



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



Rabeeh Golmohammadzadeh^a, Fereshteh Rashchi^{a,*}, Ehsan Vahidi^b

^a School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran

^b Environmental and Ecological Engineering, Purdue University, West Lafayette, IN 47907, USA

ARTICLE INFO

Article history:

Received 17 January 2017

Revised 20 March 2017

Accepted 24 March 2017

Available online 30 March 2017

Keywords:

Lithium ion battery

Leaching

Ultrasonic agitation

Organic acids

Kinetics

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⁻¹, 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.

© 2017 Elsevier Ltd. All rights reserved.

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 (LiCoO₂) 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 LiClO₄, LiBF₄, LiPF₆ and LiCF₃SO₃ (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

* Corresponding author.

E-mail address: rashchi@ut.ac.ir (F. Rashchi).

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 Cl_2 , SO_3 and 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 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 HNO_3 as the leaching agent (Lee and Rhee, 2003) and the results from activation energy calculations showed that the dissolution of 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 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 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 Abduli, 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 Abduli, 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

monohydrates ($C_6H_8O_7 \cdot H_2O$), oxalic acid dehydrate ($C_2H_2O_4 \cdot 2H_2O$), and acetic acid ($C_2H_4O_2$) with purity of 96%; were used as leaching agents and hydrogen peroxide (hydrogen peroxide with purity of 30%) was employed as a reductant. All solutions were prepared with specified concentrations using deionized water and all reagents used were of analytical grade supplied from Merck Company.

3.2. Sample preparation

To avoid self-ignition or short-circuit during dismantling process, the spent LIBs were completely discharged at the first stage. In this study, the spent LIBs were dismantled manually instead of using automatic mechanical pretreatments; because the automatic mechanical pretreatments lead to addition of impurities such as Fe, Al and Cu in the leaching system which increase the reagent consumption (Granata et al., 2012; Vassura et al., 2009; Zhang et al., 2014). The plastic and steel cases were then removed from the cells by a screwdriver and a mini grinder (Crown, CT13428, 150 W), and then cathode and anode foils were separated manually.

The black materials covered Al and Cu foils comprised mostly of $LiCoO_2$ and graphite, respectively. The cathode active materials were collected completely and were ground in a ball mill to decrease the particle size and were sieved to reduce the amount of impurities such as Al in order to promote the leaching efficiency. Afterwards, the cathode active materials were thermally treated at 700 °C for 6 h to eliminate graphite and other additives such as polyvinylidene fluoride binder and other organic compounds.

3.3. Analytical method

To completely leach the cathode materials and determine the lithium and cobalt contents before sieving, after sieving and after calcination using inductively coupled plasma optical emission spectrometry (ICP-OES, VISTA-PRO, Varian Co.), a mixed solution of hydrochloric acid and nitric acid ($HCl:HNO_3$ with 3:1 ratio) was utilized. To calculate leaching efficiency at different conditions, the concentrations of lithium and cobalt in the filtrate were also determined by ICP-OES. Table 1 shows the chemical composition of the cathode materials before sieving, after sieving and after calcination.

The cathode materials were qualitatively characterized using X-ray diffraction (XRD, Philips-3040/60 PW) before and after calcination. After the leaching tests, the residue of the leaching was also characterized by XRD to specify existing phases in the leach resi-

due after filtration. In addition, high resolution scanning electron microscopy (HR-SEM, Camscan) was utilized to analyze the surface morphology of the initial sample and that of the leaching residue. Besides, laser particle size analysis (LPSA, CILAS 1064) was used to compare the particle size of the cathode materials before and after leaching.

3.4. Design of experiment (DOE)

Maximizing the recovery of lithium and cobalt is of great importance. Conventional methods to optimize leaching parameters (one factor at a time) neglect the interactions between parameters. Therefore, to create numerical relationships between various input parameters, statistical design of experiments (DOE) as an efficient procedure for planning experiments can be employed. Screening and optimization are the two essential applications of design of experiments. In screening, influential parameters on the experiments are identified and finally, the optimal conditions of an experiment are expressed in optimization. Design of experiments, not only do survey the interactions between parameters, but also it will decrease the number of experiments (Nekouei et al., 2013).

We performed the leaching experiments in 2 steps. At first, due to the large number of parameters, 16 screening tests were designed according to orthogonal array $L_{16}(4^5)$ by Taguchi method to reduce the number of the experiments and also to identify the most influential variables. Table 2 shows the parameter and levels used in the screening tests. Based on the results obtained from the screening tests, 19 experiments were designed subsequently by response surface methodology (RSM) subdivision of D-optimal as shown in Table 3. Design Expert 7 (State-Ease Inc., Minneapolis, MN, USA) software was utilized for design and statistical analysis of the experiments.

3.5. Leaching experiments

All experiments were performed in a 500 mL three necked and round-bottomed thermostatic Pyrex reactor containing 100 mL solution. A glass condenser was also connected to the reactor to reduce the loss of water caused by evaporation. In this investigation, ultrasound waves were employed for agitation of the leaching solution using an ultrasonic bath (Ultra, VGT-1730QTD, 40 kHz, 100 W). The temperature was adjusted by means of a thermometer, controller, and sensor connected to an external heater to enhance the temperature accuracy. Time of leaching was considered 2 h in both steps; screening tests (by Taguchi) and RSM experiments. To facilitate the leaching of $LiCoO_2$ (as the cathode material), the hydrogen peroxide as a reductant was added into the solution during the leaching experiments (Li et al., 2013, 2010a,b).

After leaching, the solution was filtered and washed with deionized water and the filtrate was characterized by ICP-OES to calculate recovery of cobalt and lithium as shown in Table 3. In addition, to investigate the effect of ultrasonic-assisted agitation on recoveries of lithium and cobalt, 18 experiments were carried out by use of mechanical stirrer in the optimum condition (2 M citric acid, tem-

Table 1
Chemical composition of cathode materials.

Element	Before sieving (wt.%)	Before calcination and after sieving (wt.%)	After calcination (wt.%)
Co	27.64	32.35	46.06
Li	3.27	4.35	5.60
Cu	3.87	2.04	2.34
Ni	1.04	0.98	1.21
Al	6.36	0.20	0.24
Other elements	57.82	60.08	44.55

Table 2
Selected parameters and levels for screening tests.

Level	A: Temperature (°C)	B: H_2O_2 (Vol.%)	C: Type of acid	D: S/L ($g\ L^{-1}$)	E: Acid concentration (M)
1	25	0	DL-malic	15	1
2	50	1	Citric	30	2
3	70	2.5	Acetic	40	4
4	90	5	Oxalic	50	6

Table 3

D-optimal experimental design.

