Improvement study of hydrometallurgical treatment process for Li-ion batteries waste

Abstract

This study concerned the search for a method aimed at improving the safety of the treatment of Li-ion (Lib) battery waste. It consisted in the extraction of the electrolyte from used Libs by methanol before the hydrometallurgical treatment. As a result, the infrared extracts characterization, after concentration, revealed the presence of characteristic vibrations of organic functions or chemical bonds other than those of the methanol used, prompting the search for other constituents (P, F, Li) generally found in the electrolyte compositions of Lib. Furthermore, the pretreated cathodes are cut and subjected to selective leaching with 4N NaOH for 60 minutes according to a liquid/solid ratio L/S=10 L/Kg at ambient temperature. Alkaline leachates and black residues were quantified by X-ray fluorescence and results showed higher recovery rates for aluminum. It thus seemed that the pretreatment of the cathodic samples decreased the leaching rates. In addition, the pre-treatment of the samples has been shown to reduce the polluting nature of selective leaching, and the extraction of the electrolyte by methanol allowed the recovery of copper at the anode without any hydrometallurgical treatment.

Key words: electrolyte, methanolic pretreatment, alkaline leaching.

I. **Introduction**

In recent decades, there has been a meteoric rise worldwide in cell phones, laptops, digital devices, electric and hybrid vehicles, etc. generally operated using Li-ion batteries [1,2]. Thus, the accelerated updating of consumer electronics and advances in the promotion of the electric vehicle, have led to an increased demand for Li-ion batteries correlated with a big production of Libs waste in the world. Indeed, according to a statistical study on the consumption of Libs, the world production of Libs increased from 500 to 700 million tons from 2000 to 2004 while the number of users exceeded 6.8 billion in 2013 [3]. Therefore, based on Li-ion battery life studies [4,5], waste generation in China is predicted to be 500,000 tons in 2020 [6].

Spent Libs are concentrated precious and/or critical metals (Co, Ni, Mn, Li, Al, Cu, etc.) in their electrodes and flammable constituents (ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc.) and toxic ($LiPF_6$, $LiBF_4$, etc.) of the electrolyte [7–10]. A statistical study has therefore proven that a mass of 4000 tons of Libs waste can contain 1100 tons of heavy metals and more than 200 tons of toxic electrolyte components [3]. Therefore, decomposition in nature, improper handling, or open burning, as in some less developed countries [11], could be sources of environmental and public health problems. To this end, the management of used Li-ion batteries has an economic impact by setting up a secondary source of metallic raw materials and an environmental one by preserving nature against certain pollutants. This management of Libs waste has seen great progress with the discovery of many hydrometallurgical techniques allowing the recovery of more than 95% of the most precious design metals [8].

These techniques are endowed with a considerable selectivity allowing high recovery rates and purities [12]. However, safety remains a relevant issue regarding gaseous discharges which mark the ecological footprint of the Libs treatment process [13–15].

Previous work has led to the observation of an unpleasant and pungent odor after cutting the outer casing by the internal constituents of the accumulators, which disappears after drying the electrodes in an oven. In addition, the same phenomenon of gas evolution was noted during the leaching phases of the Libs cathodes, as well as an exothermic character of the alkaline leaching. Based on these facts, this present study aims to evaluate the impact on the ecological footprint and the efficiency of the hydrometallurgical treatment of Libs, after the prior extraction of the electrolyte.

II. Experimental

II.1. Material and methodology

The Li-ion batteries of telephones and laptops studied were purchased at the Colobane market in Dakar.

The study was conducted at the Cheikh Anta Diop University of Dakar (UCAD), at the physical, Mineral, Organic and Therapeutic Chemistry, and Analytical Chemistry and Bromatology laboratories of the Faculty of Medicine, Pharmacy and Odontology (FMPO), Organic Coordination Chemistry from the Faculty of Sciences and Technologies (FST) and the Institute of Applied Nuclear Technologies (ITNA). The reagents used were of purity for analysis.

The quantification tests of the metal compositions of the liquid and solid samples after leaching were determined by X-ray fluorescence spectroscopy (Niton XL3T XRF Analyzer).

The extracts concentrated by rotary evaporation (Büchi) and the various precipitates were characterized by infrared spectrophotometry (Perkin-Elmer Spectrum, version 10.5.4) and UV-visible spectrophotometry (Thermo scientific, UV-Vis Evolution™ 300).

