

Synthesis of Co-Al-Cl LDH by Cathodic Material Reprocessing from Cellular Phone Batteries

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The aim of this paper was the recovering of the cathodic material from discarded lithium ion batteries for obtainment of the lamellar double hydroxides (LDHs) by the co-precipitation method at variable pH in HCl and H₂O₂ 1:1 (v/v) acid solution containing Co and Al (extracted from cathodic material composed of LiCoO₂ and aluminum foil). These metals were precipitated in LiOH at pH 9 or 11, or NH₄OH at pH 9 and submitted to the hydrothermal treatment (HT) to improve the structural organization of the LDHs lamellae. After precipitation, the resulting solids were structurally characterized by XRD for phase identification and calculation of the unit cell parameter, thermally by TGA for the identification of the mass loss and morphologically by SEM. The sample obtained by precipitation with LiOH at pH 11 / hydrothermal treatment showed diffraction peaks similar to hydrotalcite, morphological and thermal characteristics similar to the pattern Co-Al-Cl LDH obtained by co-precipitation at constant pH 8.

Keywords: lithium ion batteries, LiCoO₂ and aluminum foil recovering, reprocessing of cellular phone battery and lamellar double hydroxides

1. Introduction

In the last few years the technological advances and the equipment production with portable power supply, which occupy the minimum space possible, last long and that are mainly rechargeable, drawing interest of the population in purchasing electronic products. Notebooks, *i-pods*, *tablets*, cellular phones, and digital machines are the most desirable devices. They use lithium ion batteries made up of lithiated graphite (LiC₆) as anode, lithium cobaltate (LiCoO₂) or lithium manganate (LiMn₂O₄) as cathodes and an organic electrolyte containing lithium salt (LiPF₆ or LiClO₄) in ethylene or dimethylene carbonates (EC/DMC). LiCoO₂ is frequently used due to its high charge density, long life cycles and extremely low auto-discharge charge, however, its production is highly costly and the cobalt reserves are limited¹. Although cobalt is one of the most abundant elements, it can be obtained mainly as a co-product of the copper and nickel mining. The Cobalt is part of a short list chosen as strategic metal for the economy of a country and for their critical limitations of reservation and extraction forms. On the other hand, like all human activity, these lithium ion batteries generate environmental problems due to their incorrect disposal, which is supported by legislation outdated or inadequate supervision. The rapid technological advancement of the portable electronics has emerged as a problematic disposal of appliances “old-fashioned” devices and their batteries, many batteries are constituted by lithium ion. Most of the time, this disposal is not made of proper locations which causes contamination and environmental degradation due to the battery metals. World lithium ion

batteries (LIBs) production reached 500 million units in 2000 and it is expected to reach 4.6 billion in 2010^[2-5] Brazil is a cobalt producer, but only in 2010, metal oxides and hydroxides 2401 tonnes were imported generating an expense of approximately \$ 15.4 million^[6]. The high demand and cobalt value associated with environmental damage can reach the human health, directly or indirectly. Thus, it can consider the LiCoO₂ recycling a plausible alternative for solving these problems. Since LIBs are substitutes for other secondary batteries due to lightness and good performance, the disposal of these spent LIBs will result in environmental pollution. Recycling practices are highly desirable at present and in the future from the point of view of environmental conservation⁷ and the recovery of metal values from spent LIBs and their utilization as raw materials⁸, in order to construct a sustainable and recycling-oriented society⁹. Then, it is relevant the development of batteries recovering and recycling methods. In case recovery and recycling are not possible, the environmental contamination by cumulative metals may affect the nervous system by lithium accumulation in the organism while the cobalt causes the “cobalt itch” (allergic contact dermatitis), in addition to conjunctivitis, lung lesions, asthma and bronchitis, hematologic and intestinal disturbances, cardiac effects and may also be carcinogen¹⁰. It is possible to recover cobalt in the following processes: hydrometallurgical, pyrometallurgical and electrochemical obtainment. The premise for the reprocessing of the cathodic material and the obtainment of lamellar double hydroxides (LDHs) is based on the fact that it can be made of the leaching