Run	Temperature (°C)	H ₂ O ₂ (Vol.%)	Type of acid	Responses (%)	
				Li	Co
1	70	1.25	Citric	89.92	81.43
2	60	0.50	DL-malic	87.52	79.04
3	80	2.00	DL-malic	86.67	84.02
4	60	1.23	Citric	92.46	81.06
5	69	0.50	Citric	89.81	78.19
6	80	0.50	DL-malic	86.14	83.83
7	69	0.50	Citric	87.07	78.53
8	67	1.34	DL-malic	90.13	79.25
9	70	2.00	DL-malic	90.89	80.22
10	60	0.50	DL-malic	86.83	77.76
11	80	2.00	DL-malic	86.37	83.98
12	78	1.25	DL-malic	87.34	83.01
13	60	2.00	DL-malic	88.338	78.74
14	80	1.03	Citric	84.74	84.04
15	61	2.00	Citric	84.02	78.70
16	70	0.59	DL-malic	89.13	80.59
17	71	2.00	Citric	79.00	78.72
18	60	1.23	Citric	92.45	81.87
19	80	1.03	Citric	82.58	83.15

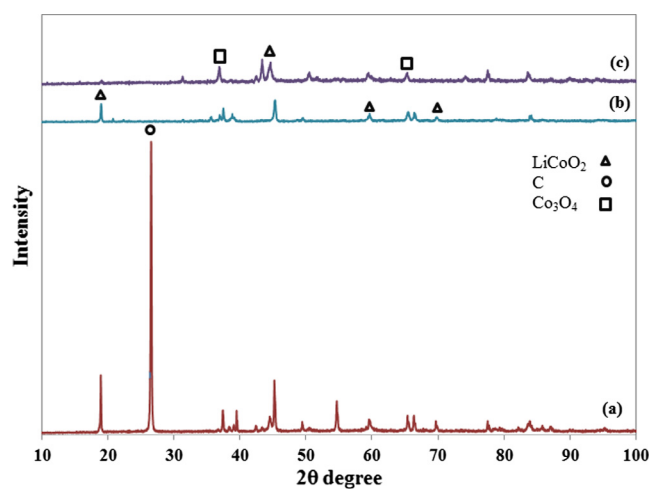


Fig. 1. XRD patterns of spent LIBs: (a) the dismantled cathode materials from spent LIBs, (b) the cathode material after dismantling and calcination at 700 °C for 6 h and (c) citric acid leaching residue.

perature of 60 °C, hydrogen peroxide concentration of 1.25 Vol.% and S/L of 30 g L⁻¹).

4. Results and discussion

4.1. Characterization of the cathode materials in spent LIBs

Spent LIBs were dismantled manually as explained in the experimental section. Fig. 1 illustrates the XRD patterns of the dismantled cathode materials from spent LIBs, the cathode material after dismantling and calcination at 700 °C for 6 h, and the citric acid leaching residue. The diffraction patterns of the sample before calcination show an intense peak of graphite which could have been transferred from anode materials during dismantling process. In addition, LiCoO₂ and Co₃O₄ were detected in the structure of the dismantled cathode materials of LIBs before calcination. Since the graphite has been burnt off during the calcination process, the XRD pattern of the cathode materials after calcination shows mainly LiCoO₂ (Li et al., 2010a, 2012). Diffraction peaks of the leaching residue are also indexed to Co₃O₄ and no diffraction peaks for LiCoO₂ can be observed, indicating that the LiCoO₂ has reacted with citric acid.

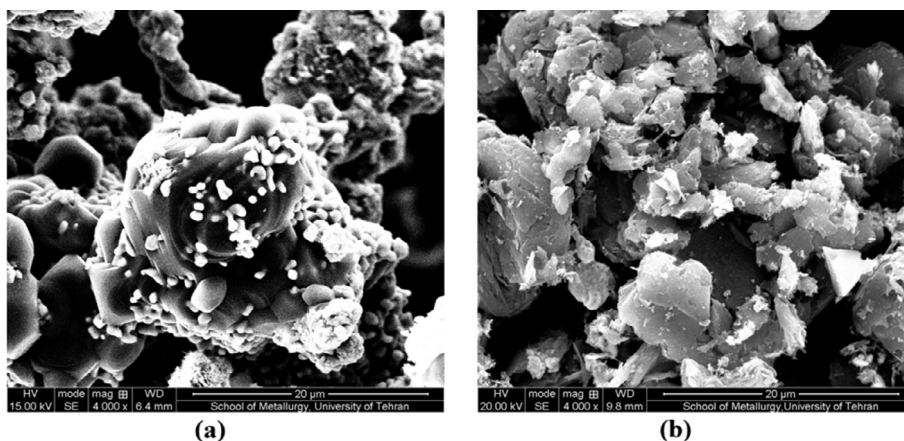


Fig. 2. The HR-SEM images of cathode materials in magnification of 4000×: (a) after dismantling and calcination (before leaching), (b) leaching residues.

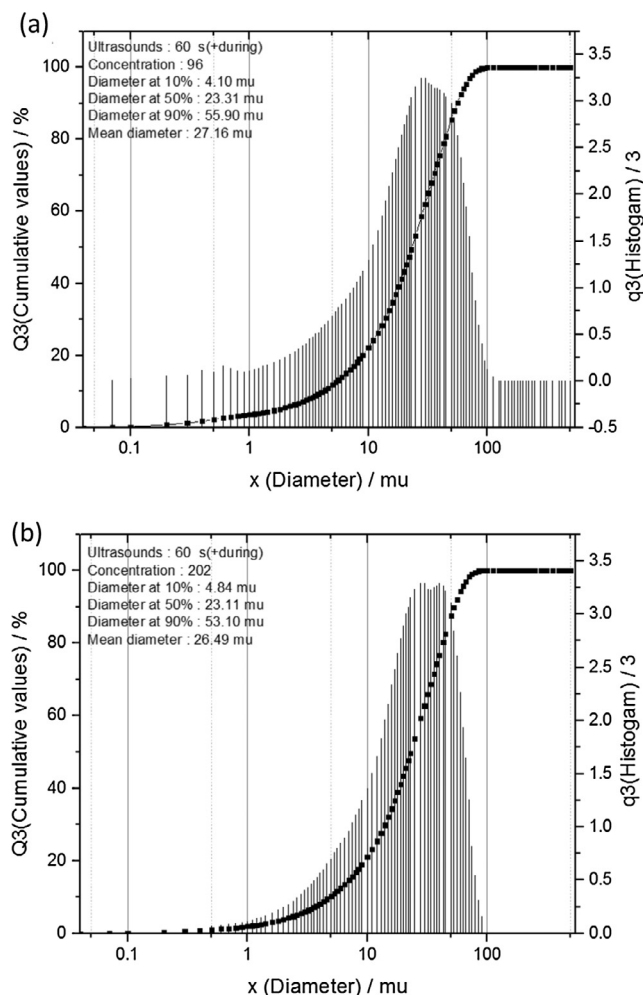


Fig. 3. Particle size distribution of cathode active materials (a) after dismantling and calcination at 700 °C for 6 h and (b) after leaching at 2 M citric acid, 60 °C, S/L: 30 g L⁻¹, H₂O₂: 1.25 Vol.%.

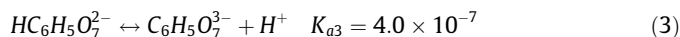
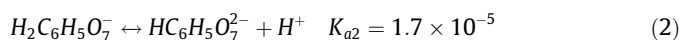
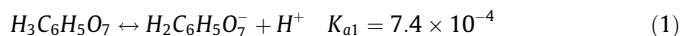
Fig. 2(a) shows the HR-SEM image of the cathode materials after dismantling and calcination at 700 °C for 6 h (before leaching). Fig. 2(b) illustrates the HR-SEM image of the leaching residue in magnification of 4000×. As it can be seen, in both images, the cathode materials demonstrate irregular shapes and agglomerated morphology.

