm{ClO^-} + 2\mathrm{H_3O^+} \rightarrow 2\mathrm{Co^{3+}} + \mathrm{Cl^-} + 3\mathrm{H_2O} \tag{25}$$

$$2\mathrm{Co^{3+}} + 6\mathrm{OH^-} \rightarrow \mathrm{Co_2O_3.3H_2O} \tag{26}$$

Recovery of cobalt by precipitation with ammonium oxalate from purified leaching solutions was also reported [30],[62].

After the recovery of Co^{2+} and Ni^{2+} by solvent extraction from leach solutions. Lithium is usually precipitated from the solution using Na_2CO_3, CO_2 or H_3PO_4 (Equations 27 and 28), [91],[140],[141].

$$2Li^+ + CO_3^{2-} \rightarrow Li_2CO_3 \quad (27)$$

$$3Li^+ + PO_4^{3-} \rightarrow Li_3PO_4 \quad (28)$$

Manganese was recovered from the solution as MnO_2 or Mn_2O_3 by adding potassium permanganate (0.5 M $KMnO_4$) [105]. Then, nickel (98.5%), cobalt (96.8%) and lithium (92.7%) were recovered as $Ni(C_4H_6N_2O_2)_2$, $CoC_2O_4.2H_2O$ and Li_3PO_4, respectively, using dimethylglyoxime (DMG, 0.2 M, $C_4H_8N_2O_2$) (Equation 29), oxalic acid (0.5 M $H_2C_2O_4$) (Equation 23) and phosphoric acid (0.5 M H_3PO_4) (Equation 24) from the purified solutions.

$$6C_4H_8N_2O_2 + Ni_3(Cit)_2 \rightarrow 3Ni(C_4H_6N_2O_2)_2 \downarrow + 2H_3Cit \quad (29)$$

Manganese was removed at pH 4 (70 °C) with ammonium persulfate (Equation 30) [140]. Then, the concentrated Co^{2+} from the purified solution by solvent extraction (P507) was recovered as cobalt oxalate (93% recovery, >99.9% purity) by adding ammonium oxalate (ratio: 1.15:1; pH: 1.5).

$$Mn^{2+} + (NH_4)_2S_2O_8 + H_2O \rightarrow MnO_2 + (NH_4)_2SO_4 + H_2SO_4 + 2H^+ \quad (30)$$

Wang et al. [105] reported the treatment of HCl leach solutions for the recovery of Mn, Ni, Co and Li. They initially precipitated Mn as MnO_2 by using $KMnO_4$ at low pH values. Then, these investigators used NH_3 to complex Ni as $[Ni(NH_3)_6]^{2+}$ and precipitated it with dimethylglyoxime at pH 9. Co was also recovered as hydroxide by further increasing the pH using NaOH to 11. A saturated solution of Na_2CO_3 was used to precipitate Li_2CO_3 from the residual solution at 100 °C. This scheme of recovery process is complex with high-consumption reagents. Nayl et al. [100] described a process in which metals are precipitated as carbonate with sodium carbonate after adjusting the pH using NaOH (Figure 9).

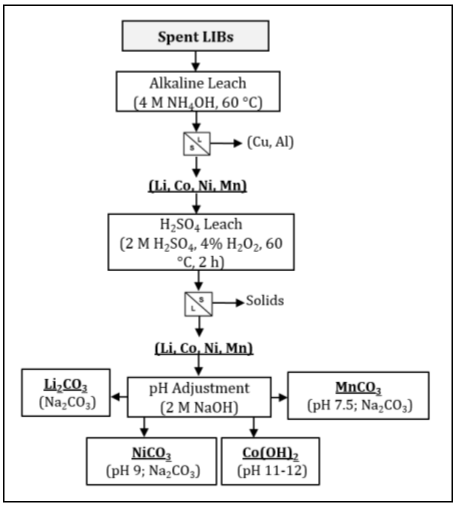

Figure 9. Recovery of Li, Co, Mn and Ni by precipitation from leaching solutions [100].

They reported 91% Ni as $NiCO_3$ recovery from the leach solution at pH 9. Then, the solution pH was increased to 11-12 with NaOH at room temperature to recover Co as cobalt hydroxide. Finally, lithium was precipitated as Li_2CO_3. by further adding Na_2CO_3 to the solution (at 90 °C). Pure Li_2CO_3 was obtained after washing the precipitate with hot water to remove the residual Na prior to drying at 100 °C.

Aktas et al. [101] investigated the crystallisation of metals from sulphuric acid solutions of waste LIBs by using ethanol. They obtained copper sulphate ($CuSO_4.3H_2O$) at 96% Cu recovery and cobalt sulphate ($CoSO_4$) at 92% Co recovery with ethanol at a solution-to-ethanol ratio of 3. Cobalt that did not precipitate with ethanol but remained in solution was precipitated as cobalt hydroxide ($Co(OH)_2$) by increasing the pH using lithium hydroxide to pH 10. After the removal of cobalt, the residual solution was acidified with sulphuric acid to precipitate lithium sulphate (Li_2SO_4) at 90% recovery with the addition of ethanol. These investigators also noted the precipitation of 99% of aluminium as aluminium hydroxide ($Al(OH)_3$).

3.3.2 Solvent extraction

Solvent extraction (SX) is the process of extracting the metal from the inorganic (aqueous) phase into the organic phase by bonding a liquid organic reagent with the metal in the solution [142]. It is used both to remove impurities and to recover metals from the leaching solutions of lithium-ion batteries (Table 8). Many SX reagents are available with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) and the hydroxy-oxime derivative (Acorga M5640) being extensively used in SX applications [143]. The main detractions to solvent extraction include the challenges in Co/Ni/Mn separation, high reagent requirements for the concentrated solutions and high operating and capital costs [5].

