



Research article

Optimization of metals extraction from spent lithium-ion batteries by sulphuric acid and sodium metabisulphite through a techno-economic evaluation



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ABSTRACT

The main factors that affect the extraction of metals from spent lithium-ion batteries by acid leaching using H₂SO₄, and sodium metabisulphite, were evaluated and optimized through a set of experiments, framed by a techno-economic approach.

The maximum value of the profit response was obtained with the highest possible values of acid concentration (2.5 M) and time (2 h), a liquid/solid ratio of 5 L/kg, and the lowest possible value of temperature (40 °C). After leaching, the electrodes active material contained in the metals decreased, while it was still significant in the graphite, as observed by scanning electron microscopy-energy dispersive spectrometry and x-ray powder diffraction. Even though the performed economic evaluation was a summarized outline it can be considered suitable to compare different leaching conditions and to determine the possible best combinations of factors that can optimize the profit response.

1. Introduction

Disposed electrical and electronic equipment (WEEE) is one of the fastest growing waste-management problems worldwide. Within the European Union (EU) represents 3–5% of the total waste produced every year (European Commission, 2017). In 2014, 11.6 Mt of WEEE were generated in Europe, corresponding to 15.6 kg/inhabitant (Baldé et al., 2015).

The high energy density of lithium-ion batteries (LIBs), associated with other properties, boosted their use on the market of portable electronic devices such as mobile phones, laptops, MP3s and others, as well as in electric vehicles, amounting to billions the number of LIBs units produced every year, thus increasing their wasting (Zeng and Li, 2014; Scrosati and Garche, 2010).

A LIB cell includes two electrodes (positive and negative), a separator, an electrolyte and a steel can. The negative electrode consists of a Cu foil coated with graphite, while the positive electrode consists of an Al foil coated with a Li-transition metal mixed oxide, such as LiCoO₂, LiMn₂O₄, or LiNiO₂. Graphite and the mixed oxide are overlaid on the foils using a polymer binder, such as polyvinylidene fluoride (PVDF).

The electrolyte is normally a lithium salt, LiPF₆, LiBF₄, LiClO₄, or LiSO₂, dissolved in an organic solvent (a mixture of several alkyl carbonates). The separator is made of microporous polypropylene (PP) (Al-Thyabat et al., 2013). Alternative materials for Li-based batteries have been studied and a remarkable recent development is the all-solid-state rechargeable Na or Li battery developed by Braga et al. (2017). This is a noncombustible device with a long life span, fast rates of charge/discharge, and higher energy density than conventional lithium-ion batteries (The University of Texas at Austin and UT News, 2017).

For several years, LiCoO₂ has been the most common LIBs active cathode material. Due to some drawbacks such as its high cost and cobalt toxicity, LiCoO₂ has been partially replaced by LiMn₂O₄ and Li(Mn,Ni,Co)O₂, particularly in high energy/power applications. As such, active cathode materials in LIBs can contain a variable concentration of Co, Ni, and Mn, making their recovery more complex (Chen et al., 2011), and more unreliable the attribution of a recycling value (Waste Management World, 2011).

Even though in theory LIBs could be totally recycled with an efficiency rate above 90% using hydrometallurgical processes, a pyrometallurgical procedure is generally applied, with Li being lost in the

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slag (Elibama, 2014). While several processes for LIBs recycling have been developed, Li global average recycling rate is less than 1% (UNEP, 2013) and the collection rate less than 10% (Ellis and Howes, 2017). Even though LIBs contains the valuable metals referred above, it is also considered a hazardous waste. The development of recycling technologies suits the global demands of energy (Choubey et al., 2017) and has positive environmental impacts (Chen et al., 2011) in resources conservation, namely reducing the risk of a shortage of raw materials (some of them critical, like Co and graphite).

Swain (2017), Heelan et al. (2016), Ordoñez et al. (Ordoñez et al., 2016), Meshram et al. (2014) and Zeng et al. (2014), have developed studies on metals recovery from LIBs. However, the focus in most studies is to maximize the metals dissolution even if the conditions are not the best from an economic point of view, because they can lead to an excessive consumption of reagents and energy. Likewise, optimization procedures are normally performed one variable at a time, without evaluating the effect and interactions between the process variables. Studies about LIBs recycling by hydrometallurgical routes normally employ hydrogen peroxide as a reducer. However, hydrogen peroxide has some drawbacks, due to its easy decomposition and usual low efficiency. Metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) is also widely used as a commercial reducer in the industry with previous research demonstrating that it can be used as a reducer in the leaching of LIBs, with a better performance when compared to other reducers (Vieceli et al., 2018). For this reason, metabisulphite as a reducer was used in this study in the leaching of LIBs with H_2SO_4 .

Considering the importance of the development of optimized solutions for metals extraction from LIBs, the central goals of this study were, (1) to evaluate the main factors that affect the extraction of metals from disposed LIBs through acid leaching with H_2SO_4 , using sodium metabisulphite as an alternative reducer (Vieceli et al., 2018) to the most common hydrogen peroxide and (2) to present an innovative approach for the optimization of the leaching process of LIBs, applying a profit function. Given that a more economic approach to optimize the recycling of LIBs has not yet been reported, this paper aims to fulfill this gap in the literature.