Fig. 3(a) and (b) illustrates the particle size distribution of cathode materials before and after leaching. It is clear that about 80% of the particles are coarser than 10 μm and also 90% of the particles (before leaching) are 55.90 μm and 90% of the particles (after leaching) are 53.10 μm. In addition, mean diameter of the particles before and after leaching are 27.16 and 26.49 μm, respectively, which means that the size of the particles can be considered practically constant.

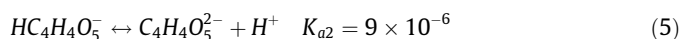
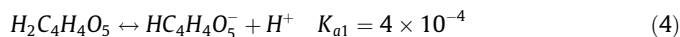
4.2. Leaching of cobalt and lithium based on the design of experiments

4.2.1. Statistical analysis

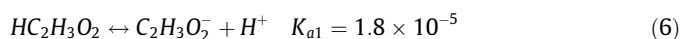
Based on the results obtained from the screening tests, temperature, hydrogen peroxide concentration and type of the acid used as the leaching agents were recognized as the most effective parameters in the leaching of LiCoO₂. Citric acid and DL-malic were chosen as the best leaching agents for the leaching of the cathode materials. Citric acid dissociates in three steps:



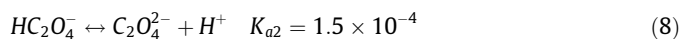
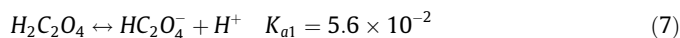
As a result, three moles of H⁺ are provided per one mole of citric acid. Therefore, it can be concluded that citric acid can produce adequate H⁺ ions in the solution (Serjeant and Dempsey, 1979). In addition, it is known that citric acid is one of the best chelating agents (Li et al., 2014). Thus, this organic acid can produce complexes with cobalt. DL-malic acid dissociates in two steps:



On the other hand, acetic acid dissociates in one step:



Therefore, two moles of H⁺ and one mole of H⁺ are released from DL-malic and acetic acids, respectively (Serjeant and Dempsey, 1979). The H⁺ concentration plays a vital role on leaching efficiency of cobalt and lithium (Li et al., 2014; Sakultung et al., 2007). Thus, DL-malic acid could be a better leaching agent in comparison with acetic acid. This is in agreement with the results obtained from the screening experiments. Dissociation steps of the other leaching agent, oxalic acid, are:



It can be observed that oxalic acid dissociates in two steps. Due to the formation of the cobalt oxalate precipitates, oxalic acid is an inappropriate reagent (Sohn et al., 2006).

Fig. 4 shows the main effect plots based on the leaching screening tests in the presence of acetic acid at 25 °C and in the absence of hydrogen peroxide. The recoveries of cobalt and lithium as a function of two variables of acid concentration and S/L are presented in the figure. As shown in Fig. 4, the optimum acetic acid concentration for the cobalt leaching is 2 M and increasing the acid concentrations more than 2 M shows no improvement in lithium recovery. Therefore, the acid concentration of 2 M was considered for the rest of the experiments. Based on the same approach, S/L of 30 g L⁻¹ resulted in the highest recoveries for both lithium and cobalt.

Fig. 5 shows the effect of leaching parameters on lithium and cobalt recoveries. Also interactions between the type of acid (DL-malic and citric), temperature and hydrogen peroxide concentration are presented in the figure. Unparalleled lines are marked as an interaction between the two parameters in interaction plots (Montgomery, 2008). The higher the slope of the lines, the more influential the related parameter is (Montgomery, 2008). Fig. 5 (a) and (c) shows that there are significant interactions between the type of acid and temperature. Using citric acid, the recovery of lithium decreases from ca. 92% to ca. 82% increasing the temperature from 60 °C to 80 °C; whereas, cobalt recovery enhances slightly from ca. 81% to ca. 83%. In the case of DL-malic acid, by increasing the temperature from 60 °C to 70 °C, the lithium recovery improved slightly from ca. 88% to ca. 90%.

By further increasing the temperature, the lithium recovery decreases slightly to ca. 86%. Increasing the temperature from 60 °C to 80 °C, the recovery of cobalt enhances from ca. 78% to ca. 83%. The increase in the cobalt recovery could be attributed to the fact that, there is a strong ionic bond between Co³⁺ and oxygen in the structure of LiCoO₂ (Li et al., 2010a; Shin et al., 2005);

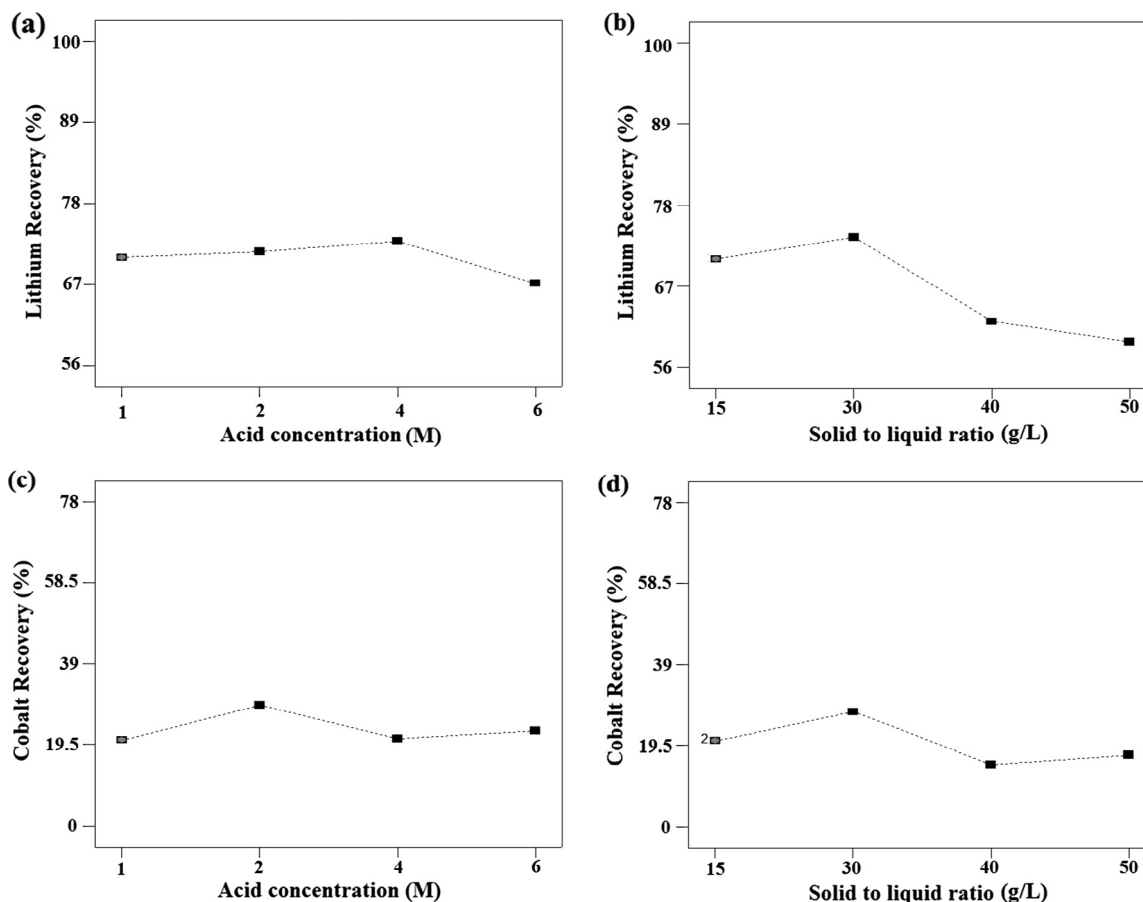
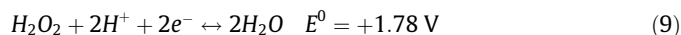