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followed by precipitation. The lamellar double hydroxides (LDHs) or hydrocalcite-type compounds are synthetic anionic clays which present structure identical to the brucite layers ($\text{Mg}(\text{OH})_2$) but with a slight load difference on the lamellae. The precipitation method with constant pH is one of the most used methods to obtain the various types of LDHs and generally presents highly satisfactory results, obtaining LDHs with excellent structural organization and high purity of phase¹¹. Thus, this paper's main objective was the establishment of a new cobalt and aluminum recovering methodology from the solution resulting from the chemical process of acid leaching followed by precipitation of the metals (Co and Al) for obtaining of the lamellar double hydroxide Co-Al-Cl.

2. Materials and Methods

2.1. Synthesis of the Co-Al-Cl LDH pattern

This synthesis method consists in the slow addition of an aqueous solution containing $1.0 \text{ mol L}^{-1} \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mol L^{-1} anhydrous AlCl_3 . Another solution containing $1.0 \text{ mol L}^{-1} \text{NaCl}$ and $3.5 \text{ mol L}^{-1} \text{KOH}$ was added to maintain the constant pH around of 8. The suspension obtained was washed with deionized water and it was subjected to a hydrothermal treatment (HT) for 100 h at $80 \text{ }^\circ\text{C}$. After treatment, the suspension was filtered and the solid washed with deionized water at pH 8 and subsequently it washed with alcohol and acetone. After washing, the material was dried under a vacuum for 48 h at room temperature.

2.2. Synthesis of the Co-Al-Cl LDH from cathodic material reprocessing

The Co-Al-Cl lamellar double hydroxide (LDH) was obtained by the cathodic material reprocessing method of lithium ion batteries (LIBs) from discarded cellular phones. The spent LIBs were submitted to physical treatment which involved a discharge pretreatment step to remove the excess capability, batteries dismantling to remove the plastic and metallic shells, scraping the cathode material, adapted from the methodology proposed by Dorella and Mansur¹². First of all, it was realized the opening of the discharged batteries. The cathodic material (LiCoO_2 , carbon black and binder) /current collector (aluminum foil) were separated of other elements of the battery as anode and electrolyte and reprocessed according to the following procedure steps:

- i The leaching was conducted with HCl acid solution followed by the addition of a hydrogen peroxide solution;
- ii Reaction system heating at $80 \text{ }^\circ\text{C}$ for 4 h with stirring speed of 300 rpm;
- iii Filtration of the leached solution for separation of carbon black and binder;
- iv Dropwise addition of 3 mol L^{-1} hydroxide solution for $30 \pm 5 \text{ min}$ until the desired pH;
- v Partial evaporation of the solvent;
- vi Filtration of the solid residue;
- vii Hydrothermal treatment (HT) in the solid residue.

In step (i), the aluminum foil and lithium cobalt oxide (LiCoO_2) were ground together in order to recover the metals which are essential for the synthesis of LDH.

- **sample (1)** – 1 g of the cathodic material (LiCoO_2 and aluminum mixture) was lixiviated with HCl/ H_2O_2 . Subsequently, the LDH was obtained by coprecipitation at variable pHs. The pH of the lixiviated solution was reached by addition of 3 mol L^{-1} lithium hydroxide (LiOH) at pH 9 or pH 11 or ammonium hydroxide at pH 9 (NH_4OH) as titrants. After the precipitation of the cobalt and aluminum hydroxide, the resulting solid residue (**step iv**) was filtered and washed with deionized water to remove any impurity in the system, and further dried. Then, the samples were structurally characterized by X ray diffraction analysis (XRD). Further, to the characterization, the solids were submitted to a hydrothermal treatment (HT), for 100 h at $70 \text{ }^\circ\text{C}$, in $1.5 \text{ mol L}^{-1} \text{NaCl}$ (**step v**). The samples were submitted again to the characterizations by XRD and TGA.
- **sample (2)** – The same process was carried out for the *sample (2)*, using of 2 g total mass (1 g of LiCoO_2 and aluminum mixture and the other 1 g only of aluminum foil) so that the oxide was previously scraped. Subsequently, it was varied the mass ratio between the aluminum and cobalt for obtaining of the Co-Al-Cl LDH.

