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CATALYTIC PASTE SOLUBILIZATION RESEARCHES REGARDING THE COBALT RECOVERY FROM USED Li-ION BATTERIES - ANOVA APPLICATION

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This paper present research regarding the cobalt recovery from the disassembled cathode from lithium-ion based secondary batteries. The experiments were carried out on the grinded material to a size appropriate to the performance of a hydrometallurgical process. Hydrometallurgical processing consisted in the involvement of different reagents that have the ability to solubilize metals of interest in the solution. In this regard, a fractional experimental plan (2^{7-2}) *was applied, thus having 2 levels of each investigated factor namely "+" and "-", and 7 investigated factors: Sulfuric acid* (H_2SO_4)*, Malic Acid* ($C_4H_6O_5$)*, Sucrose* ($C_{12}H_{22}O_{11}$)*, Oxygenated Water* (H_2O_2)*, Citric Acid* ($C_6H_8O_7$)*, Oxalic Acid* ($C_2H_2O_4$) *and Temperature. By using the analysis of variance (ANOVA) in accordance with Yates's algorithm, both the effect of the factors and their interactions has been studied.*

Keywords: ANOVA**,** Li-ion batteries, cobalt, recovery, solubilization, paste.

1. Introduction

Batteries provided the main source of electricity before the development of electric generators and electrical grids around the end of the 19th century. For over 200 years, batteries have been a vital source of energy for all users. Almost

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all the devices we use need electricity. And if there were no batteries to store it, we would be dependent on electric cables [1].

Li-Ion batteries were first produced by Sony in 1991. Currently, the lithium-ion battery industry is dominated by $LiCoO_2$cathodes and carbon anodes [2, 3]. This material was first reported by John Goodenough who admitted that this material has a layered structure and lithium can be electrochemically removed, thus being a promising cathode material [4, 5].

There are four different varieties of lithium-ion batteries currently available on the market: cylindrical, thin and flat polymer, coins and prismatic battery. Of these types of battery configurations, the most commonly used battery is the 18650 (18 x 65 mm) cylindrical type. These can usually be found on laptops and also on electric cars while prismatic batteries are found in the mobile phone [6, 7].

The base element of a battery is called a cell. A battery is made up of one or more cells connected in series or in parallel, depending on the voltage or capacity required at the output. A cell has three main components: the anode (the reducing material or negative electrode), which donates electrons to the outer circuit, being oxidized during the electrochemical reaction, the cathode (the oxidizing agent or the positive electrode) that accepts electrons from the circuit outer and the electrolyte which creates a favorable environment for ionic conduction. Electrolytes are typically liquids which have the role of separating the anode from the cathode, but there are also batteries that use solid materials that are ion conductors [5, 8, and 9].

During charging, the lithium ions pass from the cathode to the anode and the electrons are removed from the cathode through an outer field and then transferred to the anode. During discharge, the anode provides the electrolyte ions and electrons to the external circuit where the ions intersect in the cathode and the electrons in the external circuit to compensate for the charge. The redox reactions are presented below:

- Positive: $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$ (1)
- Negative: $xLi^+ + xe^- + xC_6 \leftrightarrow xLiC_6$ (2)
- General: $Li^+ + e^- + LiCoO_2 \rightarrow Li_2O + CoO$ (3)

The chemical composition of certain batteries is different and depends on the type and brand of the battery. The positive electrode is made of a paste consisting of a mixture of active material ($LiCoO_2$), black acetylene and PVDF binder polymer (polyvinylidene fluoride) and covered on both sides with an aluminum substrate. The negative electrode consists of a copper substrate which is coated with a mixture of active carbon material (MCMB) and binder polymer on both sides. Li-ion batteries contain substantial amounts of valuable metals, such as aluminum, iron, copper, lithium, cobalt, nickel and manganese. The most valuable metal is cobalt, which is contained in the battery electrode material. Therefore, cobalt recovery has a strong influence on the economic efficiency of an appropriate battery recycling process [7, 8, 9, and 10].