II.2. Results and discussion

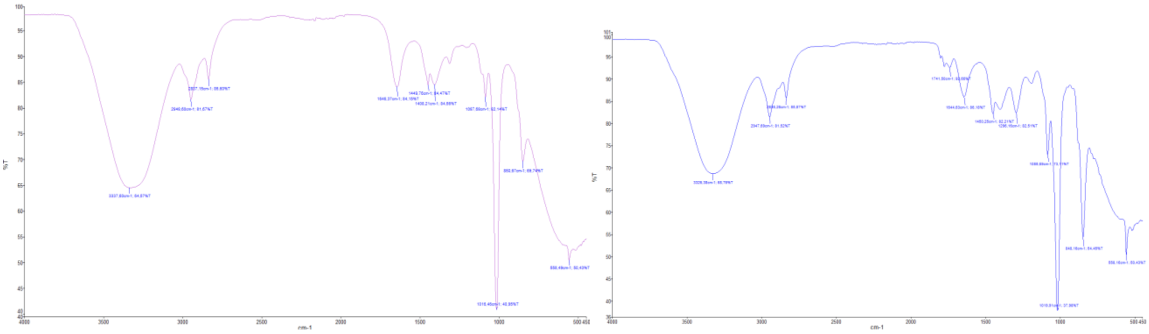
First, the Li-ion batteries were fully discharged using an ionic solution of 4N NaCl. After unloading, they were dismantled manually according to a protocol described [16] and the interior contents washed with methanol.

II.2.1. Extraction of electrolyte mixtures

The materials of the electrodes and separators immediately recovered were immersed in methanol and the whole is stirred manually every 30 minutes for 3 hours. The solids are then removed, and the filtered methanol washes are concentrated using a rotary evaporator. These concentrates are characterized by infrared spectrometer and identification tests by precipitation are carried out to determine the presence of the electrolyte components in particular, the solvents and solutes used.

II.2.1.1. Study of extraction of electrolyte solvents by methanol

Test samples of the extracts before and after concentration are characterized by infrared spectroscopy and the profiles of the samples are presented in figure 1 below.



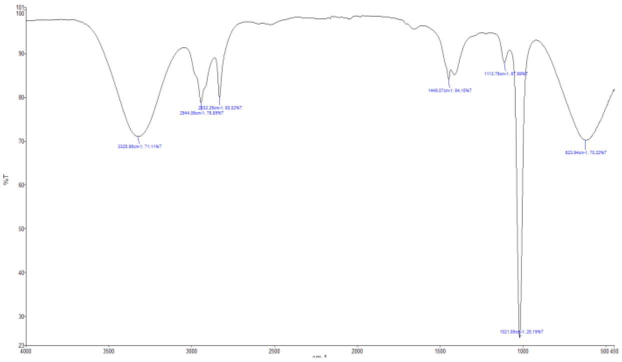


Figure 1: Infrared spectrum a) of the unconcentrated methanolic extract b), of the concentrated one and c) of the distillate recovered during the concentration.

The infrared characteristic vibration attribution study resulted in the various corresponding infrared profiles defined in Table I below.

Table I: Comparison of the infrared profiles of the methanolic extracts and proposal for the assignment of the corresponding vibrations.

Infrared absorption bands (cm^{-1})		Attributions	
$MeOH_{con}$	$MeOH_{dist}$		
1644,63		H_2O	
1741,50		C = O (carboxylic acid)	New functions
1296,16		C – OH (carboxylic acid)	
848,16		O – H (carboxylic acid)	

$MeOH_{con}$: concentrated filtrate of methanol wash liquor
$MeOH_{dist}$: methanol distillate recovered from wash liquor filtrate concentration.

After the identification of the characteristic bands of the infrared profile of methanol used during the extraction tests of the electrolyte mixtures, a specificity on the profiles of the different samples (figure 1) was noted and corresponding to the presence of absorption bands other than those characteristics of the solvent (Table II). These include an average band emerging at 1741.50 cm^{-1} and two others at 1296.16 cm^{-1} and 848.16 cm^{-1} attributable to the respective vibrations of the C=O, C–OH groups and O–H of carboxylic acid functions.

According to the literature, the organic solvents generally used as constituents of marketed electrolytes are alkyl carbonates [17,18]. Therefore, the detection of carboxylic acid function in the extracts suggests electrolyte recovery. Therefore, further studies and characterization tests are conducted to determine the presence of other electrolyte components.

II.2.1.2. Search for lithium in extracts

The lithium precipitation test is carried out in the presence of sodium carbonate. Indeed, test portions of approximately 5 mL of concentrated extract are treated with an excess of 4N Na_2CO_3. After addition of the precipitation reagent, white precipitate formed, and the infrared analysis revealed substantially identical profiles.