2.3. Characterizations of the synthesized materials

2.3.1. Structural characterization by X-ray diffraction analysis (XRD)

The powders were also characterized by X-ray diffraction analysis (XRD) using a Shimadzu model XRD 6000, Cu-K α ($\lambda = 1,5418 \text{ \AA}$) radiation (40 kV 30 mA) at 1° min^{-1} . The speed step was $0.02^\circ \text{ s}^{-1}$ and a range of $5^\circ \leq 2\theta \leq 70^\circ$. Samples are prepared from the sample powder, pressing the solid with a glass plate in aluminum sample port.

2.3.2. Thermal characterization by Thermogravimetric analyses (TGA)

The powders were characterized using a thermal analysis system Shimadzu DTG-60H simultaneous DTA-TG apparatus at $10 \text{ }^\circ\text{C min}^{-1}$ under N_2 in a heating range from $25 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$. The reference sample used was alumina.

2.3.3. Morphological characterization by Scanning Electron Microscopy (SEM)

The SEM were recorded using a scanning electron microscope (SEM) Shimadzu SSX-550 Super Scan, operated at 10 kV. Samples were supported on the door sample by dispersing the powder over the silver conductive paste, since the samples did not show sufficient conductivity to generate good images.

3. Results and Discussion

The X-ray diffractograms of the LDH obtained from the solution resulting from the chemical process of acid leaching followed by precipitation of the metals (Co and Al) in LiOH at pH 9 and 11 are shown in Figures 1 and 2, respectively, and in NH_4OH at pH 9 is shown in

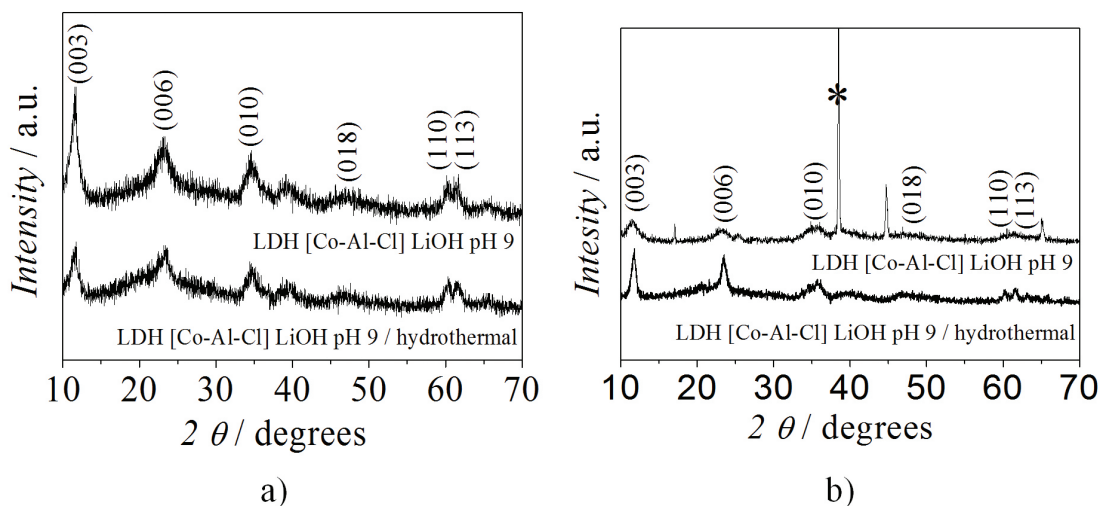


Figure 1. X ray diffractograms of the obtained LDHs by co-precipitation in LiOH at pH 9: (a) sample 1; (b) sample 2.