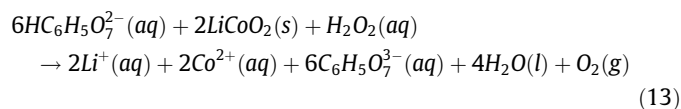
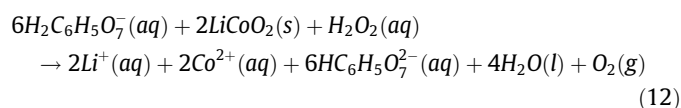
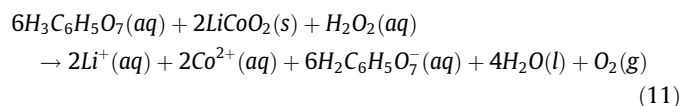
Fig. 4. Main effect plots based on screening tests in the presence of acetic acid at 25 °C and in the absence of H_2O_2 : (a) effect of acid concentration on the recovery of lithium ($S/L = 15 \text{ g L}^{-1}$), (b) effect of S/L ratio on the recovery of lithium (acetic acid: 1 M), (c) effect of acid concentration on the recovery of cobalt ($S/L = 15 \text{ g L}^{-1}$), (d) effect of S/L ratio on the recovery of cobalt (acetic acid: 1 M).

however, the reduction of Co^{3+} to Co^{2+} by hydrogen peroxide is accelerated by increasing temperature which is in agreement with previous findings (Li et al., 2013, 2010a,b).

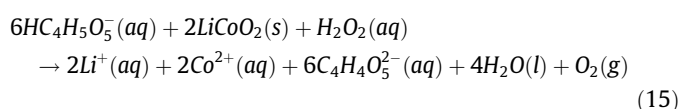
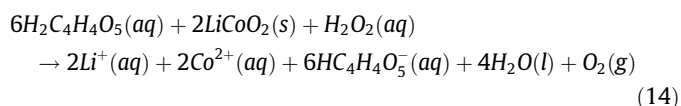
Hydrogen peroxide is an appropriate reducing agent for this leaching system. The half reactions for hydrogen peroxide in acidic solutions and for reduction of Co^{3+} to Co^{2+} are as follows (Skoog and West, 1982):



The reaction between citric acid and the metal species in the presence of hydrogen peroxide are as follows (Li et al., 2010b):



The reaction of DL-malic acid and metal species in presence of hydrogen peroxide are as follows (Li et al., 2010a):



From Eqs. (11)–(15) it can be seen that the addition of hydrogen peroxide will accelerate the forward reaction. The ability of cobalt to form chelate with organic acids is indisputable and based on the half reactions of (9) and (10), the required potential for Co^{3+} to Co^{2+} conversion is supplied in the system. In addition, due to the dissociation of organic acids at high temperatures, the chelate formation reaction of cobalt with organic acids is accelerated (Li et al., 2014).

Li et al. (2013, 2010b) claimed that since both citric and DL-malic acids start to be vaporized by increasing the temperature to 90 °C, the lithium recovery decreases. However, decompositions of citric acid and DL-malic acid start at 175 °C and 150 °C, respectively (Apelblat, 2014; Smith and Hong-Shum, 2011). It is also proposed that the lithium recovery decreases due to the decomposition of the lithium citrate at high temperatures. In other words, since lithium is an alkali metal with electron configuration

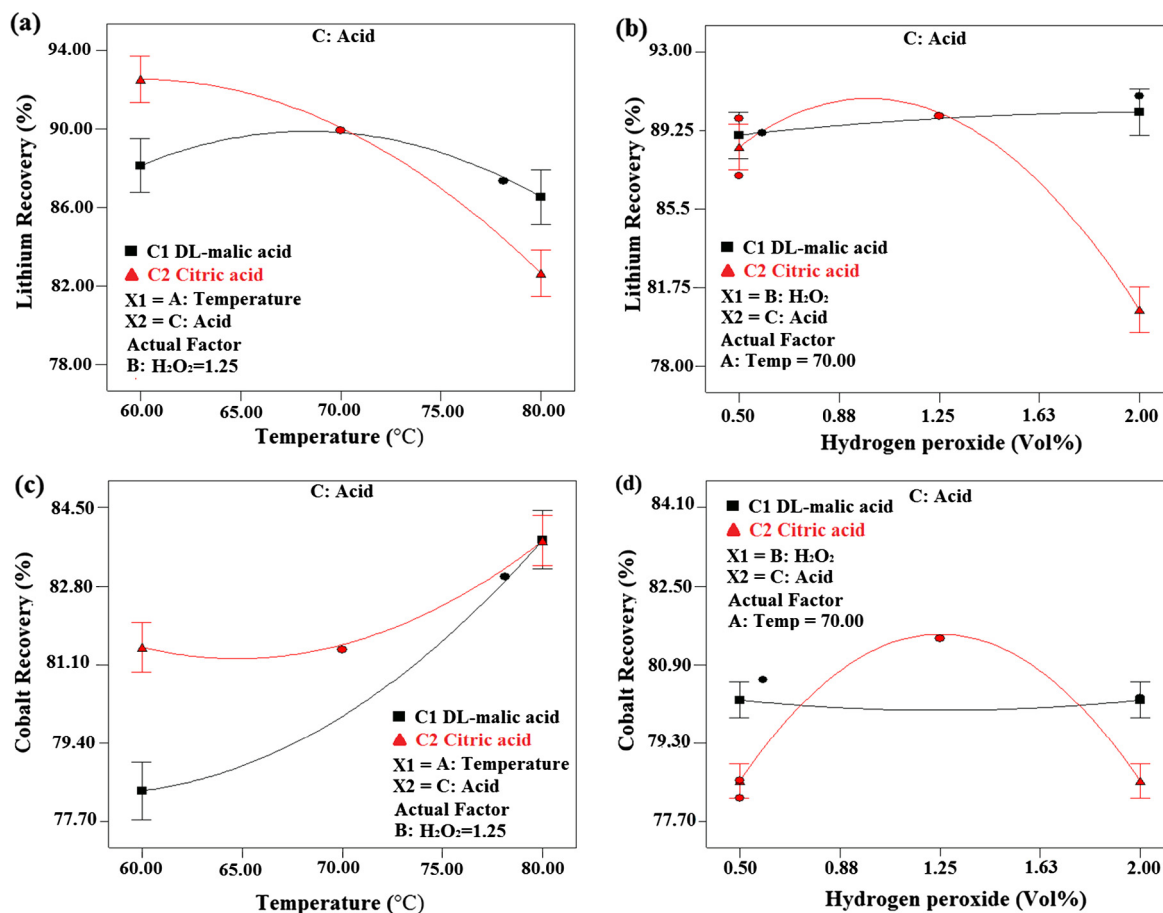


Fig. 5. Effect of leaching parameters on lithium and cobalt recoveries and interactions between type of acid and (a) H₂O₂ (Vol.%), (b) temperature, (c) H₂O₂ (Vol.%), (d) temperature.

of [2s¹], the interaction between citrate anions and lithium is weak and unstable at higher temperatures. However, in the case of cobalt as a transition metal, a chelate is formed by strong chemical bonding between the electrons of [d] orbital of cobalt cations and citrate anions. Overall, it can be concluded that to recover both lithium and cobalt from the cathode materials, citric acid shows a better performance compared to DL-malic acid.

