

ALKALINE LEACHING OF METALS FROM CATHODIC MATERIALS OF SPENT LITHIUM-ION BATTERIES

Abstract

The aim of this study was to recover metals from the positive electrode material for recycling in lithium-ion batteries. It was focused on research to optimize the hydrometallurgical pretreatment process of cathode materials for Li-ion batteries by varying parameters such as NaOH concentration, solid-liquid ratio S/L and reaction time. Thus, from used batteries collected in a local market (Colobane, Senegal), cathodic materials dried in an oven at 50°C for 24 hours, cut into small pieces, submitted to alkaline leaching with NaOH 2, 3 or 4N, followed by filtration, all at room temperature. The filtrates obtained were analyzed by atomic absorption spectrophotometry. The results obtained were showed that Al collectors could be better extracted with 4N NaOH for 5 hours at a ratio of L/S=10/1, with small quantities of the metals Co, Mn, Ni and Li found in the filtrates.

Keywords: batteries, lithium-ion, alkaline leaching, recycling

INTRODUCTION :

In recent decades, making some aspects of life much easier, smaller, easier to handle, portable electronic devices have invaded our daily lives. Indeed, there was a rapid worldwide growth of cellular phones, laptops, digital cameras, electric and hybrid vehicles, etc. [1,2]. These technologies operate with electrochemical systems (batteries) that can store (in chemical form) and reversibly release (in electrical form) energy during their operation. Since their discovery in 1959 [3], several types of batteries have been developed and the best known are lead acid batteries, nickel cadmium batteries (Ni-Cd), nickel metal hydride batteries (Ni-MH), Li-ion batteries (Libs), lithium air batteries, etc. [4,5]. A battery is mainly composed of a cathode, an anode, an electrolyte and a separator. These different components are made of materials containing relatively high concentrations of metals (Co, Li, Mn, etc.) [4].

Due to their good performance, compared to other battery types, Libs have become the most powerful energy source used [6-8]. Thus, their production and consequently, the quantities of

waste Libs used were increased considerably. For example, world Libs production of about 2044 million units in 2007 almost were up to 4.6 billion units in 2010 [5.8].

Therefore, spent Libs is defined as hazardous waste and its improper handling can cause very serious adverse effects on the environment and human health (groundwater contamination, air pollution, natural contamination) [4].

Thus, recycling processes, in addition to preserving the environment, make economic sense when metals are chemically important, relatively rare and/or valuable. Indeed, the exhaustion, scarcity, high cost or difficult exploitation of natural resources, are all justifying factors. As a result, the recycling of this electronic waste must be a necessity and a priority from both an economic and an environmental point of view.

Many studies have been devoted to the research of a process for the valorization of metals in spent Libs. Thus, various pyrometallurgical, hydrometallurgical and biometallurgical processes have been studied to leach and recover so-called precious metals in the spent Libs [6, 8, 10, 11, 12].

Recovery processes are generally carried out using thermal and/or physical separation, alkaline then acid leaching, extraction and purification processes [6, 9, 10].

In the alkaline leaching step, solvents such as N-methylpyrrolidone (NMP) [10], ammonia [1, 4, 10], sodium hydroxide [11, 12] were used to leach and separate the current collectors (Cu and Al) from the active material.

In addition, various inorganic acids were studied as solvents in the acid leaching stage. These include sulfuric acid [13.14], hydrochloric acid [15.16], orthophosphoric acid [17]. Hydrogen peroxide [13], glucose [11], sodium metabisulfite [18], ascorbic acid and tartaric acid [19] were used as reducers of M^{3+} to M^{2+} ions ($M = Co, Mn, Ni, \dots$) in the acid leaching step, due to their instability in complexes.

Organophosphorus acids such as bis (2-ethylhexyl) phosphonic acid (D2EHPA) [20], bis (2,4,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [21, 22] and 2-ethylhexyl phosphonic acid (PC88A) [23] have also been extensively studied as metal extracts. In addition, studies of combinations of different extractants were conducted to investigate the selective separation of metals in leachate liquor [21, 23, 24]. They were showed more affinity between D2EHPA and manganese, Cyanex with cobalt and PC88A with nickel [25].