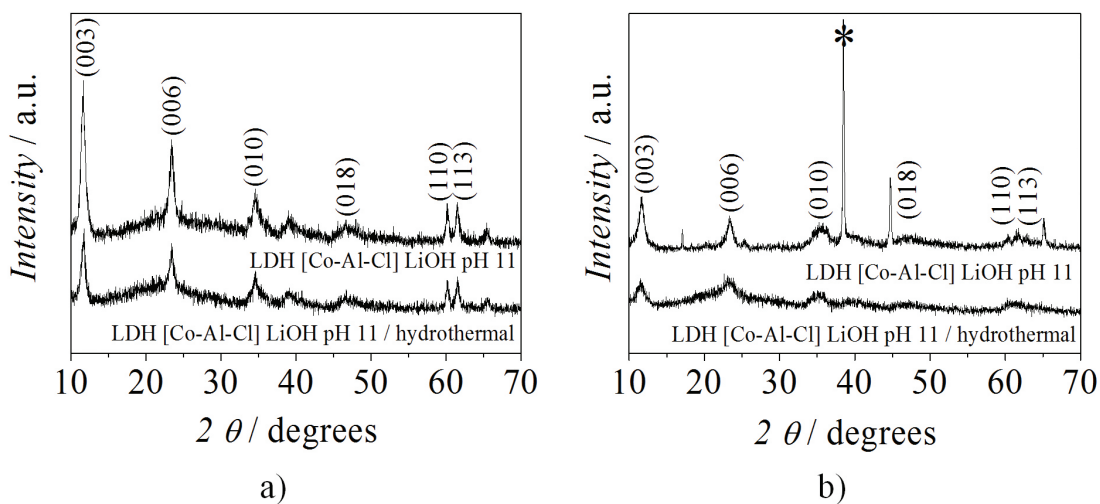


Figure 2. X ray diffractograms of the obtained LDHs by co-precipitation in LiOH at pH 11: (a) sample 1; (b) sample 2.

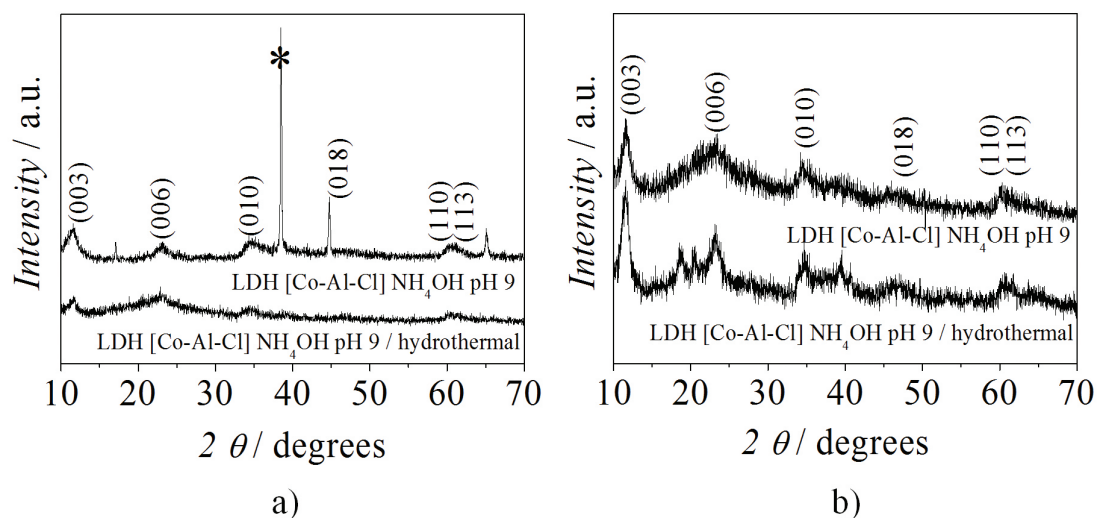


Figure 3. X ray diffractograms of the obtained LDHs by co-precipitation in NH_4OH at pH 9: (a) sample 1; (b) sample 2.