Metals such as Cu, Al, Co, Ni, Fe and Mn can be selectively extracted at pH ≤6.5 using a suitable SX process while lithium remains in solution. SX reagents, including Cyanex 272, Acorga 5640 and PC-88A, appear to be used for the treatment of pregnant leach solutions of waste LIBs [30],[62]. Pranolo et al. [144] exploited the synergistic effect of two solvents (7% PC-88A and 2% Acorga M5640) to effectively separate Fe^{3+}, Cu^{2+} and Al^{3+} from Co^{2+}, Ni^{2+} and Li^+ (pH 4-4.5).

$$2RH_{(org.)} + M^{2+}_{(aq)} \rightarrow R_2M_{(org.)} + 2H^+ \quad (31)$$

(RH: Acidic extract; M: Metal)

$$ROH_{(org.)} + A^-_{(aq)} \rightarrow RA_{(org.)} + OH^- \quad (32)$$

(RH: Alkaline extract; A: Metal complex)

Cyanex 272 is widely used commercially in the Co/Ni separation (pH 5.5-6) [62],[102],[118],[144],[145]. PC-88A is generally used in the extraction of Co from Ni and Li [3],[102],144]. Suzuki et al. [146] proposed a for the recovery of Al, Cu, Co and Li from synthetic acidic sulphate solutions (2x10^{-3} M metal, 0.2 M Na_2SO_4) by solvent extraction (Figure 10). In the first step, after copper was recovered by Acorga M5640 (pH: 1.5-2), aluminium was selectively extracted with 2-ethylhexyl 2-ethylhexylphosphonic acid (PC-88A, pH: 2.5-3). Cobalt and lithium were separated with high separation efficiency (>98%) by PC-88A/TOA (Tri-n-octylamine, pH: 5.5-6). Granata et al. [91] initially precipitated Fe, Al and Cu as hydroxide at pH 5 from the sulphuric acid-leaching solution (2M H_2SO_4, S/L: 100 g/L, 90 °C, 50% glucose).

Table 8. Removal of metals from leaching solutions by solvent extraction method.

Solvent	Metal	pH	Efficiency, %	Stripping from the organic phase	Reference
0.3 M Cyanex 272	Al	2.5-3	100% Al	-	[118]
10% Acorga 5640	Cu	1.5-1.7	98.5% Cu	2 M H_2SO_4, O:L=1:1, 2-stage	[62],[145]
7% PC-88A and 2% Acorga 5640	Al, Cu, Fe	4-4.5	100% Al, Cu, Fe	100 g/L H_2SO_4, O:L=1:8, 2-stage	[144]
10% Acorga 5640	Cu	1.5-2	100% Cu	3 M H_2SO_4	[146]
%10 PC-88A	Al	2.5-3	100% Al		

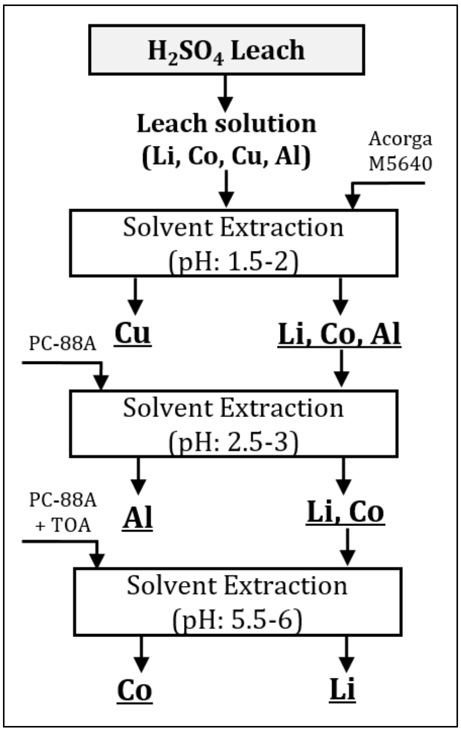

Figure 10. Recovery of Cu, Co, Li and Al from acidic sulphate solutions by solvent extraction method [146].

They used solvent extraction (Cyanex 272 and D2HEPA) to obtain a purified solution from which cobalt carbonate with high purity (47% Co) (Na_2CO_3, pH: 9-10, 2 h) was precipitated. They found that the purity of cobalt was limited to 36-37% Co without the application of SX. The researchers also reported the recovery of Li_2CO_3 with 98% purity through crystallisation at 80% yield as the final stage of the proposed solution purification and recovery process.

4 Industrial applications

There are many commercial applications for metal recovery from spent batteries (Table 9), [15],[124],[136],[147]. Toxco and Sony processes were the first commercial processes to recycle lithium-ion batteries. The Toxco process is designed for the treatment of all types of lithium-containing waste. The main products are cobalt, lithium and other important metals.

In the recycling of spent LIBs, four basic recycling technologies are mechanical pretreatment, mechanical+hydrometallurgical, pyrometallurgical, pyrometallurgical+hydrometallurgical. Some companies separate only battery components by mechanical processes and sell them to others that recover metals by hydrometallurgical or pyrometallurgical operations. While high purity lithium can be recovered in hydrometallurgical processes, it remains in the slag phase in pyrometallurgical processes [52].

4.1 Recupyl (France)

Recupyl process is a combination of physical and chemical processes to produce lithium carbonate. In this process, the mechanical treatment is carried out in an inert environment (CO_2 and 10-35% argon). Plastics, steel and copper are separated by physical separation processes such as screening, magnetic and gravity separation. The fine powder is separated by sieving and subjected to hydrolysis and leaching processes. The hydrolysis solution is filtered to obtain a pulp containing an alkaline lithium salt solution, metal oxides and carbon. Lithium is precipitated as Li_2CO_3 using CO_2 obtained from mechanical processes. Metal oxides are dissolved by sulfuric acid in the leaching process. Copper is cemented using steel balls. From the purified solution, cobalt (II) is oxidised with NaClO to precipitate as hydroxide ($Co(OH)_3$). In the process, lithium remaining in solution is precipitated with CO_2 gas (Figure 11), [52],[124],[148].

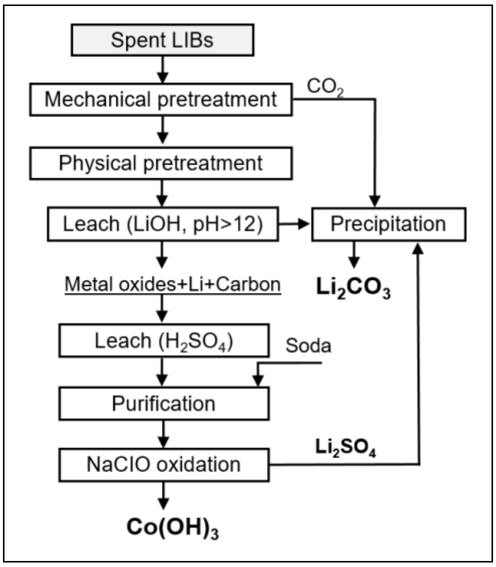

Figure 11. Flowsheet of Recupyl (France) process [124].

