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# Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects

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## ABSTRACT

An environmentally-friendly route based on hydrometallurgy was investigated for the recovery of cobalt and lithium from spent lithium ion batteries (LIBs) using different organic acids (citric acid, DL-malic acid, oxalic acid and acetic acid). In this investigation, response surface methodology (RSM) was utilized to optimize leaching parameters including solid to liquid ratio (S/L), temperature, acid concentration, type of organic acid and hydrogen peroxide concentration. Based on the results obtained from optimizing procedure, temperature was recognized as the most influential parameter. In addition, while 81% of cobalt was recovered, the maximum lithium recovery of 92% was achieved at the optimum leaching condition of 60 °C, S/L: 30 g L<sup>-1</sup>, citric acid concentration: 2 M, hydrogen peroxide concentration: 1.25 Vol.% and leaching time: 2 h. Furthermore, results displayed that ultrasonic agitation will enhance the recovery of lithium and cobalt. It was found that the kinetics of cobalt leaching is controlled by surface chemical reaction at temperatures lower than 45 °C. However, diffusion through the product layer at temperatures higher than 45 °C controls the rate of cobalt leaching. Rate of lithium reaction is controlled by diffusion through the product layer at all the temperatures studied.

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## 1. Introduction

Recycling of spent lithium ion batteries (LIBs) is not only in favor of the environmental regulations but also is economically desirable due to the growing price of cobalt (Horeh et al., 2016; Li et al., 2013). Moreover, steady evacuation of the world's primary cobalt and lithium resources has become a major concern that can be solved by recycling of LIBs (Li et al., 2009, 2012). LIBs mainly consist of an anode, a cathode, separators, and electrolyte (Li et al., 2013), in which, anode is a copper foil coated with carbon graphite and cathode is an aluminum foil coated with lithium cobalt oxide (LiCoO<sub>2</sub>) as cathode active material. The cathode materials are linked together by polyvinylidene fluoride (PVDF) as a chemically and mechanically stable material (Xu et al., 2008). The separator is made of polymeric materials, paper or paperboard, through which anode and cathode are separated (Vassura et al., 2009). Also, electrolyte of LIBs consists of organic solvents with dissolved lithium salts such as LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub> and LiCF<sub>3</sub>SO<sub>3</sub> (Horeh et al., 2016; Xu et al., 2008). Due to the presence of different substances in the spent LIBs, one of the obstacles

in efficient recycling of this waste stream is separation of the different metals from leachate (Zheng et al., 2016a). To prevail these obstacles, suitable techniques for recycling a mixture of batteries containing leaching followed by solvent extraction have been implemented (Granata et al., 2012; Vassura et al., 2009). However, carrying out a mechanical separation before recycling brings a lot of benefits including reducing amount of waste, purifying leachate, decreasing reagent consumption, saving more energy and enhancing efficiency of the desirable metals (Ordoñez et al., 2016). Zhang et al. (2014) reported that spent LIBs have appropriate selective crushing characteristic that make it a suitable material for either automatic or manual mechanical pretreatments in industrial scale.

To recover lithium and cobalt from spent LIBs, there have been some typical hydrometallurgical and pyro metallurgical processes (Li et al., 2009; Sun and Qiu, 2011). While, pyrometallurgical processes are not appropriate due to the toxic gases emissions (Kim et al., 2004), hydrometallurgical processes are alternative solutions for the environmental problems and also consume less energy in comparison with pyrometallurgical processes (Li et al., 2012; Pagnanelli et al., 2016). It has also been reported that hydrometallurgical processes have been gradually replaced by the bio-hydrometallurgical ones due to their lower costs, and fewer

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industrial requirements; however, their efficiency is low and the kinetics rate is slower and frequently requires longer time for treatment compared to the hydrometallurgical processes (Zhao et al., 2008).

In the hydrometallurgical processing of spent LIBs, it is necessary to remove carbon as the main component of anode materials to decrease acid consumption. Therefore, a pre-treatment process including crushing and calcination is expected (Li et al., 2012). Leaching of cathode materials was previously studied by inorganic leaching agents like hydrochloric acid (Dorella and Mansur, 2007; Zhang et al., 1998), nitric acid (Lee and Rhee, 2002) and sulfuric acid (Shin et al., 2005). Strong acids such as hydrochloric acids and nitric acid produce harmful fumes and gases such as  $\text{Cl}_2$ ,  $\text{SO}_3$  and  $\text{NO}_x$  and, their waste solutions can penetrate to the soil and ground waters and cause damage to local people, biodiversity, and ecosystems (Li et al., 2013). To overcome this problems, organic acids as leaching agents such as ascorbic acid (Li et al., 2012), citric acid (Li et al., 2013, 2010b, 2014), DL-malic acid (Li et al., 2013), succinic acid (Li et al., 2015a) and oxalic acid (Chen et al., 2011; Sohn et al., 2006) for the recovery of  $\text{LiCoO}_2$  have been previously investigated. A growing interest has risen in the leaching of LIBs by organic acids as degradable acids due to less emission of toxic gases during the leaching procedure (Li et al., 2013, 2012, 2014).