The typical chemical composition of Li-ion batteries is the following: Al (15-25%), amorphous carbon powder (0.1-1%), Cu foil (5-15%), diethyl carbonate (1-10%), ethylene carbonate (1-10%), methyl ethyl carbonate (1-10%), $LiPF_6$(1-5%), graphite powder (10-30%), $LiCoO_2$ (25 - 45%), polyvinylidene fluoride (PVDF) (0.5-2%), steel, Ni and inert polymer [7, 8, 9, and 11].

Recovery of Co is one of the primary goals in recycling used Li-ion batteries due to the high cost (Co is the most expensive metal in Li-ion batteries 14 $/ lb.). The price of Co is very high because there are few resources of Co in the world (the main producers of Co are Congo, Canada, China and Russia) [12].

The recycling process should reduce the waste volume, separate the components of the battery, and eliminate or reduce the risk of waste from used Li-ion batteries in the environment. Recycling processes are pyrometallurgical, hydrometallurgical and also biometalurgical, to which are added, as initial a phase, various physical processes. Physical processes generally involve mechanical processes, thermal treatments, mechanochemical processes, and dissolution processes [8, 13].

Chemical processes combine several steps - leaching in acidic or alkaline environments and purification; these two methods aim at dissolving metal fractions and recovering metals of interest that can be used in the chemical industry. Recycling through chemical processes mainly consists of leaching in acids or bases, chemical precipitation, filtration, extraction or other processes. Leaching with acids or bases is necessary in order to dissolve the metals in the solution. Once in solution, the metals can be recovered by chemical precipitation, changing the pH of the solution or by the addition of a reaction agent or by electrolysis [14].

Solubilization of $LiCoO_2$ from used Li-ion batteries is usually accomplished by using inorganic acids as leaching agents such as H_2SO_4, HCl, and HNO_3. But also, organic acids, such as malic acid, citric acid may also be used. The oxygenated water is used as a reducing agent. The addition of the reducer is necessary to ensure reduction of Co^{3+} to Co^{2+} because Co^{2+} is more soluble than Co^{3+} [15].

The reactants used in the solubilization process presented in this paper have been selected following an analysis of several works that have as subject the recovery of cobalt such as:

- In the hydrometallurgical cobalt recovery process, Jha et al., 2013 [16] used 2M solution of H_2SO_4 for 60 min, 100 g / L. The process consists in recovering Co and Li from used Li-ion batteries, using leaching and then solvent extraction. In that process 70% Co was recovered;

- Zhu et al., 2012 [17] used sulfuric acid (H_2SO_4) and oxygenated water (H_2O_2) for the leaching process. The experimental study shows that 94.7% Co can be recovered in the form of CoC_2O_4;
- For the leaching process, Granata et al., 2010 [18] used hydrochloric acid as well as sulfuric acid and glucose. Using the solvent extraction process and then the precipitation process, the high purity $CoCO_3$ product (47% Co) was obtained;
- Pagnanelli et al., 2016 [19] achieved solubilization with sulfuric acid (H_2SO_4) at 60°C, the ratio being 2:1 (2 grams of acid per gram of powder) and hydrogen peroxide (H_2O_2). High-purity products have been recovered from the process: lithium (Li_2CO_3), cobalt (Co/ $CoSO_4$/ $CoCO_3$) and nickel (Ni/ $NiCO_3$).
- Li et al., 2011 [20] in the solubilization process used 3 types of organic acids: citric, malic and aspartic, at a temperature of 90°C for 30, 40 or 120 minutes. The experiment was performed on the cathode materials of used Li-ion batteries. Using citric or malic acid, 90% Cobalt was obtained.

2. Materials and methods

2.1. Materials

In this study, spent Li-ion batteries were used. The cathode was manually cut into pieces of about 1mm² and then ground in the "Pulverisette 7" ball mill for 30 minutes at a stirring speed of 500 rotations per minute. Below we present some images on the pre-treatment applied.