4.2 Toxco (Canada)

This process is designed to treat various types of batteries. The first stage of the process involves cryogenic crushing in a liquid nitrogen environment to avoid fire hazards. After crushing, the fraction that contains protective plastic and steel mixture, referred to as 'Li-ion fluff', is removed. Large batteries are cut in an alkaline environment to neutralise acidic components and dissolve lithium salts as LiCl and Li_2SO_4. The dissolved salts are precipitated and separated in the filter press for use in the production of lithium carbonate. The waste is sent to the cobalt recovery. The lithium-bearing solution is carbonated to produce Li_2CO_3 (Figure 12). Copper is extracted in the next step [60],[124],[150].

Table 9. Industrial lithium-ion battery recycling processes [149].

Proses	Company	Material	Product
Hydrometallurgy	Recupyl, France	All batteries	$LiCoO_2$, $Co(OH)_2$
	Toxco, Canada	Li, Ni- batteries	$LiCoO_2$,
	Sony, Japan	Li-ion batteries	$Co(OH)_2$
Pyrometallurgy	Eurodieuze, France	All battery	Ni, Cd, steel
	Zimaval, France	Zn, Mn, Hg battery	Zn, Mn
	Dowa, Japan	All batteries	Co, Ni
	Batrec AG, Schweiz	Li, Hg battery	-
	Nippon, Japan	Ni-Cd, Ni-MH, LIB	Ni, Co, Cd, Al, Cu
	Accurec GmbH, Germany	All batteries	Ni, Cd, Fe, $LiCO_3$
	INMETCO, ABD	Ni-Cd	Cd, Ni, Zn
Pyro-hydrometallurgy	Umicore, Belgium	LIB's, Ni-MH	Co, Ni
	Glencore Plc., Schweiz	LIB's, EV	Cu, Ni, Zn, Li

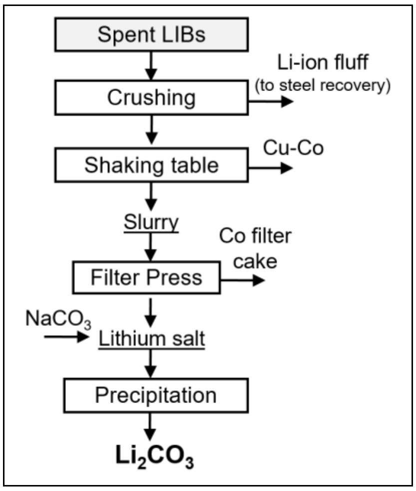

Figure 12. Flowsheet of Toxco (Canada) process [136].

4.3 Umicore (Belgium)

Umicore process is a combined pyro-and-hydro-metallurgical process. Spent waste batteries are melted (500 °C) with the patented ultra-high temperature (UHT) technology based on plasma technology to obtain a molten matte containing metals (Co, Ni, Cu, Fe). Li, Al, and Mn remain in the slag [60],[69],[124].

Metals are recovered using the hydrometallurgical treatment that involves sulphuric acid leaching and solvent extraction. Ni and Co are obtained as cobalt oxide and $Ni(OH)_2$ products [124]. A slag containing Al, Ca, Li, and Si is formed as a by-product, which can be used as a building material. Cobalt compounds are used in the production of $LiCoO_2$. Plastic, solvent and graphite are removed as a gas during smelting operation [52].

5 Environmental impacts of spent lithium-ion batteries

Mrozik et al. [151] provided a comprehensive review that identified potential routes and hazards for the environmental impacts of LIBs. There appear no universal standards on the disposal of waste LIBs worldwide. Hazardous materials that are released during the management of waste LIBs through landfilling, incineration and recycling, as well as undesired incidents such as fires and explosions, can cause environmental pollution. These materials include vapours/gases (i.e. HF, CO or HCN), heavy metals present as oxides (i.e. LMO, NMC) and degradation products of electrolyte such as alkylfluorophosphates [151],[152],[153].

6 Conclusions

The importance of lithium-ion batteries (LIBs) has increased in recent years due to the widespread use of portable electrical and electronic equipment (mobile phones, laptops, video cameras, etc.) and electric cars (EV, PHEV, HEV). Accordingly, there is a recent trend of an increase in the demand and prices of lithium and cobalt. Since LIBs contain heavy metals (Cu, Pb, Cd, Zn) and electrolytes that are harmful to the environment and human health, they should be appropriately managed. LIBs with a chemical composition of Li (1.5-7%), Co (5-20%), Cu (8-10%), Ni (5-10%), Mn (15-20%) and Al (5-8%) are regarded as a significant secondary source for these metals.

Mechanical, hydrometallurgical and pyrometallurgical treatment processes are used for the recycling process of LIBs. However, hydrometallurgical processes that often involve leaching of metals and the recovery of metals after the removal of impurities from leaching solutions, seem to have received most attention. Sulfuric acid in the presence of various reducing agents, is widely used in the leaching of LIBs. Biodegradable organic acids are also extensively promoted as environmentally-friendly alternatives. Chemical precipitation and/or solvent extraction processes are extensively exploited for the treatment of leach solutions for the recovery of metals in various forms. Production of metal hydroxides and carbonates as main products has received the most attention.

R&D studies seem to continue for the development of sustainable technologies/processes that can effectively recover metals from spent LIBs with an emphasis on minimising the environmental impact, simplifying recycling processes, and reducing costs.

7 Acknowledgment

The author would like to extend their sincere appreciations to the TÜBİTAK (Project No: 120N275) through the European Union Horizon 2020-ERAMIN2-ELiMINATE Project and to the Research Foundation of Karadeniz Technical University (Project No: FBA-2021-9432) for their financial support.

8 Author contribution statements

In the scope of this study, Oktay CELEP in the conceptualisation, writing-original draft and the literature review; Ersin Y. YAZICI in the writing-review and editing; Hacı DEVECI in writing - review and editing, supervision; the Christie DORFLING in the spelling and checking the article in terms of content were contributed.

9 Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the article prepared. There is no conflict of interest with any person/institution in the article prepared.

10 References

[1] Grey CP, Tarascon JM. "Sustainability and in situ monitoring in battery development". *Nature Material*, 16(1), 45-56, 2017.

[2] Liu C, Lin J, Cao, H, Zhang Y, Sun Z. "Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review". *Journal of Cleaner Production*, 228, 801-813, 2019.

[3] Choubey PK, Chung K, Kim M, Lee J, Srivastava RR. "Advance review on the exploitation of the prominent energy-storage element Lithium. Part II: From sea water and spent lithium ion batteries (LIBs)". *Minerals Engineering*, 110, 104-121, 2017.