According to Fig. 5(b) and (d), it is clear that there are significant interactions between type of acid and hydrogen peroxide concentration. In case of citric acid, increasing the hydrogen peroxide concentration to 1% and 1.25% enhances the leaching efficiencies of lithium and cobalt, to 90% and 81%, respectively. However, the recovery rate of both metal species decreases with further increasing of hydrogen peroxide concentration. It is worthwhile to mention that excessive amount of the hydrogen peroxide affects both oxidation and reduction half reactions (Eqs. (9) and (10)). Based on the Nernst equation, increasing the hydrogen peroxide concentration changes the reductive role of this agent to act as an oxidant. The decomposition of excess amount of hydrogen peroxide to H₂O and O₂ occurs according to the following half reaction (Skoog and West, 1982):



In the case of DL-malic acid, according to Fig. 5(b) and (d), the recovery of lithium increases slightly by increasing the hydrogen peroxide concentration, while the recovery of cobalt remains almost constant. As discussed earlier, DL-malic acid is a weaker organic acid compared to citric acid.

4.2.2. Process optimization

According to Table 3 and in order to determine the optimum condition for simultaneous recovery of lithium and cobalt, a number of experiments, were carried out using citric acid and DL-malic acid with concentration of 2 M and S/L of 30 g L⁻¹. To predict the response as a function of independent variables, multiple regression analysis was employed and the following equations were obtained:

$$\begin{aligned} \text{Cobalt recovery} = & +80.77 + 1.94A + 0.087B + 0.79C \\ & - 0.096AB - 0.78AC + 0.051BC + 1.08A^2 \\ & - 1.40B^2 - 1.64B^2C \end{aligned} \quad (17)$$

$$\begin{aligned} \text{Lithium recovery} = & +89.93 - 2.86A - 1.70B + 0.12C \\ & - 0.39AB - 2.07AC - 2.24BC - 2.48A^2 \\ & - 2.83B^2 - 2.72B^2C \end{aligned} \quad (18)$$

where A, B and C are temperature, hydrogen peroxide concentration and type of acid, respectively. The correlation coefficients (R²) for these models were calculated to be 0.96 (for lithium) and 0.98 (for cobalt) which, indicating that both the models fit adequately to the experimental data.

Fig. 6 shows the prediction of design expert 7 software from the analyzed data to reach the maximum recovery of lithium and cobalt using statistical techniques. The lines show the range of each parameter while the red points are attributed to the exact quantity of the parameters. As demonstrated in Fig. 6, 92.54% of lithium and 81.50% of cobalt can be recovered using 2 M citric acid

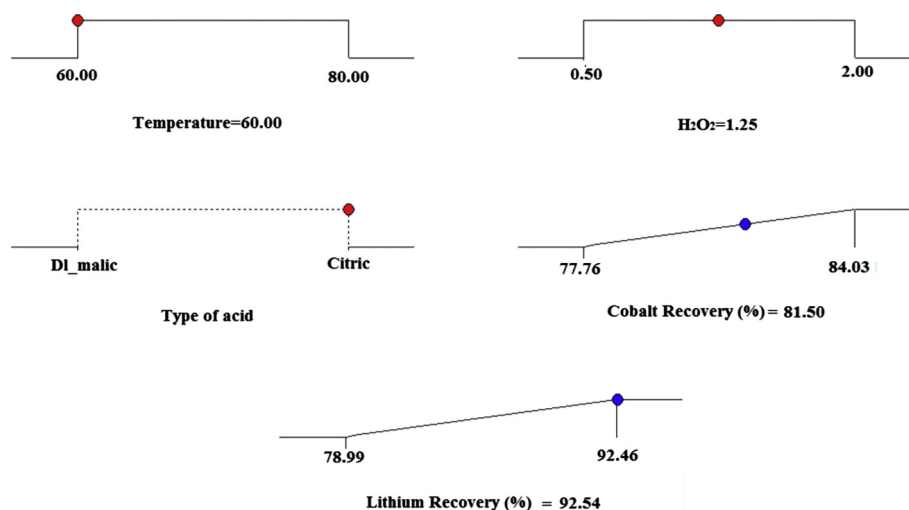


Fig. 6. Optimum conditions for maximum cobalt and lithium recovery.

in 120 min, at 60 °C. The predicted values were tested 3 times and as results, the average recovery rates of lithium and cobalt in this condition were 92.40% and 83.63% and 92.40%, respectively. Since the difference between predicted numbers and actual values are less than 5%, it can be concluded that the results are in good agreement with values provided by both models for the recovery of cobalt and lithium.

4.3. Effect of ultrasonic-assisted agitation

Ultrasonic waves have been known to enhance leaching recoveries of lithium and cobalt by the use of cavitation bubbles (Li et al., 2014). Cavitation is the formation of vapor cavities in liquid zones that are the consequence of forces acting upon the liquid (Marafi and Stanislaus, 2011). It usually occurs when a liquid is subjected to rapid changes of pressure that causing the formation of cavities where the pressure is relatively low. When subjected to higher pressures, the voids implode and provide a considerable amount of energy that reduce the energy consumption of the system (Marafi and Stanislaus, 2011). Also, the explosion of the bubbles creates several micro cracks at the surface of the solid and enhances the diffusion of the liquid to the surface of the solid by decreasing the diffusion layer (Li et al., 2015a; Marafi and Stanislaus, 2011; Tekin, 2002).

Fig. 7(a) and (b) compares the effects of ultrasonic agitation and mechanical stirring on the recoveries of lithium and cobalt at the optimum condition. According to Fig. 7(a) and regarding the lithium extraction, there is insignificant difference between the recoveries using mechanical stirrer and ultrasonic waves. However, ultrasonic agitation has higher impact on improving the leaching recovery of cobalt compared to mechanical stirrer (see Fig. 7(b)).

Fig. 8 illustrates the proposed possible interactions between citric acid and LiCoO₂ in the presence of cavitation bubbles. As depicted, the formed cavitation bubbles in the liquid explode at the surface of the LiCoO₂, leading to the formation of cobalt citrate (Co(C₆H₇O₇)₂) and lithium citrate (LiC₆H₇O₇) in the leaching solution when citric acid was the leaching agent. In addition, according to Li et al. (2014) using ultrasonic agitation, the chelating process with cobalt is speeded up and as a result, the recovery rates of lithium and cobalt are improved while the energy consumption is reduced (Bankole et al., 2013). However, they did not perform mechanical stirring for their leaching condition and merely compared their result with previous ones.