According to the literature, the recycling of used Libs mixed electrode materials remains limited. In view of these findings, it would therefore be important to develop and test a simple and optimal recycling process for the recovery of mixed batteries.

Thus, the aim of this study is to develop an optimal extraction method by testing different solvents while varying concentrations and contact times.

1. EXPERIMENTAL

1.1. MATERIAL

The Libs used in this study were purchased from the Colobane market (Dakar, Senegal) and from Samsung and Nokia (BL-5F) phones. The reagents used were of analytical purity.

The electrode materials were heated using a Memmert drying oven to remove organic components from the electrolyte. Filtrate analyses were performed using a Varian SpectrAA 220 atomic absorption/emission spectrophotometer with air/acetylene flame.

2.2. METHODOLOGY

This study was consisted of treating Libs cathode material with NaOH at different concentrations and variables reaction times and liquid/solid ratios in order to select the optimal separation parameters of the electrode material from its aluminium current collector.

2.2.1. SAMPLING

The Libs have been completely discharged to avoid any risk of explosion or ignition. They have been manually dismantled and the electrode materials were removed from the plastic and then metal shells, then dried in the oven for 24 hours at 50°C. The cathode materials were cut into small pieces with scissors and stored in glass jars for alkaline leaching studies. Figure 1 highlights the components of Libs and illustrates the different steps of this process.

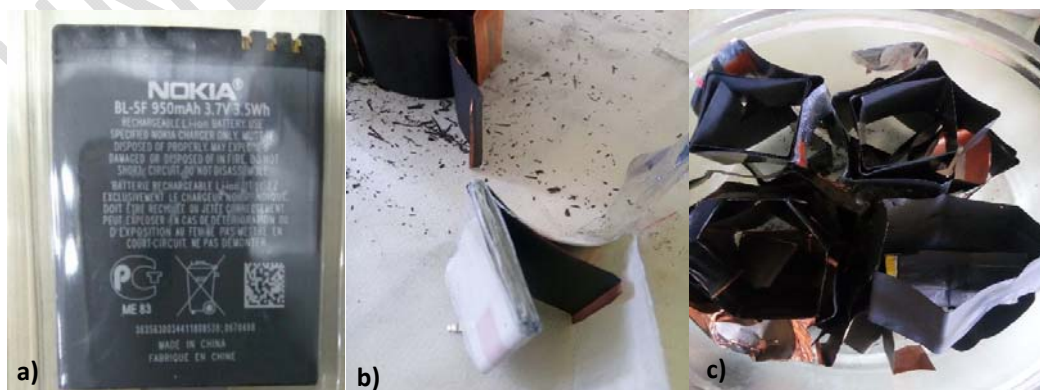


Figure 1: Li-ion battery a) electrode material and separator assembly a) and cathode and anode materials c)

2.2.2. ALKALINE LEACHING PROCESS

Test pieces of 5g of cut material were dissolved in NaOH solutions. The resulting mixtures were magnetically shaken at the ambient temperature.

After the leaching process, the final mixtures were filtered and the black residues (Figure 2) are stored for acid leaching studies. The alkaline leaching liquor was then characterized and quantified.



Figure 2 : Electrode material powder and leaching filtrate

2.2.3. ACID LEACHING PROCESS ;

The pastes obtained previously were dissolved separately in H_2SO_4 4 M and H_2O_2 4 % at an L/S ratio of 10:1. The mixtures were magnetically stirred for 60 minutes and then filtered. This leachate filtrate was analyzed while the black residue, which was supposed to concentrate in carbon black and carbon monoxide, was stored for further processing.