[4] Lv W, Wang Z, Cao H, Sun Y, Zhang Y, Sun Z. "A critical review and analysis on the recycling of spent lithium-ion batteries". *ACS Sustainable Chemistry and Engineering*, 6(2), 1504-1521, 2018.

[5] Sole KC, Parker J, Cole PM, Mooiman MB. "Flowsheet options for cobalt recovery in African copper-cobalt hydrometallurgy circuits". *Mineral Processing and Extractive Metallurgy Review*, 40(3), 194-206, 2018.

[6] European Commission. "Critical Raw Materials Resilience: Charting A Path Towards Greater Security And Sustainability". https://ec.europa.eu, (21.06.2020).

[7] Amos CD, Roldan MA, Varela M, Goodenough JB, Ferreira PJ. "Revealing the reconstructed surface of $Li[Mn_2]O_4$". *Nano Letters*, 16(5), 2899-2906, 2016.

[8] Goodenough JB, Kim Y. "Challenges for rechargeable Li batteries". *Chemistry of Materials*, 22(3), 587-603, 2010.

[9] Goodenough JB, Park KS. "The Li-ion rechargeable battery: a perspective". *Journal of the American Chemical Society*, 135(4), 1167-1176, 2013.

[10] Yuan LX, Wang ZH, Zhang WX, Hu XL, Chen JT, Huang YH, Goodenough JB. "Development and challenges of $LiFePO_4$ cathode material for lithium-ion batteries". *Energy & Environmental Science*, 4(2), 269-284, 2011.

[11] Chagnes A, Światowska J. Lithium Process Chemistry: Resources, Extraction, Batteries and Recycling. 1st ed. Amsterdam, Holland, Elsevier, 2015.

[12] Chagnes A, Pospiech B. "A brief review on hydrometallurgical technologies for recycling spent lithium ion batteries". *Journal of Chemical Technology & Biotechnology*, 88, 1191-1199, 2013.

[13] Nishi Y. *Performance of The First Lithium İon Battery and İts Process Technology*. Editors: Wakihara M, Yamamoto O. Lithium ion batteries: Fundamentals and Performance, 181-198, Tokyo, Japan, Kodansha Ltd., 1998.

[14] Zhang P, Yokoyama T, Itabashi O, Suzuki TM, Inoue K. "Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries". *Hydrometallurgy*, 47(2), 259-271, 1998.

[15] Gaines L, Cuenca R. "Costs of lithium-ion batteries for vehicles. Argonne National Laboratory". Chicago University, Illinois, USA, Scientific Report, ANDL/ESD-42, 2000.

[16] Evans KR. *Lithium*. Editor: Gunn G. Critical Metals Handbook, New Jersey, USA, Wiley-Blackwell, 230-260, 2014.

[17] Speirs J, Contestabile M, Houari Y, Gross R. "The future of lithium availability for electric vehicle batteries". *Renewable Sustainable Energy Reviews*, 35, 183-193, 2014.

[18] Gruber PW, Medina PA, Keoleian GA, Kesler SE, Everson MP, Wallington TJ. "Global lithium availability: a constraint for electric vehicles?". *Journal of Industrial Ecology*, 15(5), 760-75, 2011.

[19] Gulzar U, Goriparti S, Miele E, Li T, Maidecchi G, Toma A, Angelis FD, Capiglia C, Zaccari RP. "Next-generation textiles: from embedded supercapacitors to lithium ion batteries". *Journal of Materials Chemistry*, 4, 16771-16800, 2016.

[20] Ferreira DA, Prados LMZ, Majuste D, Mansur MB. "Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries". *Journal of Power Sources*, 187(1), 238-246, 2009.

[21] Bankole OE, Gong C, Lei L. "Battery recycling technologies: recycling waste lithium ion batteries with the impact on the environment in-view". *Journal of Ecology and Environment*, 4(1), 14-28, 2013.

[22] Zhang T, He Y, Wang F, Ge L, Zhu X, Li H. "Chemical and process mineralogical characterisations of spent lithium-ion batteries: an approach by multi-analytical techniques". *Waste Management*, 34, 1051-1058, 2014.

[23] Megahed S, Scrosati B. "Lithium-ion rechargeable batteries", *Journal of Power Sources*, 51, 79-104, 1994.

[24] Aurbach D, Talyosef Y, Markovsky B, Markevich E, Zinigrad E, Asraf L. "Design of electrolyte solutions for Li and Li-ion batteries: A review". *Electrochim Acta*, 50, 247-254, 2004.

[25] Lain MJ. "Recycling of lithium ion cells and batteries". *Journal of Power Sources*, 97-98, 736-738, 2001.

[26] Tarascon JM, Armand M. "Issues and challenges facing rechargeable lithium batteries". *Nature*, 414, 359-367, 2001.

[27] Wakihara M. "Recent developments in lithium ion batteries". *Materials Science and Engineering: R: Reports*, 33(4), 109-134, 2001.

[28] Zhang X, Cao H, Xie Y, Ning P, An H, You H, Nawaz F. "A closed-loop process for recycling $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from the cathode scraps of lithium ion batteries: process optimisation and kinetics analysis". *Separation and Purification Technology*, 150, 186-195, 2015.

[29] Vassura I, Morselli L, Bernardi E, Passarini F. "Chemical characterisation of spent rechargeable batteries". *Waste Management*, 29, 2332-2335, 2009.

[30] Swain B. "Recovery and recycling of lithium: a review". *Separation and Purification Technology*, 172, 388-403, 2017.

[31] Peng C, Hamuyuni J, Wilson BP, Lundström M. "Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system". *Waste Management*, 76, 582-590, 2018.

[32] Pindar S, Dhawan N. "Carbothermal reduction of spent mobile phones batteries for the recovery of lithium, cobalt, and manganese values". *The Journal of The Minerals, Metals & Materials Society*, 71, 4483-4491, 2019.

[33] Ordonez J, Gago EJ, Girard A. “Processes and technologies for the recycling and recovery of spent lithium-ion batteries”. *Renewable and Sustainable Energy Reviews*, 60, 195-205, 2016.

[34] Li L, Jing G, Renjie C, Feng W, Shi C, Xiaoxiao Z. “Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries”. *Waste Management*, 30, 2615-2621, 2010.

[35] Kim DS, Sohn JS, Lee CK, Lee JH, Han KS, Lee YI. “Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries”. *Journal of Power Sources*, 132(1-2), 145-149. 2004.