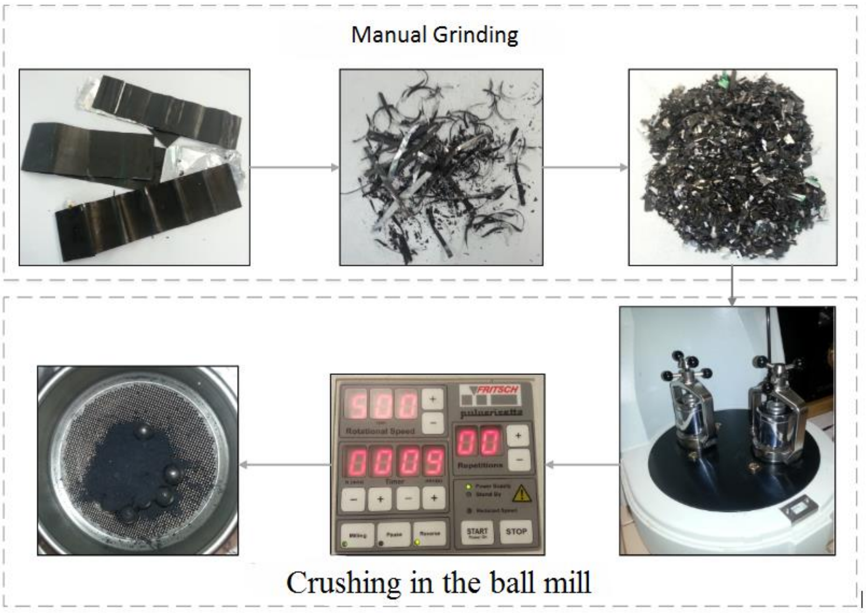


Fig.1. The pre-treatment flow on the cathode foils

By sieving this powder using a sieve of various mesh sizes, it was determined that more than 48% of the powder obtained had a size greater than 212μm, 47.62% had a size in the range of 212-63μm. The remaining 3.42% had the size of less than 63μm (fig.2). The graph below shows the granulometric curve of the powder resulted from grinding:

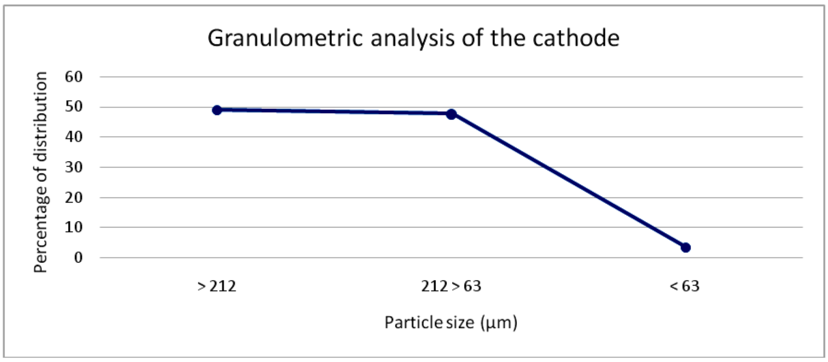


Fig.2. Granulometric analysis of the grinded cathode

To confirm the presence of Cobalt in the powder obtained, a chemical attack was made with royal water (a mixture of HCl and HNO_3 in a ratio of 3:1) using a quantity of cathodic powder. The solution obtained from this attack was then filtered under vacuum to separate the undissolved solid. Subsequently, the solution was analyzed by both atomic absorption spectrometry and X-ray fluorescence spectrometry. Thus, it was observed that the powder contained approximately 42.16% Cobalt.