2.3. ANALYTICAL METHODS ;

Filtrate analysis were performed using a Varian SpectrAA 220 atomic absorption/emission spectrophotometer using SpectrAA software version 4.10. Spraying was carried out using an air/acetylene flame with an air flow rate of 3.5 L/min, an acetylene flow rate of 1.5 L/min and a nebulizer flow rate of 5 mL/min. The samples were prepared by diluting the filtrates (1/10th, 1/100th, 1/1000th). The calibration solutions were prepared by dissolving the metal salts in ultra pure water. All dilutions have used this type of water. For each of the elements studied (Al, Ca, Cu, Co, Co, Cr, Mg, K, Fe, Li, Mn, Ni, Na), calibration was performed using individual solutions prepared at 2, 4, 6, 8 and 10 and 50 mg/L. The elements Fe, Co, Ni, Mn, Cu, Cu, Cr were analyzed by absorption using the same SpectrAA Lamp Varian hollow cathode lamp. The Ca and Mg elements were analyzed by absorption using another SpectrAA

Lamp Varian hollow cathode lamp. The elements Al, K, Li and Na were analyzed by emission. For each prepared solution (calibration and diluted sample), 3 measurements were made for 3 seconds, leaving a delay of 10 seconds between each measurement.

3. RESULTS AND DISCUSSION ;

To study the effect of NaOH concentration, samples (5g) were dissolved in NaOH 2N, 3N and 4N at a ratio of L/S=10L/Kg. After 5 hours of stirring time (magnetic stirrer), the mixtures obtained were filtered and the black residues recovered and then stored for further purification studies. The filtrates were then analysed by atomic absorption spectrophotometer (SAA) and the results obtained were illustrated in Figure 3 above.

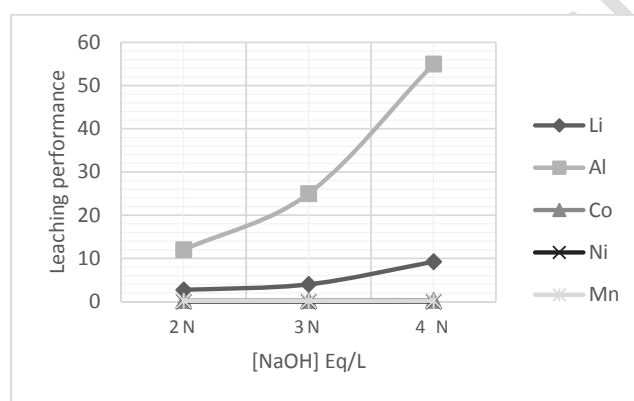


Figure 3 : Percentage of dissolution of Libs metals as a function of NaOH concentration

These results were showed that a decrease in NaOH concentration was leaded to a decrease in leaching performance of all metals analyzed with higher leaching performance percentages for Al (12 % to 55 %) followed by Li (2.70 % to 9.23 %). However, the metals Mn, Co and Ni are found in trace amounts in the aqueous phases.

A combined study of the L/S ratio and reaction time of the alkaline leaching process was conducted on six (6) samples of cathodic materials from used batteries. The NaOH concentration used was set at 4 N, the reaction medium was at room temperature and the reaction times were 5h and 24h (Table I).

Table I : Percentage of metals dissolution with NaOH 4N, L/S=10/1.

NaOH, 4N	Al	Li	Co	Mn	Ni	Fe (II)
L/S= 10, 5h	55,00 %	9,23 %	0,30 %	0,14 %	Traces	Traces
L/S= 11, 5h	56,25 %	7,92 %	0,32 %	0,18 %	Traces	Traces

L/S= 12, 5h	57,36 %	9,21 %	0,47 %	0,18 %	Traces	Traces
L/S=10, 24h	52,25 %	8,51 %	0,98 %	0,10 %	Traces	Traces
L/S=11, 24h	55,00 %	8,87 %	0,158 %	0,17 %	Traces	Traces
L/S=12, 24h	59,31 %	9,44 %	0,34 %	0,22 %	Traces	Traces

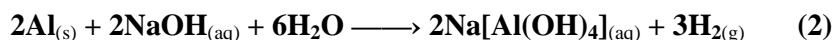
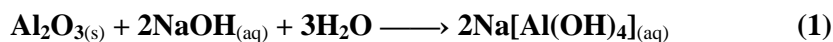
Based on the results obtained, the effectiveness of alkaline leaching with 4N NaOH of Li and Al was varied slightly with the amount of solvent.