[36] Dorella G, Mansur MB. “A study of the separation of cobalt from spent Li-ion battery residues”. *Journal Power Sources*, 170(1), 210-215, 2007.

[37] Paulino JF, Busnardo NG, Afonso JC. “Recovery of valuable elements from spent Li-batteries”. *Journal of Hazardous Materials*, 150(3), 843-849, 2008.

[38] Li L, Ge J, Wu F, Chen R, Chen S, Wu B. “Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant”. *Journal of Hazardous Materials,* 176, 288-293, 2010.

[39] Li J, Wang G, Xu Z. “Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent LiCoO2/graphite lithium batteries”. *Journal of Hazardous Materials,* 302, 97-104. 2016.

[40] Santos VEO, Celante VG, Lelis MFF, Freitas MBJG. “Chemical and electrochemical recycling of the nickel, cobalt, zinc and manganese from the positives electrodes of spent NieMH batteries from mobile phones”. *Journal of Power Sources*, 218, 435-444, 2012.

[41] Bertuol DA, Machado CM, Silva ML Calgaro, C.O, Dotto GL, Tanabe EH. “Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction”. *Waste Management*, 51, 245-251, 2016.

[42] Nayaka GP, Manjanna J, Pai KV, Vadavi R, Keny SJ, Tripathi V.S. “Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids”. *Hydrometallurgy*, 151, 73-77, 2015.

[43] Zheng Y Long, HL, Zhou L, Wu ZS, Zhou X, You L, Yang Y, Liu J.W. “Leaching procedure and kinetic studies of cobalt in cathode materials from spent lithium ion batteries using organic citric acid as leachant”. *International Journal of Environmental Research,* 10(1), 159-168, 2016.

[44] Wang H, Huang K, Zhang Y, Chen X, Jin W, Zheng S, Zhang Y, Li P. “Recovery of lithium, nickel, and cobalt from spent lithium-ion battery powders by selective ammonia leaching and an adsorption separation system”. *ACS Sustainable Chemistry & Engineering,* 5(12), 11489-11495, 2017.

[45] Lee CK, Rhee KI. “Preparation of $LiCoO_2$ from spent lithium-ion batteries”. *Journal of Power Sources*, 109, 17-21. 2002.

[46] Li J, Zhao R, He X, Liu H. “Preparation of $LiCoO_2$ cathode materials from spent lithium-ion batteries”. *Ionics,* 15, 111-113, 2009.

[47] Meshram P, Pandey BD, Mankhand TR. “Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects”. *Waste Management*, 45, 306-313, 2015.

[48] Liu YJ, Hu QY, Li XH, Wang ZX, Guo HJ. “Recycle and synthesis of $LiCoO_2$ from incisors bound of Li-ion batteries”. *Transaction Nonferrous Metals Society*, 16, 956-959, 2006.

[49] Shin SM, Kim NH, Sohn JS, Yang DH, Kim YH. “Development of a metal recovery process from Li-ion battery wastes”. *Hydrometallurgy*, 79, 172-181, 2005.

[50] Sun L, Qiu K. “Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries”. *Journal of Hazardous Materials*, 194, 378-384, 2011.

[51] Gao W, Zhang X, Zheng X, Lin X, Cao H, Zhang Y, Sun Z. “Lithium carbonate recovery from cathode scrap of spent lithium-ion battery: a closed-loop process”. *Environmental Science & Technology*, 51, 1662-1669, 2017.

[52] Ekberg C, Petranikova M. *Lithium Batteries Recycling*. Editors: Chagnes A, Swiatowska J. Lithium Process Chemistry: Resources, Extraction, Batteries and Recycling, 233-265, Amsterdam, Holland, Elsevier, 2015.

[53] Fergus JW. “Recent developments in cathode materials for lithium ion batteries”. *Journal of Power Sources*, 195(4), 939-954, 2010.

[54] Scrosati B, Garche J. “Lithium batteries: status, prospects and future”. *Journal of Power Sources*, 195(9), 2419-2430, 2010.

[55] Zeng X, Li J. “Spent rechargeable lithium batteries in e-waste: Composition and its implications”. *Frontiers of Environmental Science & Engineering*, 8, 792-796, 2014.

[56] Gratz E, Sa Q, Apelian D, Wang Y. “A closed loop process for recycling spent lithium ion batteries”. *Journal of Power Sources*, 262, 255-262, 2014.

[57] Nitta N, Wu F, Lee JT, Yushin G. “Li-ion battery materials: present and future”. *Materials Today*, 18(5), 252-264, 2015.

[58] Huang B, Pan Z, Su X, An L. “Recycling of lithium-ion batteries: Recent advances and perspectives”. *Journal of Power Sources*, 399, 274-286, 2018.

[59] Winslow KM, Laux SJ, Townsend TG. “A review on the growing concern and potential management strategies of waste lithium-ion batteries”. *Resources, Conservation and Recycling*, 129, 263-277, 2018.

[60] Liu F, Peng C, Porvali A, Wang Z, Wilson BP, Lundström M. “Synergistic recovery of valuable metals from spent nickel-metal hydride batteries and lithium ion batteries”. *ACS Sustainable Chemistry & Engineering*, 19, 16103-16111, 2019.

[61] Mossali E, Picone N, Gentilini l, Rodriguez O, Perez JM. “Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments”. *Journal of Environmental Management*, 2020. Doi: 10.1016/j.jenvman.2020.110500.

[62] Nan J, Han D, Zuo X. “Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction”. *Journal of Power Sources*, 152, 278-284, 2005.

[63] Diekmann J, Hanisch C, Froböse L, Schälicke G, Loellhoeffel, T, Fölster AS, Kwade A. “Ecological recycling of lithium-ion batteries from electric vehicles with focus on mechanical processes”. *Journal of the Electrochemical Society*, 164, A6184-A6191, 2016.

[64] Chen X, Ma H, Luo C, Zhou T. "Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid". *Journal of Hazardous Materials*, 326, 77-86, 2017.

[65] Kükrer T. Taşınabilir Elektronik Atık Pillerinden Lityum ve Kobalt Geri Kazanımı. Doktora Tezi, Süleyman Demirel Üniversitesi, Isparta, Türkiye, 2010.

[66] Nie H, Xu L, Song D, Song J, Shi X, Wang X, Zhang L, Yuan Z. "$LiCoO_2$: recycling from spent batteries and regeneration with solid state synthesis". Green Chemistry, 17(2), 1276-1280, 2015.