Figure 3. The diffractograms of the samples containing a high concentration of aluminum called **sample 2** – it was precipitated at pH 9 and 11 using LiOH. The XRD of this sample a diffraction peak at $2\theta = 38^\circ$ degree which is not relative to the characteristic lamellar structure of the LDH and it have been caused by the residual NaCl in the LDH. **Sample (1)** obtained with NH_4OH at pH 9 did not show characteristic diffraction peak of the LDH even with the lowest amount of aluminum used in relation to the others.

Sample (1) at pH 9 and 11 using LiOH and **sample (2)** at pH 9 using NH_4OH did not present well defined diffraction peaks, which can infer that there was no influence of the amount of aluminum present in the probable LDHs obtained. Subsequently, the LDHs were subjected to a hydrothermal treatment in order to obtain a structure more orderly and without the mixture of phases. Then, LDH suspension was put in a reactor containing 1.5 mol L^{-1} NaCl at 70°C for 100 h ^[13,14] X ray diffractograms of the LDH obtained by precipitation in LiOH at pH 9 after hydrothermal treatment (HT) presented a better definition of the diffraction peaks correspondent to the planes: 003, 006 and 110 (Figure 1b). In the XRD of the Figure 4 it observes among the synthesized LDH from the cathodic material those obtained by precipitation at pH 11 with LiOH presented structure similar to the synthesized Co-Al-Cl LDH by the co-precipitation method at constant pH 8 (LDH pattern)¹⁵. The synthesized LDH by the method described in this paper

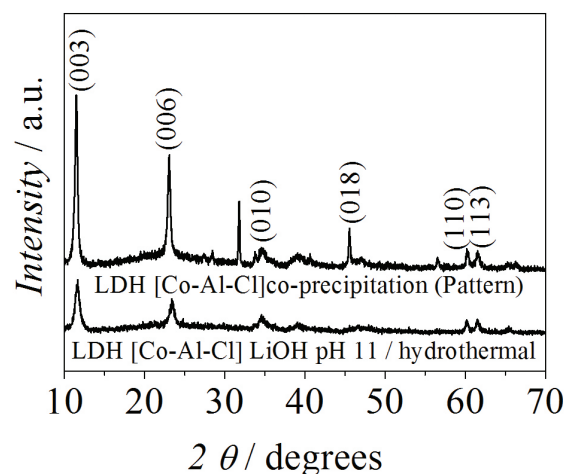


Figure 4. X ray diffractograms of the obtained LDHs by co-precipitation in LiOH at pH 11/ hydrothermal treatment (reprocessing method) and co- precipitation at pH 8 (pattern).

presented diffraction peaks centered at 11.66° , 23.38° , 34.56° , 46.66° and 60.16° which correspond to reflections 003, 006, 010, 018 and 110 according to the literature^{16,17}. The basal spacing values – d (003), the distance between cations (a) and the unit cell height (c) were calculated using a Peakfit software, version 4, and are shown in the Table 1. It was observed in this Table that the highest diffraction peak correspondent to the plan 003 represents the d value relative to the sum of the lamellae thickness and the interlamellar region height, and may range between 7.6 and 7.8 Å, depending on the degree of hydration of the material¹⁶⁻¹⁸. Hydrocalcite parameter c corresponds to the unit cell height, whereas parameter a is attributed to the distance between the cations on the calcite-type layer. Thus, the synthesized LDH in this paper presented the parameter d within the theoretical parameter and it is similar to that attributed to the hydrocalcite (2.9942 Å). In addition, the diffraction peak intensity rate corresponding to the plan 003 (7.55752 Å) is approximately the double of plan 006 (3.79694 Å). Then, the synthesized LDH in this paper presents the parameter d within the theoretical parameter and it is similar to that obtained for the Co-Al-Cl LDH pattern obtained from co-precipitation at pH 8. As the diffraction peaks of the Co-Al-Cl LDH obtained by the precipitation with LiOH at pH 11 were similar to the pattern, then this route was established as main LDH synthesis. The LDH followed by hydrothermal treatment was submitted for the thermal and morphological characterizations by thermogravimetry (TGA) and SEM, respectively.