After 5 hours of reaction, the dissolution rates of the metals were varied from 55.00 % to 57.36 % for Al, from 0.30 % to 0.47 % for Co and from 0.14 % to 0.18 % for Mn. However, the variation in the Li rate was decreased from 9.23 % to 7.92 % and then was increased to 9.21 %.

At 24 hours of agitation, leaching efficiency was increased from 52.25 % to 59.31 % for Al, from 8.51 % to 9.44 % for Li and at the end from 0.10 % to 0.22 % for Mn. The variation in the dissolution rate of Co, on the other hand, was not monotonous. It was carried out by a decrease from 0.98 % to 0.16 % and then an increase to 0.34 %. At both reaction times, the metals Ni and Fe (II) were remained in trace amounts in the leaching liquors.

Compared to the two reaction times, a slight variation in the dissolution rates of Al and Li was noted. Still with these two reaction times (5 h and 24 h), the Al leaching rate was the same 55.00 % for the ratio L/S=10L/Kg. However, these rates had varied slightly from 55.00 % to 56.36 % and 55.00 % to 57.36 % for 5 h and 24 h respectively. The dissolution efficiency of Li had varied respectively from 6.85 % to 9.21 % and from 8.51 % to 9.44 % for 5 h and 24 h agitation. These results had highlighted the small influence of solvent volume on the efficiency of the process of separating Al from the active material. Therefore, the Liquid-Solid ratio that had provided the highest dissolution rate for Al and the lowest for Li, Co, Mn and Ni metals had been the most appropriate. These results was confirmed, according to the literature, by the work of Ferreira (2009), with a dissolution rate of about 58 % for Al, 12 % for Li and trace Co [26]. In view of the results obtained, i. e. an increase of 2 % for each additional litre of volume, and according to the literature, the L/S ratio of 10 L/Kg had chosen for subsequent studies with a reaction time of 5 hours.

During the alkaline leaching process, the attack of the metal Al (s) by soda is only possible after its oxidation to Al^{3+} by oxygen from the air. This dissolution of the aluminium current collector by NaOH is illustrated by the following chemical equations 1 and 2[27].



The aluminium oxide Al_2O_3 reagent comes from the protective layer that is deposited on the cathode collector. This layer, normally formed during the first life cycles of the material, prevents degradation of the collector and improves the cyclability of the material.

In view of the difference in redox potential of the Al^{3+}/Al ($E=-1.67\text{V}$) and O_2/OH^- ($E=0.40\text{V}$) pairs, the oxidation of the metal Al cannot be spontaneous [28]. As a result, the dissolution of the aluminium leaf in NaOH cannot be spontaneously total, which is verified by the results obtained, varying between 52.25 % and 59.31 %.

According to the results obtained, relatively high concentrations of NaOH were resulted in more significant dissolution rates. These results were confirmed by the work of Ferreira et al. and Chen et al. with dissolution rates of about 58 % and 99.9% respectively [12, 26].

In addition, Li had higher dissolution rates than the metals Co, Mn and Ni of the material. This work was substantiated by those of D. Majuste et al. with a dissolution rate of about 12 % for Li and at trace levels for Co [26]. According to the composition of the matrix of materials, Li has more mobility than these metals. Therefore, its dissolution in solvents will be more effective than the metals complexed in this matrix. These higher leaching rates of Li can also be justified by the mobility of Li^+ in the material, according to the Libs operating principle [29].

Finally, by comparing the two reaction times studied, it can be concluded that approximately half of the metals are dissolved after 5 hours and that after 24 hours, the levels obtained are lower or comparable.