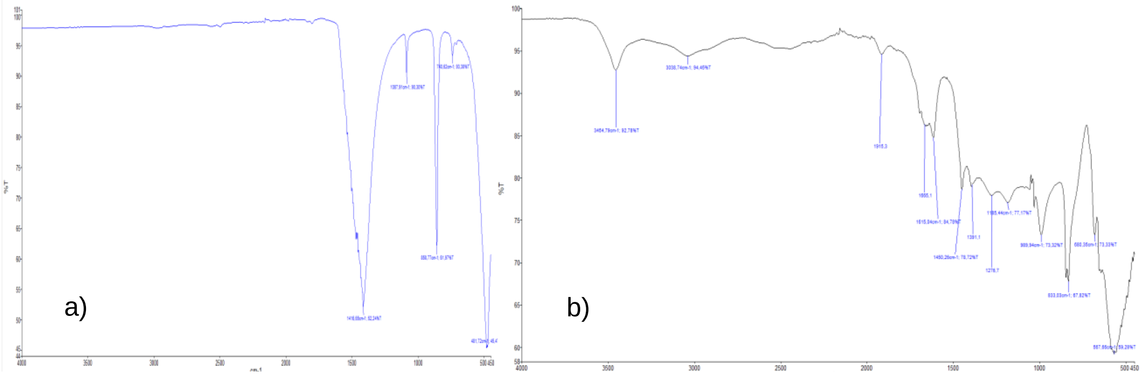


Figure 2: IR spectra a) of a Li_2CO_3 powder and b) of the precipitate formed by the action of Na_2CO_3.

The results of the study of attribution of the vibrational bands characterized on the infrared profiles of the samples are reported in Table II.

Table II: Attribution of the vibrations of the infrared spectra of the methanolic extract and the Li_2CO_3 powder taken as reference.

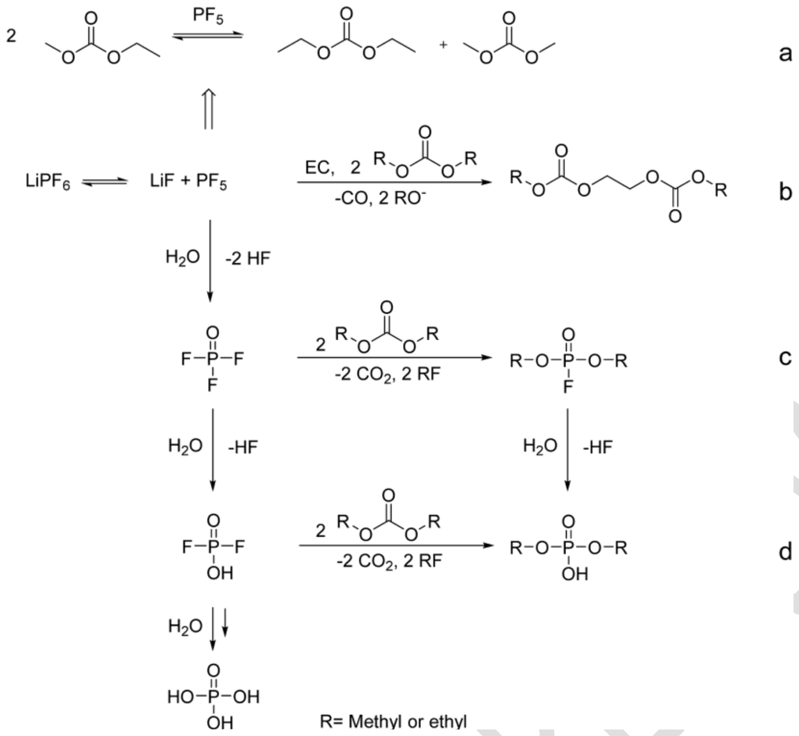
IR absorption bands (cm^{-1})		Attribution
Precipitate	Li_2CO_3	
3454,79		O – H (linked) acid
3038,74		O – H (linked) alcohol
1915,3		
1665,1		C = O (acid)
1615,04		H_2O
1450,04		O – H
1391,1	1416,65	Li_2CO_3
1276,7		C – O acid
1185,44		
989,94	1087,91	Li_2CO_3
833,03	858,77	Li_2CO_3
680,35	740,62	Li_2CO_3
567,66	481,72	Li_2CO_3

II.2.1.3. Search for phosphorus in extracts

According to the literature [18,19], the $LiPF_6$ salt most used in the design of batteries is very unstable in the presence of traces of water which promotes its decomposition as presented by the reaction below:

$$LiPF_6 \rightleftharpoons LiF + PF_5$$

According to Schultz et al., (2017), the phosphate pentafluoride (PF_5) formed can undergo a series of reactions in contact with water up to the formation of phosphoric acid (H_3PO_4) or phosphates and hydrofluoric gas (HF). In addition, PF_5 can also react with organic solvent constituents of the electrolyte to form alkyl phosphates as shown:



This series of interdependent decomposition reactions leads to a very complex mixture with the release of gases that can pollute the atmosphere.