2. Materials and methods

2.1. Sampling and physical separation

279 batteries from laptops were classified in classes according to their brands and models. After that operation and considering the number of batteries in each class, a representative sample of 40 batteries for further analysis was set aside. The plastic cases and printed circuit boards (PCB) of these 40 batteries were removed and the six Li-ion cells contained in each one of them were separated for physical processing. The total weigh of Li-ion cells submitted to physical processing was about 10.4 kg. In order to prevent short circuits and risks of explosion during the fragmentation, the Li-ion cells were subjected to a cryogenic pre-treatment, by dipping them into liquid nitrogen (4–6 min). Then, they were shredded using a grab shredder with a 6 mm bottom discharge grid (Erdwich EWZ 2000). Although about 20% of the material did not pass the grid (staying with a size bigger than 6 mm), this was mixed with the material with a size smaller than 6 mm to be used in the subsequent physical separation steps.

The physical separation procedure consisted of: (1) a magnetic separation to remove iron scrap, mainly from steel cans; (2) removal of the coarse fraction (bigger than 6.7 mm), constituted mainly by plastics and some large Al and Cu foils; and (3) density separation using water to allow some residual plastic strips from the separator to float. After these steps, a fraction rich in active electrode materials (high content of Li, Co, Mn and Ni), usually designated as black mass was obtained. Due to the great material heterogeneity, it was crushed a second time in a cutting mill (Retsch SM2000, with a 2 mm discharge grid). Representative samples for the leaching tests (about 5 g) were obtained with a rotary sample splitter.

Table 1
Selected factors and respective levels.

| Factors | | Levels | | | Units |
|---|-------|----------|--------------|-----------|--------------------|
| | | Low (−1) | Standard (0) | High (+1) | |
| H_2SO_4 concentration | x_1 | 1.5 | 2 | 2.5 | M |
| $\text{Na}_2\text{S}_2\text{O}_5$ concentration | x_2 | 0.25 | 0.325 | 0.4 | M |
| L/S ratio | x_3 | 3 | 5 | 7 | L/kg |
| Leaching temperature | x_4 | 40 | 60 | 80 | $^{\circ}\text{C}$ |
| Leaching time | x_5 | 0.5 | 1.25 | 2 | h |

2.2. Leaching experiments

Samples from the physical separation were leached in 250 mL glass flasks using a thermostatic orbital shaker (150 min^{-1}). Reagents used (H_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_5$) were of analytical grade and the solutions were prepared just before each experiment. Leaching parameters were studied using a full 2^k factorial design of experiments with five factors ($k = 5$), and two levels (25 factorial design). Replicates of experiments ($n_c = 4$) were performed at the central level of the design to estimate the experimental error. Given the obtained curvature, 2^k axial variable combinations were added (distance of $\alpha = \pm 1$ from the design center), resulting in a face-centered central composite design (CCD). Tests were randomly performed. Preliminary tests helped to define the factors, these being the acid concentration (x_1), the reducer concentration (x_2), the liquid to solid (L/S) ratio (x_3), the leaching temperature (x_4) and the leaching time (x_5). The selected levels are presented in Table 1. The low and high levels expressed as (−1) and (+1) according to the commonly used coded factors nomenclature are those used in the 2^k experiments, while the standard level (0) was performed to evaluate the experimental error.

The experimental results were analysed and statistically treated and they can be represented in a function, by the adjustment to a polynomial model, which can be obtained using multiple linear regression. This regression model can be used to represent the process studied.

The effect of the factors on the metals recovery was evaluated, and a profit function was adopted as the process response (y).

The significance of the regression model was assessed by analysis of variance (ANOVA), the model significance by the F -test, while the model inadequacy was evaluated by a lack-of-fit test (LOF). The percentage of the response variation explained by the model was evaluated by the coefficient of determination (R^2) and the existence of pure curvature was assessed by an hypothesis test.

Response surfaces and contour plots assisted the model interpretation and optimization. This methodology can be found in Montgomery (2012).

2.3. Characterization techniques

Chemical analysis to determine metals content and leaching yields were performed by atomic absorption spectrometry (AAS) using a SOLAR 969 AA Spectrometer (Thermo Elemental). The composition of the initial sample was assessed by the same technique, after digestion in a microwave with aqua regia. Morphological transformations were observed through a Scanning Electron Microscopy with secondary electron imaging (SEM/SE, JEOL JSM 7001F microscope, 15 kV). Structural and compositional changes were evaluated by X-ray powder diffraction (XRPD) using a PANalytical XPERT-PRO diffractometer (Cu $K\alpha$ radiation, scan from 5 to $100^{\circ} 2\theta$ with a step size of $0.050^{\circ} 2\theta$, step time 150s, generator settings of 35 mA and 40 kV). The analytical interpretation of results was performed using the X'PERT HIGHSCORE PLUS software and the PDF-2 $^{\circ}$ data base (PDF-2).

2.4. Profit function

Usually, the optimization of the experimental conditions for a

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