4. CONCLUSION

In this work, a hydrometallurgical pretreatment process, consisting of separating the aluminum foil from the active material of the electrode material, was evaluated in order to develop an optimal method for the selective dissolution of the Al cathodic collector. Thus, alkaline leaching was relatively effective with soda, which is a cheap solvent, and after a relatively short time. However, this average separation of the active ingredient from the

material in its aluminium collector leads to a more detailed study of reaction and thermodynamic kinetics as well as the analysis of acid leaching with the use of organic acid solvents.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

BIBLIOGRAPHICAL REFERENCES

- [1] X. Zheng, W. Gao, X. Zhang, M. He, X. Lin, H. Cao, Y. Zhang, Z. Sun, Spent lithium-ion battery recycling – Reductive ammonia leaching of metals from cathode scrap by sodium sulphite, *Waste Management*. 60 (2017) 680–688. doi:10.1016/j.wasman.2016.12.007.
- [2] M.K. Jha, A. Kumari, A.K. Jha, V. Kumar, J. Hait, B.D. Pandey, Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone, *Waste Management*. 33 (2013) 1890–1897. doi:10.1016/j.wasman.2013.05.008.
- [3] Historique de la batterie | Batteries Accus AJS, (n.d.). <http://www.accus-ajs.com/historique-de-la-batterie/> (accessed December 11, 2018).
- [4] A.A. Nayl, R.A. Elkhashab, S.M. Badawy, M.A. El-Khateeb, Acid leaching of mixed spent Li-ion batteries, *Arabian Journal of Chemistry*. 10 (2017) S3632–S3639. doi:10.1016/j.arabjc.2014.04.001.
- [5] H. Leridon, Chaire Développement durable – environnement, énergie et société: Année académique 2008-2009, *La lettre du Collège de France*. (2009) 9. doi:10.4000/lettre-cdf.501.
- [6] W. Gao, C. Liu, H. Cao, X. Zheng, X. Lin, H. Wang, Y. Zhang, Z. Sun, Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries, *Waste Management*. 75 (2018) 477–485. doi:10.1016/j.wasman.2018.02.023.

- [7] X. Wang, G. Gaustad, C.W. Babbitt, C. Bailey, M.J. Ganter, B.J. Landi, Economic and environmental characterization of an evolving Li-ion battery waste stream, *Journal of Environmental Management*. 135 (2014) 126–134. doi:10.1016/j.jenvman.2014.01.021.
- [8] G. Zeng, X. Deng, S. Luo, X. Luo, J. Zou, A copper-catalyzed bioleaching process for enhancement of cobalt dissolution from spent lithium-ion batteries, *Journal of Hazardous Materials*. 199–200 (2012) 164–169. doi:10.1016/j.jhazmat.2011.10.063.
- [9] J. Ordoñez, E.J. Gago, A. Girard, Processes and technologies for the recycling and recovery of spent lithium-ion batteries, *Renewable and Sustainable Energy Reviews*. 60 (2016) 195–205. doi:10.1016/j.rser.2015.12.363.
- [10] Xiaohong Zheng, Z. Zhu, X. Lin, Y. Zhang, Y. He, H. Cao, Z. Sun, A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries, *Engineering*. 4 (2018) 361–370. doi:10.1016/j.eng.2018.05.018.
- [11] Q. Meng, Y. Zhang, P. Dong, Use of glucose as reductant to recover Co from spent lithium ions batteries, *Waste Management*. 64 (2017) 214–218. doi:10.1016/j.wasman.2017.03.017.
- [12] L. Chen, X. Tang, Y. Zhang, L. Li, Z. Zeng, Y. Zhang, Process for the recovery of cobalt oxalate from spent lithium-ion batteries, *Hydrometallurgy*. 108 (2011) 80–86. doi:10.1016/j.hydromet.2011.02.010.
- [13] X. Chen, Y. Chen, T. Zhou, D. Liu, H. Hu, S. Fan, Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries, *Waste Management*. 38 (2015) 349–356. doi:10.1016/j.wasman.2014.12.023.
- [14] C. Peng, J. Hamuyuni, B.P. Wilson, M. Lundström, Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system, *Waste Management*. 76 (2018) 582–590. doi:10.1016/j.wasman.2018.02.052.
- [15] Y. Guo, F. Li, H. Zhu, G. Li, J. Huang, W. He, Leaching lithium from the anode electrode materials of spent lithium-ion batteries by hydrochloric acid (HCl), *Waste Management*. 51 (2016) 227–233. doi:10.1016/j.wasman.2015.11.036.
- [16] M. Contestabile, S. Panero, B. Scrosati, A laboratory-scale lithium-ion battery recycling process, *Journal of Power Sources*. 92 (2001) 65–69. doi:10.1016/S0378-7753(00)00523-1.