2.2. Solubilization of solutions

To solubilize the metals of interest in the solution, various reagents were used according to the fractional factorial design and their concentrations were determined depending on the redox chemical reactions:

$$12LiCoO_2 + 18H_2SO_4 + C_4H_6O_5 \rightarrow 12CoSO_4 + 6Li_2SO_4 + 4CO_2 + 21H_2O \qquad (4)$$

$$48LiCoO_2 + 78H_2SO_4 + C_{12}H_{22}O_{11} \rightarrow 48CoSO_4 + 24Li_2SO_4 + 12CO_2 + 83H_2O \qquad (5)$$

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow 2CoSO_4 + Li_2SO_4 + 4H_2O_2 + O_2 \qquad (6)$$

$$18LiCoO_2 + 27H_2SO_4 + C_6H_8O_7 \rightarrow 18CoSO_4 + 9Li_2SO_4 + 6CO_2 + 31H_2O \qquad (7)$$

$$2LiCoO_2 + 3H_2SO_4 + C_2H_2O_4 \rightarrow 2CoSO_4 + Li_2SO_4 + 2CO_2 + 4H_2O \qquad (8)$$

The experimental process in this study is presented in the figure below:

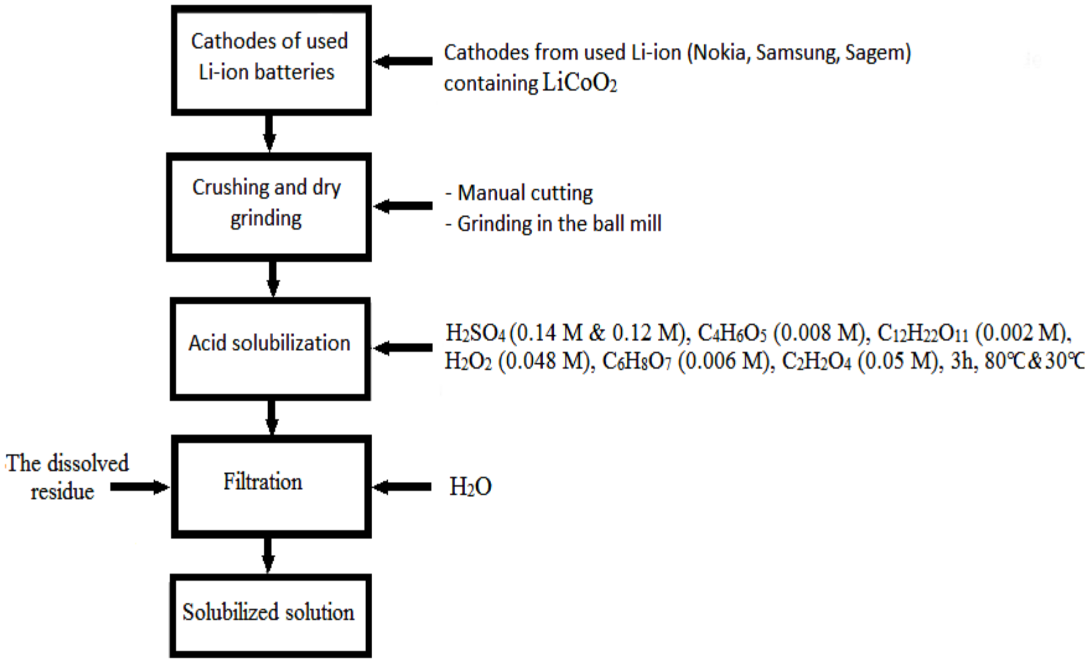
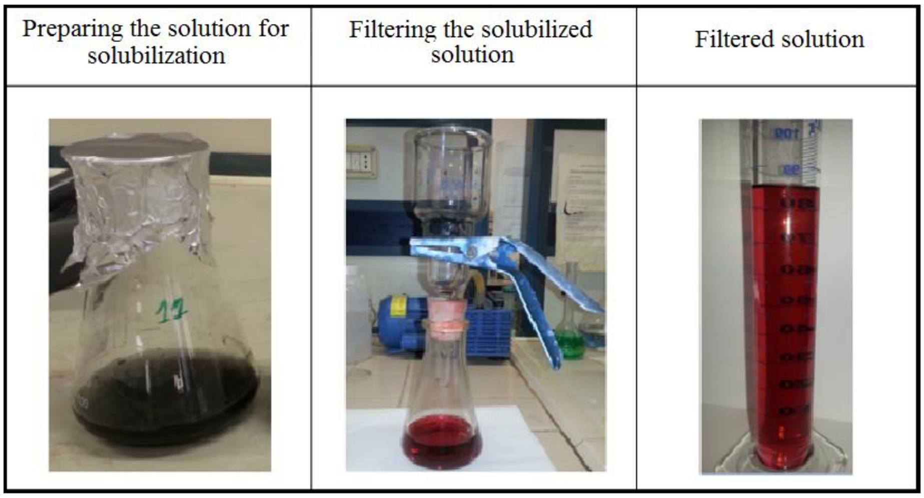


