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# Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction

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## ABSTRACT

Continuing technological development decreases the useful lifetime of electronic equipment, resulting in the generation of waste and the need for new and more efficient recycling processes. The objective of this work is to study the effectiveness of supercritical fluids for the leaching of cobalt contained in lithium-ion batteries (LIBs). For comparative purposes, leaching tests are performed with supercritical CO<sub>2</sub> and co-solvents, as well as under conventional conditions. In both cases, sulfuric acid and H<sub>2</sub>O<sub>2</sub> are used as reagents. The solution obtained from the supercritical leaching is processed using electrowinning in order to recover the cobalt. The results show that at atmospheric pressure, cobalt leaching is favored by increasing the amount of H<sub>2</sub>O<sub>2</sub> (from 0 to 8% v/v). The use of supercritical conditions enable extraction of more than 95 wt% of the cobalt, with reduction of the reaction time from 60 min (the time employed in leaching at atmospheric pressure) to 5 min, and a reduction in the concentration of H<sub>2</sub>O<sub>2</sub> required from 8 to 4% (v/v). Electrowinning using a leach solution achieve a current efficiency of 96% and a deposit with cobalt concentration of 99.5 wt%.

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## 1. Introduction

The useful lifespans of electronic products, especially portable devices such as cell phones and laptops, have decreased due to the constant introduction of new technologies. This has resulted in the generation of large quantities of waste electrical and electronic equipment (WEEE), including spent lithium-ion batteries (LIBs) (M.K. Jha et al., 2013; Shin et al., 2005). The inappropriate disposal of these batteries can cause serious environmental problems due to their hazardous constituents, such as heavy metals and electrolytes. However, some of these materials, for example cobalt and lithium, are strategic and valuable metals and must therefore be recycled (Zhu et al., 2012).

In addition to protecting the environment, the recycling of LIBs improves the use of natural resources and can contribute to decreasing the cost of battery production. These wastes are an important secondary source of metals; in some cases, the concentrations of metals present in batteries are higher than in ores (A.K. Jha et al., 2013; Dorella and Mansur, 2007). Moreover, the price of cobalt has increased significantly in recent years, making it economically feasible to recycle this metal (L. Li et al., 2013). In

2007, approximately 25% of global demand for cobalt was for battery applications (Dewulf et al., 2010).

The widespread use of LIBs is mainly due to their high energy density, low weight, high cell voltage, low self-discharge rate, and wide operating temperature range, when compared to nickel-cadmium or nickel-metal hydride batteries used in mobile phones and other electronic devices (Swain et al., 2007; Bertuol et al., 2015a). LIBs consist of an anode, a cathode, electrolytes, a separator, and an outer shell (Bertuol et al., 2015a; Bernardes et al., 2004; Ferreira et al., 2009). The anode is composed of a copper foil covered by a layer of powdered graphitic carbon, while the cathode consists of an aluminum foil coated with a layer of metal oxide such as LiCoO<sub>2</sub> powder (L. Li et al., 2013). This compound is most widely employed as the cathode in LIBs, due to its good electrochemical performance. However, disadvantages are its high cost, limited cobalt resources, and toxicity (Bertuol et al., 2015a; Li et al., 2010). The separators are made of polymeric materials, and the external case is usually constructed of steel or aluminum (Wu et al., 2000; Bertuol et al., 2015b). The typical composition of these batteries is 5–20 wt% Co, 5–10 wt% Ni, 5–7 wt% Li, 15 wt% organics, and 7 wt% plastics (Bertuol et al., 2015b; Kang et al., 2010). The composition varies slightly, depending on the manufacturing process.

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Different technologies based on pyrometallurgical or hydrometallurgical processes can be used for the recycling of LIBs (Freitas et al., 2010). Pyrometallurgical processes are commonly used in industry for the recovery of valuable metals, providing high productivity and efficiency, but drawbacks are high energy consumption and the emission of hazardous gases (Joulié et al., 2014). Hydrometallurgical processes involve the dissolution of metals in alkaline or acid medium (Birloaga et al., 2013). Hydrometallurgical processes are more benign from an environmental point of view and usually involve mechanical separation processes for battery dismantling, followed by dissolution of the electrodes in concentrated acids (Bertuol et al., 2015a, 2015b). After the leaching step, the resulting solution containing the metallic ions is usually submitted to precipitation, extraction, and electrowinning processes in order to recover the desired metals (Bertuol et al., 2015a; Freitas et al., 2010).