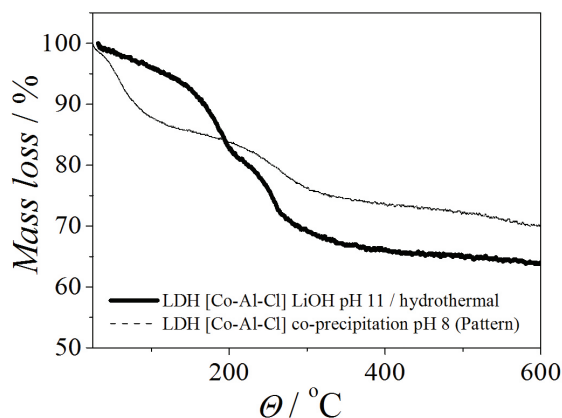


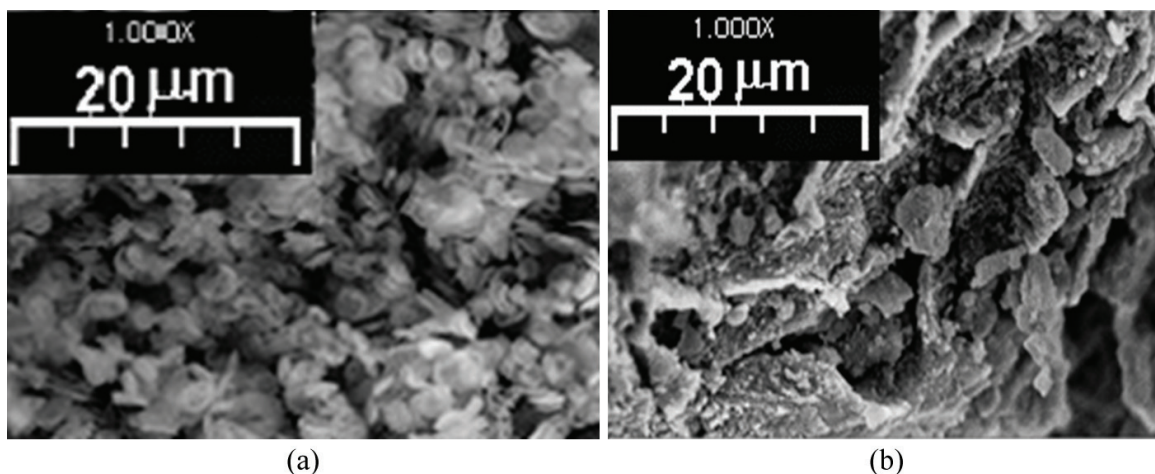
Figure 5. Thermogravimetric curves of the obtained LDHs by co-precipitation in LiOH at pH 11/ hydrothermal treatment (reprocessing method) and co- precipitation at pH 8 (pattern).

Table 1. Basal spacing values of the obtained LDHs by co-precipitation in LiOH at pH 8 (pattern) and by co-precipitation in LiOH at pH 11/ hydrothermal treatment (reprocessing method).

Unit Cell parameter	LDH [Co-Al-Cl] co-precipitation at pH 8 (pattern)	LDH [Co-Al-Cl] LiOH at pH 11 (reprocessing)
$d/\text{Å}$	7.6885	7.55752
$d(003)$		
$a/\text{Å}$	3.1556	3.14786
$2 \times d$ (110)		
$c/\text{Å}$	23.5752	23.43959
$C=3 \times d(003)$		

Table 2. Variance analysis by TGA of the co-precipitation in LiOH at pH 8 (pattern) and by co-precipitation in LiOH at pH 11/ hydrothermal treatment (reprocessing method).