Fig.3. Experimental process flowchart

The solubilization was performed (as shown in Figure 4) on the powder with the average size of the particles of 212 µm, maintaining a solid: liquid ratio of 1:100 and a reaction time of 3 hours. These tests were carried out in Erlenmeyer flasks (250 ml) which were placed in the Dubnoff thermostatic bath in order to heat and shake the samples.



Preparing the solution for solubilization

Filtering the solubilized solution

Filtered solution

Fig.4. Images from the solubilization process of the cathode foil

Throughout the process, a mechanical stirring speed of 200 rpm was applied, and at an interval of one hour, samples were taken from each solution to determine the concentration of the elements of interest in the solution by spectral atomic absorption analysis. The final solution was then filtered under vacuum (Greiffenberger vacuum pump) using a 44 mm filter.

In order to obtain the optimal conditions for the solubilization of valuable materials contained in the cathode of the Li-ion secondary batteries, a series of solubilization processes were performed, in which the 6 reagents were used at different concentration – mixing the lower and the highest level of each one, at 30°C and respectively 80°C.

The methods of mixing the levels (high/low) is presented in section 2.3 “The ANOVA application” and in Table 1 are presented the levels of each reagent.

Table 1.

Solubilization Parameters

		Level		
		High (+)	**Medium (0)**	**Low (-)**
A	Process temp., °C	30	50	80
B	Conc. of H_2SO_4, M	0.14	0.13	0.12
C	Conc. of $C_4H_6O_5$, M	0.008	0.004	0
D	Conc. of $C_{12}H_{22}O_{11}$, M	0.002	0.001	0
E	Conc. of H_2O_2, M	0.048	0.024	0
F	Conc. of $C_6H_8O_7$, M	0.006	0.003	0
G	Conc. of $C_2H_2O_4$, M	0.05	0.025	0

2.3. The ANOVA application

This experimental work is based on a fractional experimental plan 2^{7-2}→ thus we have 2 levels of each investigated factor: "+" and "-", and 7 investigated factors:

- A – Temperature;
- B – Sulfuric acid (H_2SO_4),
- C – Malic acid ($C_2H_6O_5$),
- D - Sucrose ($C_{12}H_{22}O_{11}$),
- E – Hydrogen peroxide (H_2O_2),
- F – Citric acid ($C_6H_8O_7$),
- G – Oxalic acid ($C_2H_2O_4$),

of which 2 generators (F and G) are composed of the interactions generated between the first five factors: F=A*B*C*D and G=B*C*D*E.

Table 2.

The fractional factorial model applied in the experiment

Factors		**Temperature**	**Sulfuric Acid**	**Malic Acid**	**Sucrose**	**Hydrogen Peroxide**	**Citric Acid**	**Oxalic Acid**
No.	Test	A	B	C	D	E	F=ABCD	G=BCDE
1	1	-1	-1	-1	-1	-1	1	1
2	a	1	-1	-1	-1	-1	-1	1
3	b	-1	1	-1	-1	-1	-1	-1
4	ab	1	1	-1	-1	-1	1	-1
5	c	-1	-1	1	-1	-1	-1	-1
6	ac	1	-1	1	-1	-1	1	-1
7	bc	-1	1	1	-1	-1	1	1
8	abc	1	1	1	-1	-1	-1	1
9	d	-1	-1	-1	1	-1	-1	-1
10	ad	1	-1	-1	1	-1	1	-1
11	bd	-1	1	-1	1	-1	1	1
12	abd	1	1	-1	1	-1	-1	1
13	cd	-1	-1	1	1	-1	1	1
14	acd	1	-1	1	1	-1	-1	1
15	bcd	-1	1	1	1	-1	-1	-1
16	abcd	1	1	1	1	-1	1	-1
17	e	-1	-1	-1	-1	1	1	-1
18	ae	1	-1	-1	-1	1	-1	-1