The recovery of valuable metals from spent LIBs usually employs acid leaching in the presence of a reducing agent that converts the metals to a more soluble oxidation state.  $H_2O_2$  in sulfuric acid solution acts as an effective reducing agent, which enhance the percentage leaching of metals (M.K. Jha et al., 2013).

The metals in solution can then be readily separated by techniques such as electrowinning or precipitation (L. Li et al., 2013). The literature reports several studies that have evaluated the recovery of cobalt after leaching with  $H_2SO_4$  (Table 1). In most of the studies, reaction times longer than 60 min were required.

The present work evaluates a more efficient method for cobalt recovery, with faster reaction kinetics, using supercritical  $CO_2$  modified with co-solvents. The use of supercritical fluids is an attractive option, due to the interesting properties of these solvents and the fact that they can be recycled and reused, hence providing environmental benefits (Herrero et al., 2010). Among the various fluids used for extraction,  $CO_2$  stands out because of its low cost, good chemical stability, relatively low critical point ( $T_c = 31.1\text{ }^\circ\text{C}$ ,  $P_c = 7.38\text{ MPa}$ ), high diffusivity, low viscosity, wide range of applications, and easy handling (Lin et al., 2014).

Calgaro et al. (2015) developed an alternative method for recovery of Cu from the printed circuit boards (PCBs) of obsolete mobile phones, employing supercritical  $CO_2$  modified with sulfuric acid and hydrogen peroxide. They concluded that supercritical leaching with  $CO_2$  and co-solvents provided faster reaction kinetics for Cu recovery. The supercritical extraction was 9 times faster, compared to atmospheric pressure extraction.

In addition, the use of supercritical  $CO_2$  using water as co-solvent, in order to de-laminate the PCB and separate its constituent materials by removing the polymers was studied (Sanyal et al., 2013). The use of water under supercritical conditions has also been employed for removal of the polymer fraction by the degradation of brominated epoxy resins, constituting a pretreatment step for recovery of the metals present (Xiu and Zhang, 2009; Xing and Zhang, 2013; Xiu et al., 2013).

Supercritical fluids such as  $CO_2$ , modified with complexing or chelating agents, have also been employed for the extraction of metal ions from various solid or liquid matrices (Herrero et al., 2010). Chelation or complexation is responsible for converting the metal species into soluble neutral complexes in the supercritical  $CO_2$  (Sunarso and Ismadji, 2009). For example, Cu was extracted from waste wood containing chromated copper arsenate using supercritical  $CO_2$  and Cyanex 302 as co-solvent (Wang and Chiu, 2008).

In many environmental applications, water is often present in a supercritical fluids extraction system as a part of the original sample or added deliberately. Water in contact with carbon dioxide becomes acidic due to the formation and dissociation of carbonic acid (Toews et al., 1995):

**Table 1**  
Studies reported in the literature for cobalt recovery from LIBs by acid leaching.

Reference	$H_2SO_4$	$H_2O_2$ (v/v)	Solid-liquid ratio (g/L)	Reaction time (min)	Temperature ( $^\circ\text{C}$ )	Method	Cobalt recovery (wt%)
M.K. Jha et al. (2013)	2 M	5%	100	60	75	Leaching of the anode and cathode, with sizes of 4 mm	70
Zhu et al. (2012)	2 M	2%	33	120	60	$LiCoO_2$ leaching assisted by ultrasound	96.3
Dorella and Mansur (2007)	6% (v/v)	1%	33.33	60	65	Manual dismantling, simultaneous leaching of cathode and anode	80
Swain et al. (2007)	2 M	5%	100	30	75	Leaching of $LiCoO_2$ waste generated during the manufacture of lithium-ion batteries	93
Ferreira et al. (2009)	0.75 M	1%	33.33	60	40	Cathode leaching in two steps: first with NaOH to selectively leach of Al, then acid leaching to extract cobalt and lithium	97
Kang et al. (2010)	2 M	6%	100	60	60	Discharge, dehydration, drying, and grinding of the battery as a physical pretreatment, followed by leaching of 16-mesh powder	98
Chen et al. (2011)	4 M	10%	100	120	85	Manual battery disassembly followed by leaching of the anode and cathode	95
Sun and Qiu (2011)	2 M	5%	50	60	80	Pretreatment by vacuum pyrolysis followed by acid leaching of the $LiCoO_2$	99

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