[67] Xu J, Thomas HR, Francis RW, Lum KL, Wang J, Liang B. "A review of processes and technologies for the recycling of lithium-ion secondary batteries". *Journal of Power Sources*, 177, 512-527, 2008.

[68] Fan B, Chen X, Zhou T, Zhang J, Xu B. "A sustainable process for the recovery of valuable metals from spent lithium-ion batteries". *Waste Management Research*, 34, 474-481, 2016.

[69] Georgi-Maschler T, Friedrich B, Weyhe R, Heegn H, Rutz M. "Development of a recycling process for Li-ion batteries". *Journal of Power Sources*, 207, 173-182, 2012.

[70] Yang Y, Huang G, Xu S, He Y, Liu X. "Thermal treatment process for the recovery of valuable metals from spent lithium-ion batteries". *Hydrometallurgy*, 165, 390-396, 2016.

[71] Guo H, Kuang G, Yang JX, Hu S. "Fundamental research on a new process to remove Al^{3+} as potassium alum during lithium extraction from lepidolite", *Metallurgical and Materials Transactions B*, 47(6), 3557-3564, 2016.

[72] Zeng X, Li J, Shen B. "Novel approach to recover cobalt and lithium from spent lithium-ion battery using oxalic acid". *Journal of Hazardous Materials*, 295, 112-118, 2015.

[73] Golmohammadzadeh R, Faraji F, Rashchi F. "Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review". *Resources, Conservation & Recycling*, 136, 418-435, 2018.

[74] Sun L, Qiu K. "Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries". *Waste Management*, 32, 1575-1582, 2012.

[75] Lee CH, Chen MJ, Tsai SL. *Treatment and Recycling of Scrap Lithium Battery*. Editor: Warey P.B. New research on hazardous materials, 209-224, Hauppauge, New York, USA, Nova Science Pub In., 2007.

[76] Garcia EM, Federal U, Carlos DS, Pereira EC. "Electrodeposition of cobalt from spent Li-ion battery cathodes by the electrochemistry quartz crystal microbalance". *Journal of Power Sources*, 185, 549-553, 2008.

[77] Wang D, Wen H, Chen H, Yang Y, Liang H. "Chemical evolution of $LiCoO_2$ and $NaHSO_4 \cdot H_2O$ mixtures with different mixing ratios during roasting process". *Chemical Research in Chinese Universities*, 32, 674-677, 2016.

[78] Amato A, Rocchetti L, Fonti V, Atia TA, Altimari P, Moscardini E, Toro L, Pagnanelli F, Beolchini F. "Recovery of critical metals from LCDs and Li-ion batteries". *Electronics Goes Green 2016*, Berlin, Germany, 07-09 September 2016.

[79] Guzolu JS, Gharabaghi M, Mobin M, Alilo H. "Extraction of Li and Co from Li-ion batteries by chemical methods". *Journal of The Institution of Engineers (India): Series D*, 98, 43-48, 2017.

[80] Zheng X, Gao W, Zhang X, He M, Lin X, Cao H, Zhang Y, Sun Z. "Spent lithium-ion battery recycling-reductive ammonia leaching of metals from cathode scrap by sodium sulphite". *Waste Management*, 60, 680-688, 2017.

[81] Yang Y, Xu S, He Y. "Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes". *Waste Management*, 64, 219-227, 2017.

[82] Li L, Qu W, Zhang X, Lu J, Chen R, Wu F, Amine K. "Succinic acid-based leaching system: A sustainable process for recovery of valuable metals from spent Li-ion batteries". *Journal of Power Sources*, 282, 544-551, 2015.

[83] Sa Q, Gratz E, He M, Lu W, Apelian D, Wang Y. "Synthesis of high performance LiNi1/3Mn1/3Co1/3O2 from lithium ion battery recovery stream". *Journal of Power Sources* 282, 140-145, 2015.

[84] Zou H, Gratz E, Apelian D, Wang Y. "A novel method to recycle mixed cathode materials for lithium ion batteries". *Green Chemistry*, 15(5), 1183-1191, 2013.

[85] Chen X, Kang D, Cao L, Li J, Zhou T, Ma H. "Separation and recovery of valuable metals from spent lithium ion batteries: Simultaneous recovery of Li and Co in a single step", *Separation and Purification Technology*, 210, 690-697, 2019.

[86] Meshram P, Pandey BD, Mankhand TR. "Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching". *Chemical Engineering Journal*, 281, 418-427, 2015.

[87] Pagnanelli F, Moscardini E, Granata G, Cerbelli S, Agosta L, Fieramosca A, Toro L. "Acid reducing leaching of cathodic powder from spent lithium ion batteries: Glucose oxidative pathways and particle area evolution", *Journal of Industrial and Engineering Chemistry*, 20(5), 3201-3207, 2014.

[88] Wang J, Chen M, Chen H, Luo T, Xu Z. "Leaching study of spent Li-ion batteries". *Procedia Environmental Sciences*, 16, 443-450, 2012.

[89] Vieceli N, Nogueira CA, Guimarães C, Pereira MFC, Durão FO, Margarido F. "Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite". *Waste Management*, 71, 350-361, 2018.

[90] Chen X, Fan B, Xu L, Zhou T, Kong J. "An atom-economic process for the recovery of high value-added metals from spent lithium-ion batteries". *Journal of Cleaner Production*, 112, 3562-3570, 2016.

[91] Granata G, Moscardini E, Pagnanelli F, Trabucco F, Toro L. "Product recovery from Li-ion battery wastes coming from an industrial pre-treatment plant: Lab scale tests and process simulations". *Journal of Power Sources*, 206, 393-401, 2012.

[92] Chen X, Luo C, Zhang J, Kong J, Zhou T. "Sustainable recovery of metals from spent lithium-ion batteries: A green process". *ACS Sustainable Chemistry & Engineering*, 3(12), 3104-3113, 2015, 2015.

[93] Zhang Y, Meng Q, Dong P, Duan J, Lin Y. “Use of grape seed as reductant for leaching of cobalt from spent lithium-ion batteries”. *Journal of Industrial and Engineering Chemistry*, 66, 86-93, 2018.

[94] Wu Z, Soh T, Chan JJ, Meng S, Meyer D, Srinivasan M, Tay CY. “Repurposing of fruit peel waste as a green reductant for recycling of spent lithium-ion batteries”. Environmental Science & Technology, 54, 9681-9692, 2020.