Consequently, reactions were carried out on test portions of the concentrated extracts to precipitate the phosphorus into phosphoric acid or phosphate. After 72 h, yellow precipitate formed. It was then recovered by filtration, washed with distilled water, dried at room temperature, and subjected to characterization tests. Samples of the precipitates are subjected to infrared characterization tests (Figure 3).

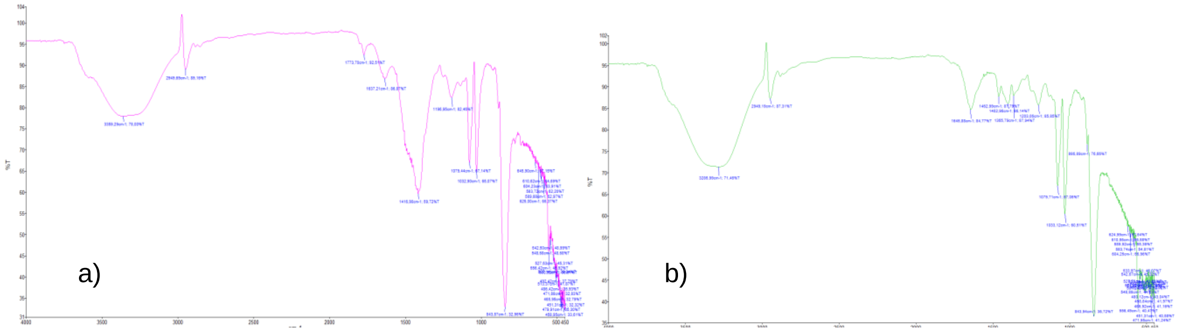


Figure 3: Infrared spectrum of the precipitates a) from the methanolic extract and b) from the ethanolic one.

Table III: Interpretation table of the infrared spectra of the precipitates obtained from samples of concentrated washing liquors.

IR absorption bands (cm^{-1})		Attributions
Méthanolic extract	Ethanolic extract	
3359,29	3285,99	OH

2949,69	2949,19	
1773,70		ethanol
1637,21	1645,88	H_2O
	1462,99	ethanol
1416,90	1402,96	
	1365,79	ethanol
1196,95	1203,06	P = O
1079,44	1079,71	
1032,90	1033,12	
	886,89	ethanol
843,87	843,94	

The vibrational band assignment study showed that the absorption bands of the two spectra came out at the same places except for a few chemical shifts. This suggests that the same precipitate formed. Furthermore, it is noted on the spectra, a vibration absorbing around 1200 cm^{-1} attributed to the phosphine function (P=O). Therefore, phosphate assay tests are performed in the presence of sodium hydrogen molybdate, ammonia and acetic acid.

A mass of 2 g of powder from the precipitate is dissolved in 20 mL of distilled water. 5 ml of 4N acetic acid are added to this solution and the mixture obtained is homogenized. Then, 5 ml of a 4 N sodium molybdate solution are added, then 5 ml of ammonia. After mixing the reagents, an orange-blue color appears in the test tubes.

A reference sample prepared from solutions of sodium phosphate and sodium phospho-molybdate in the presence of ammonia is prepared for the absorbance measurements in the UV-visible spectrometer.

In the light of the results, quite high UV absorptions of the order of 0.400 in the 750 – 800 cm-1 range are noted. These absorption phenomena observed with the reference solution confirm the presence of ammonium phospho-molybdate, hence the presence of phosphate in the precipitates. However, further studies are needed to determine its exact chemical form.

II.2.2. Alkaline leaching of cathodes previously washed with ethanol or methanol

Test portions of the sample of cathodes previously treated with alcohols (ethanol, methanol) are leached in the presence of a 4N NaOH solution, at room temperature according to a ratio L/S = 10 L/Kg. After addition of the reagents, the reaction media are placed under stirring. After 2 hours of reaction, a sample of 2 mL of leachate is taken and repeated every hour until 5 a.m. At the end, the leachates are recovered by filtration (FisherbrandTM grade 143) to undergo quantification tests by XRF.