Temperature Range/ °C	Mass Loss events	Mass Loss LDH co-precipitation at pH 8 (pattern)/ (%)	Mass Loss LDH precipitation in LiOH at pH 11 (reprocessing) (%)	Variance
25.5-100	Extrinsic Water	12.09	3.94	4.075
100-195	Intrinsic Water	3.70	13.51	4.905
195-310	Lamellae Dehydroxylation	8.60	13.89	2.645
500-600	Hydroxyl Decomposition	2.10	1.13	0.485
> 600	Formation of Mixed Oxide	30.21	37.54	3.665

**Figure 6.** SEM of the obtained LDHs by (a) co-precipitation in LiOH at pH 11/ hydrothermal treatment (reprocessing method); (b) co-precipitation at pH 8 (pattern).

In the Figure 5 is shown TGA of the obtained Co-Al-Cl LDH by co-precipitation at pH 8 (constant pH method), used as pattern and the obtained Co-Al-Cl LDH from the precipitation with LiOH at pH 11. It was observed the respective mass loss: the first from 25.5 °C to approximately 100 °C, corresponding to a mass loss of 12.09% associated to the elimination of water adsorbed in the material. The second mass loss of 3.70% occurs from 100 °C to 190 °C is attributed to the interlamellar water loss. The final decomposition phase from 195 °C to 310 °C with a mass loss of 8.6% associated to the dihydroxylation of the LDH lamellae and finally from 500 °C to 600 °C, a mass loss of 2.1% related to the remaining part of the hydroxyl decomposition and formed of a Co and Al mixed oxide, corresponding to the 30.21% of the initial mass. The TGA for the obtained LDH by the reprocessing of the lithium ion battery cathodic material. It was observed the first 3.94% mass loss from 25.5 °C to approximately 100 °C, correspondent to the adsorbed water elimination in the material structure. The mass loss second (13.51%) from 100 °C to 195 °C is associated to the loss of the interlamellar water correspondent to the solvated anions. The final decomposition phase from 195 °C to 310 °C with a mass loss of 13.89 % is associated to the LDH lamellae dihydroxylation. Finally from 500 °C to 600 °C, there is a mass loss of 1.13% related to the remaining part of the hydroxyl decomposition. From 600 °C there is a constant residual mass attributed to the formation of the Co and Al

mixed oxide, corresponding to the 37.54% of the initial mass. All TGA results are summarized in the Table 2.

SEM of the LDH obtained by co-precipitation at pH 8 (pattern) (Figure 6a) with 1000 times amplification presented superimposed inorganic boards and with a hexagonal shape, such results were similar to the morphologies obtained for LDH by the co-precipitation method¹⁸. Figure 6b shows SEM of the LDH obtained by reprocessing cathodic material from lithium ion batteries (with LiOH at pH 11 after hydrothermal treatment). It was observed an irregular shape of the LDH, with high porosity and some clustering. This morphology was similar to those obtained by Reis et al. for Mg-Al-CO₃ LDH¹⁹.

These materials will test as adsorbents of pesticides and herbicides in contaminated waters²⁰.

4. Conclusions

The X ray diffractograms of the sample obtained by the coprecipitation with LiOH at pH 11 / hydrothermal treatment showed diffraction peaks similar to the Co-Al-Cl LDH pattern.

From the TGA data of the Co-Al-Cl LDH obtained by reprocessing method it was verified four (4) mass loss characteristics events of the thermal decomposition of the LDH.

From the SEM of the Co-Al-Cl LDH, it was possible to observe an irregular shape of the LDH, with high porosity and some clustering. Thus, the synthesized LDH by reprocessing method presented structural, thermal and morphological characteristics similar to the Co-Al-Cl LDH/LDH pattern obtained at pH 8, becoming possible its application as adsorbent of pesticides and herbicides in contaminated waters.

The Co-Al-Cl LDH obtained by precipitation with LiOH at pH 11 / hydrothermal treatment showed structural,

morphological and thermal characteristics similar to the pattern Co-Al-Cl LDH obtained by co-precipitation at constant pH 8.

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