[95] Zhao J, Zhang B, Xie H, Qu J, Qu X, Xing P, Yin H. “Hydrometallurgical recovery of spent cobalt-based lithium-ion battery cathodes using ethanol as the reducing agent”. *Environmental Research*, 2020. https://doi.org/10.1016/j.envres.2019.108803.

[96] Contestabile M, Panero S, Scrosati B. “A laboratory-scale lithium ion battery recycling process”. *Journal of Power Sources*, 92, 65-69, 2001.

[97] Shuva MAH, Kurny ASW. “Hydrometallurgical recovery of value metals from spent lithium ion batteries”. American *Journal of Materials Engineering and Technology*, 1(1), 8-12, 2013.

[98] Castillo S, Ansart F, Laberty R, Portal J. “Advances of recovering of spent lithium battery compounds”. *Journal of Power Sources*, 112, 247-254, 2002.

[99] Chen L, Tang XC, Zhang Y, Li LX, Zeng ZW, Zhang Y. “Process for the recovery of cobalt oxalate from spent lithium-ion batteries”. *Hydrometallurgy*, 108, 80-86, 2011.

[100] Nayl AA, Elkhashab RA, Badaw SM, El-Khateeb MA. “Acid leaching of mixed spent Li-ion batteries”. *Arabian Journal of Chemistry*, 10, 3632-3639, 2017.

[101] Aktas S, Fray DJ, Burheim O, Fenstad J, Acma E. “Recovery of metallic values from spent Li ion secondary batteries”. *Mineral Processing and Extractive Metallurgy*, 115(2), 95-100, 2006.

[102] Kang J, Senanayake G, Sohn J, Shin SM. “Recovery of cobalt sulphate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272”. *Hydrometallurgy*, 100, 168-171, 2010.

[103] Kang JG, Sohn JS, Chang HK, Senanayake G, Shin SM. “Preparation of cobalt oxide from concentrated cathode material of lithium ion batteries by hydrometallurgical methods”. *Advanced Powder Technology*, 21, 175-179, 2010.

[104] Swain B, Jeong J, Lee JC, Lee GH, Sohn JS. “Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries”. *Journal of Power Sources*, 167, 536-544, 2007.

[105] Wang RC, Lin YC, Wu SH. “A novel recovery process of metal values from the cathode active materials of the lithium-ion secondary batteries”. *Hydrometallurgy*, 99(3), 194-201, 2009.

[106] Li L, Chen R, Sun F, Wu F, Liu J. “Preparation of $LiCoO_2$ films from spent lithium-ion batteries by a combined recycling process”. *Hydrometallurgy*, 108(3), 220-225, 2011.

[107] Myoung J, Jung Y, Lee J, Tak Y. “Cobalt oxide preparation from waste $LiCoO_2$ by electrochemical-hydrothermal method”. *Journal of Power Sources*, 112 (2), 639-642, 2002.

[108] Lee CK, Rhee KI. “Reductive leaching of cathodic active materials from lithium ion battery wastes”. *Hydrometallurgy*, 68, 5-10, 2003.

[109] Porvali A, Shukla S, Lundström M. “Low-acid leaching of lithium-ion battery active materials in Fe-catalyzed Cu-H_2SO_4 system”. *Hydrometallurgy*, 2020. https://doi.org/10.1016/j.hydromet.2020.105408.

[110] Zhu SG, He WZ, Li GM, Zhou X, Zhang XJ, Huang JW. “Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation”. *Transactions of Nonferrous Metals Society of China*, 22, 2274-2281, 2012.

[111] Jha AK, Jha MK, Kumari A, Sahu SK, Kumar V, Pandey BD. “Selective separation and recovery of cobalt from leach liquor of discarded Li-ion batteries using thiophosphinic extractant”. *Separation and Purification Technology*, 104, 160-166, 2013(b).

[112] Meshram P, Abhılash Pandey BD, Mankhand TR, Deveci H. “Comparision of different reductants in leaching of spent lithium ion batteries”. *The Journal of The Minerals, Metals & Materials Society*, 68(10), 2613-2623, 2016.

[113] Yang J, Jiang LX, Liu FY, Jia M, Lai YQ. “Reductive acid leaching of valuable metals from spent lithium-ion batteries using hydrazine sulfate as reductant”. *Transactions of Nonferrous Metals Society of China*, 30, 2256-2264, 2020.

[114] Pagnanelli F, Moscardini E, Altimari P, Atia TA, Toro L. “Leaching of electrodic powders from lithium ion batteries: Optimization of operating conditions and effect of physical pretreatment for waste fraction retrieval”. *Waste Management*, 60, 706-715, 2017.

[115] Chen X, Guo C, Ma H, Li J, Zhou T, Cao L, Kang D. “Organic reductants based leaching: A sustainable process for the recovery of valuable metals from spent lithium ion batteries”. *Waste Management*, 75, 459-468, 2018.

[116] Chen Y, Chang D, Liu N, Hu F, Peng C, Zhou X, He J, Jie Y, Wang H, Wilson BP, Lundstrom M. “Biomass-assisted reductive leaching in H_2SO_4 medium for the recovery of valuable metals from spent mixed-type lithium-ion batteries”. *The Journal of The Minerals, Metals & Materials Society*, 71(12), 4464-4472, 2019.

[117] Jian G, Guo J, Wang X, Sun C, Zhou Z, Yu L, Kong F, Qiu J. “Study on separation of cobalt and lithium salts from waste mobile-phone batteries”. *Procedia Environmental Sciences,* 16, 495-499, 2012.

[118] Mantuano DP, Dorella G, Elias RCA, Mansur MB. “Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272”. *Journal of Power Sources*, 159, 1510-1518, 2006.

[119] Yazıcı EY. Elektronik Atıklardan Metallerin Fiziksel ve Hidrometalurjik Yöntemlerle Geri Kazanımı. Doktora Tezi, K.T.Ü., Trabzon, Türkiye, 2012.

[120] Li YJ, Zeng GS. “Hydrometallurgical process for recovery and synthesis of $LiCoO_2$ from spent lithium-ion batteries”. *International Conference on Electric Technology and Civil Engineering (ICETCE)*, Lushan, China, 22-24 April 2011.

[121] Xia Z, Xie XQ, Shi YW, Lei YP, Guo F. “Recycling cobalt from spent lithium ion battery”. *Frontiers of Materials Science in China*, 2(3), 281-285, 2008.

[122] Jha MK, Kumari A, Jha AK, Kumar V, Hait J, Pandey BD. “Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone”. *Waste Management*, 33(9), 1890-1897, 2013(a).