The analytical results showed higher aluminum contents compared to those of cobalt, manganese, nickel, copper, etc. which are at trace levels in the leachate (figure 4).

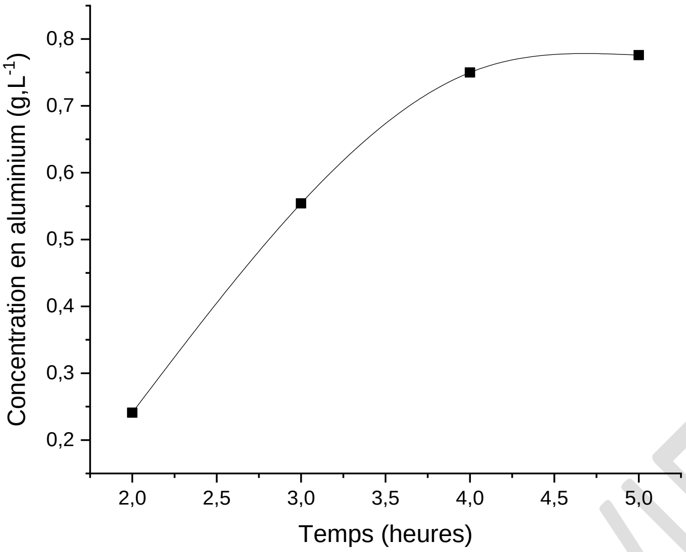


Figure 4: Curve of evolution of the aluminum concentration as a function of time (NaOH 4 N, L/S = 10 L/Kg, T_{amb})

This curve characterizes the evolution of the leaching efficiency of aluminum from the cathode by a sodium hydroxide solution (NaOH 4 N) as a function of time. This highlighted two phases of evolution at 2 h and 4 h and showed a clear improvement in leaching efficiency. At the level of the second, a tray appeared which began to settle around four hours of reaction with a slight variation in the aluminum content. These results corroborated data from the literature which support that a sodium hydroxide solution is capable of attacking the aluminum of Libs cathode design. However, the aluminum recovery efficiency is quite low compared to literature data [16,21]. Ferreira et al., (2009) and Gaye et al., (2019) respectively obtained recovery rates of up to around 59% and 55% in aluminum after 60 minutes of agitation. Moreover, according to the literature, the soluble complex most generally formed with Al is $[Al(OH)_4]^-$) [21]. Since literature data have revealed that $[Al(OH)_n]^{3-n}$ complexes (with $n \geq 4$), due to a lack of stability, generally lead to the precipitation of $Al(OH)_3$ in a very alkaline medium (high pH), in the presence of CO_2, etc. [22–25], the composition of the residual powders was determined by XRF and the contents of the most representative metals are reported in Table IV below.

Table IV: Composition of residual powder from the leaching of cathodic materials with 4 N NaOH, L/S = 10 mL/g.

Element oxides	*Al*	*Co*	*Cu*	*Fe*
Percentage %	15,31	76,14	0,02	0,09

These results show a very concentrated composition of cobalt with 76.14%, aluminum with 15.31% and traces of copper and iron. This presence of aluminum in high content in the leaching residues confirms the precipitation of aluminum hydroxide.

II.2.3. Recovery of copper anode connector

The prior extraction of the electrolyte from a used Libs played a major protective role in its treatment by hydrometallurgy. Contrary to previous work, the pungent gas release observed during the dismantling phases and the alkaline and acid leaching phases was significantly reduced or even absent.

At the end of the electrolyte extraction tests, the electrodes are rinsed several times with distilled water, and it is noted at the level of the anodes, a separation of the black layer of active material and of the electronic connector. The analysis confirmed that the nature of the metal sheet of the connector is not altered and that it retains its conductive properties. Figure 5 below shows metallic sheets of anode connector separated from the layer of active material after rinsing with distilled water.

III. Conclusion

Li-ion battery waste management is an active area of research and has seen remarkable advances with thousands of techniques developed. However, it still faces limitations in terms of effectiveness and safety. Thus, a preliminary alcoholic treatment of the cathode clearly improves the non-polluting character. On the other hand, this pretreatment seemed to constitute an unfavorable factor in the selectivity of the alkaline leaching. Finally, the recovery of the electrolyte allowed a clear separation of the anode black mass from the copper sheet and characterization tests showed that the connector can be used in other batteries.

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