- [17] X. Chen, H. Ma, C. Luo, T. Zhou, Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid, *Journal of Hazardous Materials*. 326 (2017) 77–86. doi:10.1016/j.jhazmat.2016.12.021.
- [18] N. Vieceli, C.A. Nogueira, C. Guimarães, M.F.C. Pereira, F.O. Durão, F. Margarido, Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite, *Waste Management*. 71 (2018) 350–361. doi:10.1016/j.wasman.2017.09.032.
- [19] G.P. Nayaka, K.V. Pai, G. Santhosh, J. Manjanna, Dissolution of cathode active material of spent Li-ion batteries using tartaric acid and ascorbic acid mixture to recover Co, *Hydrometallurgy*. 161 (2016) 54–57. doi:10.1016/j.hydromet.2016.01.026.
- [20] J. Li, X. Yang, Z. Yin, Recovery of manganese from sulfuric acid leaching liquor of spent lithium-ion batteries and synthesis of lithium ion-sieve, *Journal of Environmental Chemical Engineering*. 6 (2018) 6407–6413. doi:10.1016/j.jece.2018.09.044.
- [21] J.M. Zhao, X.Y. Shen, F.L. Deng, F.C. Wang, Y. Wu, H.Z. Liu, Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A, *Separation and Purification Technology*. 78 (2011) 345–351. doi:10.1016/j.seppur.2010.12.024.
- [22] J. Kang, G. Senanayake, J. Sohn, S.M. Shin, Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272, *Hydrometallurgy*. 100 (2010) 168–171. doi:10.1016/j.hydromet.2009.10.010.
- [23] S.-H. Joo, S.M. Shin, D. Shin, C. Oh, J.-P. Wang, Extractive separation studies of manganese from spent lithium battery leachate using mixture of PC88A and Versatic 10 acid in kerosene, *Hydrometallurgy*. 156 (2015) 136–141. doi:10.1016/j.hydromet.2015.06.002.
- [24] Y. Pranolo, W. Zhang, C.Y. Cheng, Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system, *Hydrometallurgy*. 102 (2010) 37–42. doi:10.1016/j.hydromet.2010.01.007.
- [25] X. Chen, B. Xu, T. Zhou, D. Liu, H. Hu, S. Fan, Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries, *Separation and Purification Technology*. 144 (2015) 197–205. doi:10.1016/j.seppur.2015.02.006.

- [26] D.A. Ferreira, L.M.Z. Prados, D. Majuste, M.B. Mansur, Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries, *Journal of Power Sources*. 187 (2009) 238–246. doi:10.1016/j.jpowsour.2008.10.077.
- [27] D.A. Ferreira, L.M.Z. Prados, D. Majuste, M.B. Mansur, Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries, *Journal of Power Sources*. 187 (2009) 238–246. doi:10.1016/j.jpowsour.2008.10.077.
- [28] couples_redox.pdf, (n.d.). http://mslp.ac-dijon.fr/IMG/pdf/couples_redox.pdf (accessed January 18, 2019).

UNDER PEER REVIEW