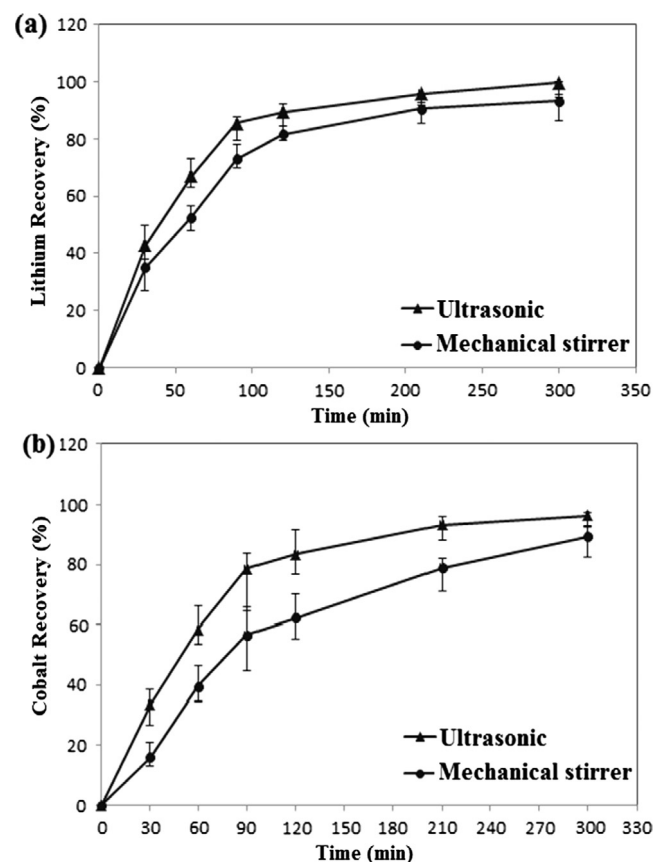


Fig. 7. Effect of ultrasonic agitation and mechanical stirrer on leaching recovery of: (a) lithium; and (b) cobalt, (citric acid: 2 M, S/L: 30 g L⁻¹, H₂O₂ = 1.25 Vol.%, temperature = 60 °C).

4.4. Kinetic modeling

Based on the optimum condition obtained from the optimization step, citric acid was chosen as the best leaching agent and 24 experiments were designed to investigate the effect of temperature and time of leaching on the leaching recoveries of lithium and cobalt. The samples were quantitatively analyzed by ICP-OES to determine the lithium and cobalt recoveries.

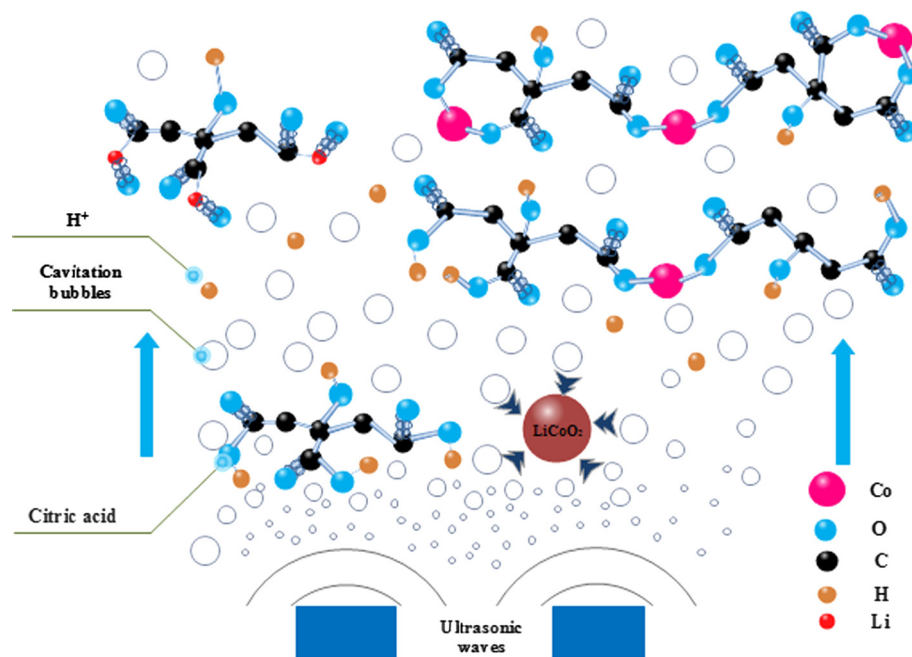


Fig. 8. Proposed possible interaction between LiCoO_2 and citric acid in presence of cavitation bubbles.

Knowing that the particles size before and after leaching has remained constant, it can be concluded that the shrinking core model (SCM) for spherical particles of unchanging size can be applied to describe the kinetics of cobalt and lithium leaching during the recovery process. According to this model, the inner cores of the particles shrink with time while the size of particle remains unchanged. According to the shrinking core model, the rate of leaching is limited to the rate of slower step and there are 3 steps in the SCM occurring simultaneously during the process (Levenspiel, 1999; Nazemi et al., 2011):

Step 1: Diffusion of the leaching agent within the liquid film surrounding the particle.

Step 2: Diffusion of the leaching agent through the solid product layer of particle up to the surface of the inner core.

Step 3: Chemical reaction of the leaching agent at the surface of the inner core.

In order to specify the controlling mechanism of the leaching reaction, plot of various kinetic model formulas verses time should be drawn according to experimental data gained from the leaching experiments (Levenspiel, 1999). The formula of each controlling step is explored against the experimental data and the controlling mechanism is defined as the step that best fits the experimental data (Jha et al., 2013; Takacova et al., 2016). Sometimes correlation coefficients are very close to each other, thus, excess experiments are required to specify the rate controlling mechanism. Furthermore, this method not only consists of complicated calculations, but also is incapable of detecting mixed control mechanisms (Jha et al., 2013; Li et al., 2015a; Takacova et al., 2016). To overcome these difficulties, a method was proposed by Nazemi et al. (2011) to determine the controlling mechanism by SCM taking into account, all of the above three steps c at the same time as follows:

$$t = \tau_f X + \tau_p \left[1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) \right] + \tau_R \left[1 - (1-X)^{\frac{1}{3}} \right] \quad (19)$$

Share of each of the above mentioned steps in the kinetics of leaching can be revealed by fitting the experimental data to Eq. (19) and evaluating the constants of this equation. In this case,

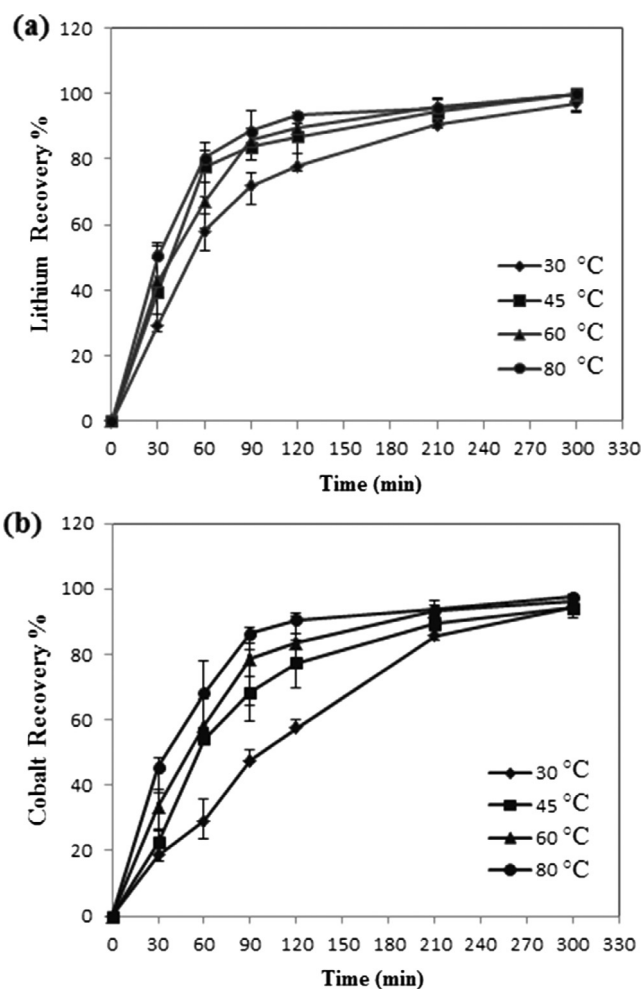


Fig. 9. Effect of temperature on citric acid leaching (citric acid: 2 M, S/L: 30 g L⁻¹, H₂O₂ = 1.25 Vol.%): (a) lithium; and (b) cobalt.