19	be	-1	1	-1	-1	1	-1	1
20	abe	1	1	-1	-1	1	1	1
21	ce	-1	-1	1	-1	1	-1	1
22	ace	1	-1	1	-1	1	1	1
23	bce	-1	1	1	-1	1	1	-1
24	abce	1	1	1	-1	1	-1	-1
25	de	-1	-1	-1	1	1	-1	1
26	ade	1	-1	-1	1	1	1	1
27	bde	-1	1	-1	1	1	1	-1
28	abde	1	1	-1	1	1	-1	-1
29	cde	-1	-1	1	1	1	1	-1
30	acde	1	-1	1	1	1	-1	-1
31	bcde	-1	1	1	1	1	-1	1
32	abcde	1	1	1	1	1	1	1

Using this fractional factorial plan with seven factors at two levels (2^{7-2}), 32 experiments were performed.

3. Experimental results and discussion

The experimental procedure consisted in the solubilization process of the cathode material and the analysis of the samples in order to determine the best extraction yield of cobalt from the solutions and at the same time the determination of the best reactant used in this process.

In table 3 are presented the results for extraction yields of cobalt from the solutions (mostly greater than 60%) at certain time intervals and in table 4 the quantities of reactants used for these samples:

Table 3.

The extraction yields greater of cobalt

No.	**Test**	**Extraction yield of Co (%)**		
		1h	**2h**	**3h**
4	AB (III)	61.87332	*64.59489*	55.26718
6	AC	59.88123	*63.92203*	53.87532
8	ABC	56.50180	*62.74308*	61.49684
12	ABD (I)	55.93856	***71.16825***	55.05635
14	ACD (II)	64.03142	*69.78802*	63.53102
16	ABCD	60.41483	*61.30534*	60.02945
20	ABE	57.15397	*63.17440*	62.11285
22	ACE	57.56899	*64.18082*	61.63024
24	ABCE	53.00378	*60.47145*	57.07808
28	ABDE	58.36938	*62.08172*	56.29547
30	ACDE	56.38322	*60.55771*	56.96128
32	ABCDE	60.47412	*64.03705*	62.29723

Table 4.

The quantities of reactants used for samples

No.	**Temp.**	**H_2SO_4**	**$C_2H_6O_5$**	**$C_{12}H_{22}O_{11}$**	**H_2O_2**	**$C_6H_8O_7$**	**$C_2H_2O_4$**
	A	B	C	D	E	F= ABCD	G=BCDE
4	80	0.38	0	0	0	0.057	0
6	80	0.32	0.0536	0	0	0.057	0
8	80	0.38	0.0536	0	0	0	0.022
12	**80**	**0.38**	**0**	**0.0342**	**0**	**0**	**0.022**
14	80	0.32	0.0536	0.0342	0	0	0.022
16	80	0.38	0.0536	0.0342	0	0.057	0
20	80	0.38	0	0	0,24	0.057	0.022
22	80	0.32	0.0536	0	0,24	0.057	0.022
24	80	0.38	0.0536	0	0,24	0	0
28	80	0.38	0	0.0342	0,24	0	0
30	80	0.32	0.0536	0.0342	0,24	0	0
32	80	0.38	0.0536	0.0342	0,24	0.057	0.022

Considering the results obtained, the maximum value for cobalt extraction, 71.17%, was obtained for the "*ABD*" test. This is due to the combination of sulfuric acid, sucrose and oxalic acid at a temperature of 80°.