[123] Joulié M, Laucournet R, Billy E. “Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminium oxide based lithium ion batteries”. *Journal of Power Sources*, 247, 551-555, 2014.

[124] Li J, Li X, Zhang Y, Hu Q, Wang Z, Zhou Y, Fu F. “Study of spent battery material leaching process”. *Transactions of Nonferrous Metals Society of China*, 19, 751-755, 2009a.

[125] Bas AD, Deveci H, Yazici EY. “Treatment of manufacturing scrap TV boards by nitric acid leaching”. *Separation and Purification Technology*, 130(10), 151-159, 2012.

[126] Li L, Jun L, Yang R, Xiao XZ, Ren JC, Feng W, Khalil A. “Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries”. *Journal of Power Sources*, 218, 21-27, 2012.

[127] Zeng X, Li J, Singh N. “Recycling of spent lithium-ion battery: A critical review”. *Critical Reviews in Environmental Science and Technology*, 44(10), 1129-1165, 2014.

[128] Nayaka GP, Pai KV, Santhosh G, Manjanna J. “Dissolution of cathode active material of spent Li-ion batteries using tartaric acid and ascorbic acid mixture to recover Co”. *Hydrometallurgy*, 161, 54-57. 2016a.

[129] Nayaka GP, Pai KV, Santhosh G, Manjanna J. “Recovery of cobalt as cobalt oxalate from spent lithium ion batteries by using glycine as leaching agent”. *Journal of Environmental Chemical Engineering*, 4(2), 2378-2383, 2016b.

[130] Musariri B, Akdogan G, Dorfling C, Bradshaw S. “Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries”. *Minerals Engineering*, 137, 108-117, 2019.

[131] Wang B, Lin XY, Tang Y, Wang Q, Leung MKH, Lu XY. “Recycling $LiCoO_2$ with methanesulfonic acid for regeneration of lithium-ion battery electrode materials”. *Journal of Power Sources*, 2019. http://dx.doi.org/10.1016/j.jpowsour.2019.226828.

[132] Yadav P, Jie CJ, Tan S, Srinivasan M. “Recycling of cathode from spent lithium iron phosphate batteries”. *Journal of Hazardous Materials*, 2020. https://doi.org/10.1016/j.jhazmat.2020.123068.

[133] He LP, Sun SY, Mu YY, Song XF, Yu JG. “Recovery of lithium, nickel, cobalt, and manganese from spent lithium-ion batteries using L-tartaric acid as a leachant”. *ACS Sustainable Chemistry & Engineering*, 5, 714-721, 2017.

[134] Chen X, Zhou T. “Hydrometallurgical process for the recovery of metal values from spent lithium-ion batteries in citric acid media”. *Waste Management & Research*, 32, 1083-1093, 2014.

[135] Al-Thyabat S, Nakamura T, Shibata S, Lizuka A. “Adaptation of minerals processing operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling: critical review”. *Minerals Engineering*, 45, 4-17, 2013.

[136] Meshram P, Pandey BD, Mankhand TR. “Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review”. *Hydrometallurgy*, 150, 192-208, 2014.

[137] Haavanlammi L, Hietala K, Karonen J. “Hydrocopper® for treating variable copper concentrates”. *International Symposium on Copper Hydrometallurgy*, Toronto, Canada, 369-377, 2007.

[138] Habashi, F. *Kinetics of Metallurgical Processes*, 1st ed. Quebec, Canada, Metallurgie Extractive Quebec, 1999.

[139] Chen X, Zhou T, Kong J, Fang H, Chen Y. “Separation and recovery of metal values from leach liquor of waste lithium nickel cobalt manganese oxide based cathodes”. *Separation and Purification Technology*, 141, 76-83, 2015.

[140] Chen X, Xu B, Zhou T, Liu D, Hu H, Fan S. “Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries”. *Separation and Purification Technology*, 144, 197-205, 2015(b).

[141] Pant D, Dolker T. “Green and facile method for the recovery of spent Lithium Nickel Manganese Cobalt Oxide (NMC) based Lithium ion batteries”. *Waste Management*, 60, 689-695, 2017.

[142] Sole KC. *Solvent Extraction in the Hydrometallurgical Processing And Purification of Metals: Process Design and Selected Applications.* Editors: Aguilar M, Cortina J.L. Solvent Extraction and Liquid Membranes, 141-200, Boca Raton, Florida, USA, CRC Press, 2008.

[143] Ritcey GM, Ashbrook AW. *Solvent Extraction. Principles and applications to process metallurgy*. Part 1. Elsevier, Amsterdam, Netherlands, 1984.

[144] Pranolo Y, Zhang W, Cheng CY. “Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system”. *Hydrometallurgy*, 102, 37-42, 2010.

[145] Nan J, Han D, Yang M, Cui M, Hou X. “Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries”. *Hydrometallurgy*, 84, 75-80, 2006.

[146] Suzuki T, Nakamura T, Inoue Y, Niinae M, Shibata J. “A hydrometallurgical process for the separation of aluminum, cobalt, copper and lithium in acidic sulfate media”. *Separation and Purification Technology*, 98, 396-401, 2012.

[147] Espinosa DCR, Bernardes AM, Tenório JAS. “An overview on the current processes for the recycling of batteries”. *Journal of Power Sources,* 135, 311-319, 2004.

[148] Recupyl Process. “Flowsheet of Recupyl Process”. http://www.recupyl.com/157-process.html (15.05.2020).

[149] Meshram P, Mishra A, Abhilash Sahu R. “Environmental impact of spent lithium ion batteries and green recycling perspectives by organic acids-A review”. *Chemosphere*, 2020. https://doi.org/10.1016/j.chemosphere.2019.125291.

[150] Ekermo, V. Recycling opportunities for Li-ion batteries from hybrid electric vehicles. MSc Thesis, Chalmers University of Technology, Gothenburg, Swedish, 2012.

[151] Mrozik W, Rajaeifar MA, Heidrich O, Christensen P. “Environmental impacts, pollution sources and pathways of spent lithium-ion batteries”. *Energy and Environmental Science*, 14, 6099-6121, 2021.

[152] Larsson F, Bertilsson S, Furlani M, Albinsson I, Mellander BE. “Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-$LiCoO_2$ cells at different levels of ageing”. *Journal of Power Sources*, 373, 220-231, 2018.

[153] Wang Q, Mao B, Stoliarov SI, Sun J. “A review of lithium ion battery failure mechanisms and fire prevention strategies”. *Progress in Energy and Combustion Science*, 73, 95-131, 2019.