when there is only one controlling mechanism, the related coefficient in Eq. (19) is non-zero and the other two would be zero. Furthermore, if there are more than one mechanism influencing the kinetics of leaching, more than one of these coefficients would be non-zero. The constants of Eq. (19) can be calculated by a multi-linear regression analysis, using the least square technique proposed by Nazemi et al. (2011). This technique can be formulated as:

$$\phi = \sum_i \left[\tau_f X_i + \tau_p (1 - 3(1 - X_i)^{\frac{2}{3}} + 2(1 - X_i)) + \tau_r (1 - 1(1 - X_i)^{\frac{1}{3}}) - t_i \right]^2 \quad (20)$$

Minimize ϕ .

Subject to τ_f , τ_p and $\tau_r > 0$.

Eq. (20) is an optimization problem from which τ_f , τ_p and τ_r can be calculated by any optimization technique. Using this technique eliminates the requirements of repeating calculations and it determines the controlling mechanisms by solving the above mentioned optimization problem.

Fig. 9(a) shows the relationship between lithium extraction and time at different temperatures. The lithium recovery increased with increasing the leaching time and after 5 h almost 100% of lithium is recovered at 45 °C using 2 M citric acid, S/L of 30 g L⁻¹ and hydrogen peroxide concentration of 1.25 Vol.%. Results of fitting experimental data in Fig. 9(a) to Eq. (20) by technique proposed by Nazemi et al. (2011), are shown in Table 5. Standard deviation of calculated parameters were evaluated by the method explained by Constantinides and Mostoufi (1999) and are also reported in this table. At all the temperatures applied, the coefficients related to chemical reaction and diffusion through the liquid film are equal to zero and the main controlling mechanism is diffusion through the product layer.

Fig. 9(b) illustrates the recovery of cobalt as a function of time at different leaching temperatures. The 97.68% of cobalt was recovered at an experimental condition of: 80 °C, 2 M citric acid, S/L of 30 g/L and hydrogen peroxide concentration of 1.25 Vol.%, after 5 h of leaching. Table 4 shows the constants obtained by fitting the experimental data represented in Fig. 9(b) to Eq. (19) by the constrained least square technique developed by Nazemi et al. (2011). Standard deviation of calculated parameters were evaluated by the method explained by Constantinides and Mostoufi (1999) and are also reported in this table. It can be concluded that at temperatures greater than 45 °C, diffusion through the product

layer is the controlling mechanism and at 30 °C, chemical reaction is the controlling step.

Leaching of lithium depends on the amount of H⁺ available in the solution (Li et al., 2014). Leaching of cobalt not only depends on the concentration of H⁺, but also it depends on the type of anion produced by the dissociation of the selected acid. This is due to the chelate formation between the cobalt ions and the anions of the selected acid when dissociated (Li et al., 2010b; Shin et al., 2005). In other words, there are two essential steps in cobalt leaching including, dissociation reaction at the solid and liquid interface and chelating process between metal ions and anions in the selected acid (Li et al., 2013).

5. Conclusions

In this study, we tried to expand the knowledge of recycling with emphasis on an eco-friendly method including three main sections; optimizing of the leaching parameters, investigating the effect of ultrasonic agitation on the leaching recoveries of lithium and cobalt in comparison with the effect of mechanical stirrer and eventually, studying the leaching kinetics of cobalt and lithium based on constrained multi-linear regression analysis using the least square technique.

Under the optimum condition of leaching (S/L ratio of 30 g L⁻¹, temperature of 60 °C, citric acid concentration of 2 M, hydrogen peroxide concentration of 1.25 Vol.%, and leaching time of 2 h), 92.53% and 81.50% of lithium and cobalt were recovered respectively; Increasing the time of leaching to 5 h and keeping the other parameters constant lead to 99.80% and 96.46% recoveries for lithium and cobalt, respectively. Besides, comparing mechanical stirrer and ultrasonic agitation, it was concluded that cavitation enhances both recoveries of cobalt and lithium.

Based on the kinetic study results, the rate of cobalt leaching is controlled by diffusion of the reactant through the product layer, at temperatures greater than 45 °C. Moreover, chemical reaction on the surface of unreacted core particles controls the kinetic rate at lower temperatures. The rate of lithium leaching at all the temperatures studied is controlled by diffusion of the reactant through the product layer.

References

- Apelblat, A., 2014. *Citric Acid*. Springer.
- Bahaloo-Horeh, N., Mousavi, S.M., 2016. Enhanced recovery of valuable metals from spent lithium ion batteries through optimization of organic acids produced by *Aspergillus niger*. *Waste Manage.* 51, 239–244.
- Bankole, O.E., Gong, C., Lei, L., 2013. Battery recycling technologies: recycling waste lithium ion batteries with the impact on the environment in-view. *J. Environ. Eco.* 4, 14–28.
- Chen, L., Tang, X., Zhang, Y., Li, L., Zeng, Z., Zhang, Y., 2011. Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy* 108, 80–86.
- Constantinides, A., Mostoufi, N., 1999. *Numerical Methods for Chemical Engineers With MATLAB Applications*. Prentice Hall PTR, Upper Saddle River New Jersey.
- Dorella, G., Mansur, M.B., 2007. A study of the separation of cobalt from spent Li-ion battery residues. *J. Power Sources* 170, 210–215.
- Gaines, L., Nelson, P., 2010. *Lithium-ion Batteries: Examining Material Demand and Recycling Issues*. Minerals, Metals and Materials Society/AIME, Warrendale PA 15086 USA.
- Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., Rutz, M., 2012. Development of a recycling process for Li-ion batteries. *J. Power Sources* 207, 173–182.
- Granata, G., Pagnanelli, F., Moscardini, E., Takacova, Z., Havlik, T., Toro, L., 2012. Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: accomplishment of European guidelines by optimizing mechanical pre-treatment and solvent extraction operations. *J. Power Sources* 212, 205–211.
- Guo, Y., Li, F., Zhu, H., Li, G., Huang, J., He, W., 2016. Leaching lithium from the anode electrode materials of spent lithium-ion batteries by hydrochloric acid (HCl). *Waste Manage.* 51, 227–233.
- Horeh, N.B., Mousavi, S., Shojaosadati, S., 2016. Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using *Aspergillus niger*. *J. Power Sources* 320, 257–266.

Table 4

Coefficients of Eq. (20) for leaching of cobalt. Values in parentheses are standard deviation of the calculated parameter.

Temperature (°C)	τ_R (min)	τ_P (min)	τ_F (min)	R ²
30	471 (19.9)	0	0	0.99
45	0	413 (36.0)	0	0.98
60	0	347 (44.8)	0	0.97
80	0	299 (60.5)	0	0.93

Table 5

Coefficients of Eq. (20) for leaching of lithium. Values in parentheses are standard deviation of the calculated parameter.