Kinetic aspects of cobalt and lithium recovery from spent LIBs using sulfuric acid have also been studied. Meshram et al. (2015) claimed that diffusion of the leaching agent on the surface of cathode materials controls the rate of leaching for both lithium and cobalt. However, Jha et al. (2013) reported that leaching rate of lithium and cobalt is controlled by chemical reaction and diffusion through the ash, respectively. In addition, Takacova et al. (2016) studied the kinetics of cobalt and lithium using both sulfuric acid and hydrochloric acid and the results showed that chemical reaction controls cobalt extraction at the first stage of leaching (0–90 min) and diffusion controls the rate of reaction at the second stage of leaching (90–180 min). In addition, at the first stage of lithium leaching (0–90 min), a mixed mode (both chemical reaction and diffusion) controls the rate of reaction while, diffusion controls the rate of reaction at the second stage (90–180 min). Moreover, leaching of the cathode materials of spent LIBs has also been studied using  $\text{HNO}_3$  as the leaching agent (Lee and Rhee, 2003) and the results from activation energy calculations showed that the dissolution of  $\text{LiCoO}_2$  is controlled by chemical reaction. Zheng et al. (2016b) studied the kinetics of cobalt recovery from spent LIBs using citric acid at temperatures higher than 70 °C and based on their results, leaching of cobalt is controlled by chemical reaction. The kinetics studies of cobalt and lithium recovery from spent LIBs using succinic acid at temperatures higher than 50 °C indicated that chemical reaction controls leaching at the first step (0–10 min) and diffusion controls the rate of leaching at the second stage (20–40 min) (Li et al., 2015a). It is clear from the aforementioned discussion that different results have been reported on the leaching kinetics of the cathode material of LIBs. Besides, the researches on the kinetics of ultrasonic assisted leaching of LIBs using organic acids at low temperatures are few.

Conventional stirring is regularly used in metals extraction; however, recently the effect of ultrasonic agitation in comparison with mechanical stirring on the kinetics of the dissolution of phosphate rock in HCl solution and extraction of valuable metals from spent hydro processing catalysts have been investigated. Results indicated that the ultrasonic agitation is more efficient for the extraction of metals present in the both phosphate rock and spent catalyst (Marafi and Stanislaus, 2011; Tekin, 2002). Li et al. (2014) explained the mechanism of ultrasonic agitation on the leaching of spent  $\text{LiCoO}_2$  with sulfuric acid, hydrochloric acid and citric acid. However, the effect of ultrasonic agitation in comparison with

mechanical stirring in the organic acid leaching of  $\text{LiCoO}_2$  have not been studied.

In this study, recovery of lithium and cobalt from spent LIBs was explored by using four organic acids as leaching agents which imitate bioleaching processes. The effects of acid concentration, S/L, temperature and hydrogen peroxide concentration as reducing agent on the recovery of lithium and cobalt were investigated and the leaching parameters were optimized by response surface methodology. The effect of cavity action of ultrasonic agitation on the kinetics of the lithium and cobalt recovery in a wide range of temperatures was also investigated. For the first time the interactions between influential parameters was interpreted and the effect of ultrasonic agitation in comparison with mechanical stirrer on the leaching efficiency of lithium and cobalt was also surveyed.

## 2. Waste battery management

LIBs have been widely used in laptop computers, mobile phones, video cameras, portable music players, and electric vehicles (Li et al., 2009). As a mean to develop sustainable mobility, the new generation of electric vehicles will drive the growth, and it is expected that the global lithium demand of about 110,000 metric tons per year may triple by 2020 to support the electrified vehicles industry and other existing applications (Gaines and Nelson, 2010; Wanger, 2011).

The drastic increase in the waste stream causes a series of environmental issues which resulted in setting up strict policies in manufacturing, usage, collection, recycling and safe disposal of LIBs in Europe and USA (Bahaloo-Horeh and Mousavi, 2016). Thus, it is crucial to take effective steps to minimize the waste pile up. Disposal of spent LIBs in landfill sites or incinerators leads to air and ground water pollutions due to the existence of heavy metals and toxic substances in these waste (Guo et al., 2016; Pietrelli et al., 2005). Besides, high operation and maintenance costs of incinerator facilities are indisputable (Li et al., 2015b). Another contributing factor is existence of valuable metals in LIBs such as cobalt and lithium that by landfilling or incineration will be lost (Zand and Abdul, 2008).

To undertake these problems, the most practically reasonable remedy seems to be recycling of spent LIBs which is not only eco friendly but also consumes less energy and reduce demand for virgin raw materials. Nevertheless, this fact cannot be ignored that the collection process of spent LIBs is incompetent around the world (Xu et al., 2008). Therefore, efficient acts are imposed in order to regulate the collection of spent LIBs; i.e., based on European guideline 2006/66/EC, 45% of the spent LIBs must be collected and also 50% of the average weight of spent LIBs should be recycled by 2016 (Granata et al., 2012; Zand and Abdul, 2008).

For this purpose, suitable technologies for recycling of spent LIBs have been developed such as pyrometallurgy and hydrometallurgy (Zheng et al., 2016a). Despite the fact that pyrometallurgical technology is used in industrial scale recycling of spent LIBs, it has serious downsides such as severe environmental impacts, high operating costs and high energy consumption (Georgi-Maschler et al., 2012). On the other hand, hydrometallurgical technologies employing organic acids are eco-friendly and leach metals by either replacing the hydrogen ions and metal ions or soluble complex formation (Ren et al., 2009).

## 3. Experimental

### 3.1. Materials and reagents

Spent LIBs with different sizes from Lenovo and IBM laptops were used in this investigation. DL-malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ), citric acid

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