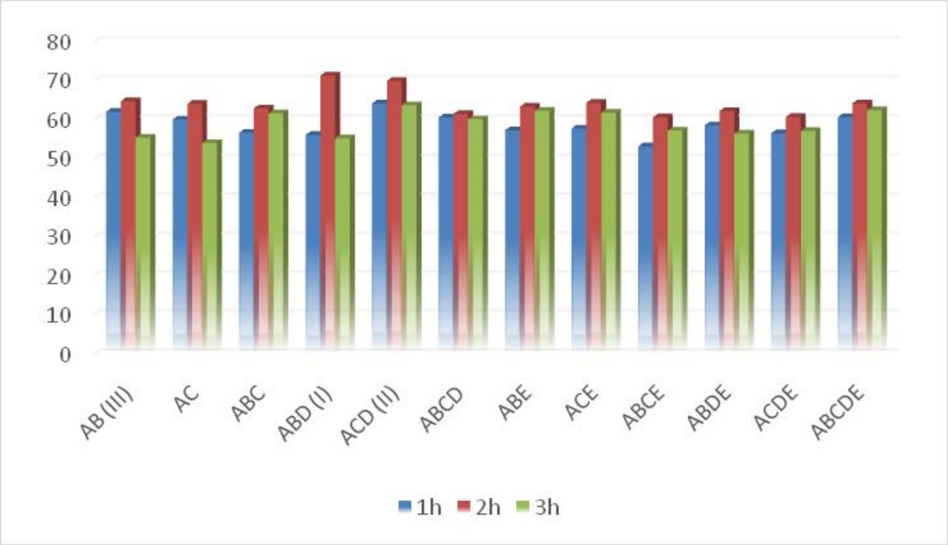


Fig.5. The effect of Time on yield of Co extraction

Factor A, the process temperature, with the tested values of 30°C and 80°C, has a significantly positive effect on Cobalt extraction. From ANOVA, it results that by raising the temperature, the extraction yield can be improved by about 23%. This is because both the velocity of the chemical reaction and the ion transfer is significantly influenced by the temperature.

Factor B, the sulfuric acid concentration with the tested values: 0.14M and 0.12M, positively affect the extraction of cobalt. With the increase in sulfuric acid concentration, the Co extraction yield improves by about 1.9%.

According to the table above, it is observed that the extraction yield of cobalt increases up to 2 hours, followed by a slight decrease. This is due to the precipitation phenomenon of both metals once the reagents in the solution have been consumed. The combination of sulfuric acid, sucrose and oxalic acid at 80°C shows the highest degree of solubilization of cobalt.

The solubilization efficiency of cobalt is relatively low at a leaching temperature of 30°C, but rising when temperature reaches 80°C. Thus, the temperature of 80°C will be chosen as the optimal solubilization temperature. At the same time, the solubilization of cathode materials increases with the increase in time. Thus, we will choose the optimal solubilization time as being 2 hours.

4. Conclusions

Hydrometallurgical processing of lithium-ion based secondary batteries includes as the main operation the process of solubilization. For the recovery of cobalt from the $LiCoO_2$ active material we used different reagents as sulfuric acid (H_2SO_4), malic acid ($C_2H_4O_5$), sucrose ($C_{12}H_{22}O_{11}$), hydrogen peroxide (H_2O_2), citric acid ($C_6H_8O_7$), oxalic acid ($C_2H_2O_4$) by varying the concentrations of solutions and temperatures of process.

The ANOVA application used in this research paper allowed optimization of the solubilization process. Through this experimental plan it is possible to determine with sufficient precision the effect produced by the input variables of the solubilization process because they are confused only with the effects of the interactions of three factors that are generally considered negligible when analyzing the main effects.

The maximum value f of 71.17% for cobalt extraction was obtained during the "ABD" test. This is due to the combination of sulfuric acid, sucrose and oxalic acid at a temperature of 80ºC. It is necessary to continue the research in order to recover the cobalt from the solubilized solution, using the precipitation process.

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