Temperature (°C)	τ_R (min)	τ_P (min)	τ_F (min)	R ²
30	0	376 (20.3)	0	0.99
45	0	280 (33.9)	0	0.97
60	0	280 (35.4)	0	0.97
80	0	258 (51.0)	0	0.94

- Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J., Pandey, B.D., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manage.* 33, 1890–1897.
- Kim, D.S., Sohn, J.S., Lee, C.K., Lee, J.H., Han, K.S., Lee, Y.I., 2004. Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries. *J. Power Sources* 132, 145–149.
- Lee, C.K., Rhee, K.I., 2002. Preparation of LiCoO_2 from spent lithium ion batteries. *J. Power Sources* 109, 17–21.
- Lee, C.K., Rhee, K.I., 2003. Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* 68, 5–10.
- Levenspiel, O., 1999. *Chemical Reaction Engineering*. John Wiley & Sons, New York.
- Li, J., Shi, P., Wang, Z., Chen, Y., Chang, C.-C., 2009. A combined recovery process of metals in spent lithium ion batteries. *Chemosphere* 77, 1132–1136.
- Li, L., Ge, J., Chen, R., Wu, F., Chen, S., Zhang, X., 2010a. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manage.* 30, 2615–2621.
- Li, L., Ge, J., Wu, F., Chen, R., Chen, S., Wu, B., 2010b. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.* 176, 288–293.
- Li, L., Lu, J., Ren, Y., Zhang, X.X., Chen, R.J., Wu, F., Amine, K., 2012. Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. *J. Power Sources* 218, 21–27.
- Li, L., Dunn, J.B., Zhang, X.X., Gaines, L., Chen, R.J., Wu, F., Amine, K., 2013. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. *J. Power Sources* 233, 180–189.
- Li, L., Zhai, L., Zhang, X., Lu, J., Chen, R., Wu, F., Amine, K., 2014. Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. *J. Power Sources* 262, 380–385.
- Li, L., Qu, W., Zhang, X., Lu, J., Chen, R., Wu, F., Amine, K., 2015a. Succinic acid-based leaching system: a sustainable process for recovery of valuable metals from spent Li-ion batteries. *J. Power Sources* 282, 544–551.
- Li, Y., Zhao, X., Li, Y., Li, X., 2015b. Waste incineration industry and development policies in China. *Waste Manage.* 46, 234–241.
- Marafi, M., Stanislaus, A., 2011. Waste catalyst utilization: extraction of valuable metals from spent hydroprocessing catalysts by ultrasonic-assisted leaching with acids. *Ind. Eng. Chem. Res.* 50, 9495–9501.
- Meshram, P., Pandey, B., Mankhand, T., 2015. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: leaching and kinetic aspects. *Waste Manage.* 45, 306–313.
- Montgomery, D.C., 2008. *Design and Analysis of Experiments* seventh ed. John Wiley & Sons.
- Nazemi, M., Rashchi, F., Mostoufi, N., 2011. A new approach for identifying the rate controlling step applied to the leaching of nickel from spent catalyst. *Int. J. Miner. Process.* 100, 21–26.
- Nekouei, R.K., Rashchi, F., Amadeh, A.A., 2013. Using design of experiments in synthesis of ultra-fine copper particles by electrolysis. *Powder Technol.* 237, 165–171.
- Ordoñez, J., Gago, E., Girard, A., 2016. Processes and technologies for the recycling and recovery of spent lithium ion batteries. *Renew. Sustain. Energy Rev.* 60, 195–205.
- Pagnanelli, F., Moscardini, E., Altimari, P., Atia, T.A., Toro, L., 2016. Cobalt products from real waste fractions of end of life lithium ion batteries. *Waste Manage.* 51, 214–221.
- Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M., 2005. Characterization and leaching of NiCd and NiMH spent batteries for the recovery of metals. *Waste Manage.* 25, 221–226.
- Ren, W.-X., Li, P.-J., Geng, Y., Li, X.-J., 2009. Biological leaching of heavy metals from a contaminated soil by *Aspergillus niger*. *J. Hazard. Mater.* 167, 164–169.
- Sakultung, S., Pruksathorn, K., Hunsom, M., 2007. Simultaneous recovery of valuable metals from spent mobile phone battery by an acid leaching process. *Korean J. Chem. Eng.* 24, 272–277.
- Serjeant, E.P., Dempsey, B., 1979. *Ionisation Constants of Organic Acids in Aqueous Solution*. Pergamon, Oxford.
- Shin, S.M., Kim, N.H., Sohn, J.S., Yang, D.H., Kim, Y.H., 2005. Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy* 79, 172–181.
- Skoog, D.A., West, D.M., 1982. *Fundamentals of Analytical Chemistry*, fourth ed. Holt Rinehart Winston.
- Smith, J., Hong-Shum, L., 2011. *Food Additives Data Book*. John Wiley & Sons.
- Sohn, J.S., Shin, S.M., Yang, D.H., Kim, S.K., Lee, C.K., 2006. Comparison of two acidic leaching processes for selecting the effective recycle process of spent lithium ion battery. *Geosyst. Eng.* 9, 1–6.
- Sun, L., Qiu, K., 2011. Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries. *J. Hazard. Mater.* 194, 378–384.
- Takacova, Z., Havlik, T., Kukurugya, F., Orac, D., 2016. Cobalt and lithium recovery from active mass of spent Li-ion batteries: theoretical and experimental approach. *Hydrometallurgy* 163, 9–17.
- Tekin, T., 2002. Use of ultrasound in the dissolution kinetics of phosphate rock in HCl. *Hydrometallurgy* 64, 187–192.
- Vassura, I., Morselli, L., Bernardi, E., Passarini, F., 2009. Chemical characterisation of spent rechargeable batteries. *Waste Manage.* 29, 2332–2335.
- Wanger, T.C., 2011. The Lithium future resources, recycling, and the environment. *Conserv. Lett.* 4, 202–206.
- Xu, J., Thomas, H., Francis, R.W., Lum, K.R., Wang, J., Liang, B., 2008. A review of processes and technologies for the recycling of lithium-ion secondary batteries. *J. Power Sources* 177, 512–527.
- Zand, A.D., Abdul, M., 2008. Current situation of used household batteries in Iran and appropriate management policies. *Waste Manage.* 28, 2085–2090.
- Zhang, P., Yokoyama, T., Itabashi, O., Suzuki, T.M., Inoue, K., 1998. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy* 47, 259–271.
- Zhang, T., He, Y., Wang, F., Ge, L., Zhu, X., Li, H., 2014. Chemical and process mineralogical characterizations of spent lithium-ion batteries: an approach by multi-analytical techniques. *Waste Manage.* 34, 1051–1058.
- Zhao, L., Yang, D., Zhu, N.-W., 2008. Bioleaching of spent Ni–Cd batteries by continuous flow system: effect of hydraulic retention time and process load. *J. Hazard. Mater.* 160, 648–654.
- Zheng, X., Gao, W., Zhang, X., He, M., Lin, X., Cao, H., Zhang, Y., Sun, Z., 2016a. Spent lithium ion battery recycling – reductive ammonia leaching of metals from cathode scrap by sodium sulphite. *Waste Manage.*
- Zheng, Y., Long, H., Zhou, L., Wu, Z., Zhou, X., You, L., Yang, Y., Liu, J., 2016b. Leaching procedure and kinetic studies of cobalt in cathode materials from spent lithium ion batteries using organic citric acid as leachant. *Int. J. Environ. Res.* 10, 159–168.