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A Review on Nickel Recovery of Batteries by chemical Process

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Abstract— *There is a growing concern about the environmental impacts that batteries can cause if there is no correct destination at the time of disposal. Therefore, this article presents a review on the recovery of nickel and metals that are contained in batteries through chemical processes. With this study, it is possible to better understand how some processes available for nickel restoration work and, after recovery, their possible applications in different areas. It is possible to notice during the review that many authors cite the use of some additives or alloys for doping, which brings higher rates of nickel recovery and reuse. The main objective of this review is to form a database with recent research and that it is possible to give direction to new laboratory experiments and future work.*

I. INTRODUCTION

The generation of sustainable energy has been increasing every year, and consequently, it is necessary to store this energy for later use. Thus, it is recommended that this storage be in sustainable and economical energy converter systems. An energy storage system that is gaining ground are batteries, as they have different sizes, models and capacities. However, there is still much to be evaluated in this area, especially about the environmental impacts caused both in the production and disposal stages [4].

Studies in relation to environmental impacts have been carried out and updated every year. A way to get to know these studies better is through the International Conference on Heavy Metals in the Environment, which was created in 1975 in Toronto, Canada, where every two years it publishes research on topics related to heavy metals, soil contamination and consequences for the environment. Many of these surveys indicate that there are significant numbers of people with high levels of contamination and diseases caused by heavy metals. This is mainly due to incorrect disposal, which end up falling into fertile planting soil and river sources that supply communities and irrigate crops [23].

World battery production accounts for several billion per year, and Ni-Cd and Ni-MH batteries are among the most used systems in recent decades, however, there has been a great concern regarding the disposal of used batteries, because the species of metals used to manufacture these batteries are highly toxic [8].

In addition to high production, there is another question that must be taken into account, which is the illegal import of batteries from Paraguay. As the city of Foz do Iguaçu is a triple border city, it becomes more susceptible to the illegal importation and commercialization of this material. According to data from the customs balance issued and published by the Federal Revenue, in 2019 there was an increase of approximately 150% in the seizure of batteries and approximately 66% in electronics, these numbers are a comparison between the years 2018 and 2019 [19].

In Europe, there are already regulations and legislation that require manufacturers of Ni-Cd and Ni-Zn batteries to recycle at least 75% of their weight and cadmium recovery to be as complete as possible. An advantage of these batteries is the recovery of nickel, as it is considered a strategic metal with great value in the market [8]. In the United States there are already programs for the collection and recycling of electronic waste, which is where the largest volume of batteries with these components is concentrated. In Brazil, it has not yet been possible to implement these programs, as the greatest difficulty encountered is the collection system, cooperation of people and efficiency in the process, there are only small actions in some Brazilian states that work trying to minimize the incorrect disposal of these materials [29].

In view of the above, a review of some recent studies was carried out dealing with the recovery of nickel and metals found in batteries, through different chemical processes, with the objective of formulating a database for new research and studies in the scope of recovery of these materials.

II. MATERIAL AND METHODS

To select the articles used in this narrative literature review, the following keywords were used: (nickel and recovery); (batteries and recovery); (Ni-Cd). Web of Science, Scopus and Science Direct databases. After an electronic search, the complete articles were reviewed and the most suitable were included in this article.

2.1 Batteries

By general definition, the battery is also known as an electrochemical cell, and its main function is the conversion of chemical energy into electrical energy. This released electrical energy is generally the difference in binding energies of the metals, oxides, and molecules undergoing the electrochemical reaction [24].

Basically, batteries are formed by cathode, anode and electrolyte, and their reactions are known as redox reactions. The cathode and anode are electronic conductors, and the electrolyte is the ionic conductor. The anode is considered the negative pole because it is where the oxidation reaction takes place, that is, it is in this electrode where there is the process of loss of electrons. The cathode is considered the positive pole, where the reduction reaction takes place, that is, the gain of electrons during the process. The electrolyte is an ion-conducting liquid solution whose main function is to improve the performance of the electrodes [24].

Within this definition there are two groups of batteries that stand out, they are: the primary batteries, which are sets of cells that do not perform inversion in their electrolytic reactions, that is, they cannot be recharged. And the secondary batteries, which are sets of cells that use electrochemical reactions that can be reversed, that is, the reagents that make up this system, can return quantities close to the initial ones only with the passage of electric current in their interior [20].

Taking as an example the secondary Ni-Cd batteries. In this type of battery, the positive electrode (cathode) is Nickel, and the negative electrode (anode) is Cadmium. The reduction and oxidation reactions, which occur at these electrodes, respectively, at the time of the electrochemical reaction, can be represented by (1) and (2). The electrolyte applied to these batteries is potassium hydroxide (KOH), along with small amounts of additives. with the aim of improving the performance of the electrodes [24]. In Fig.1 demonstrates the basic schematic of a Ni-Cd battery.

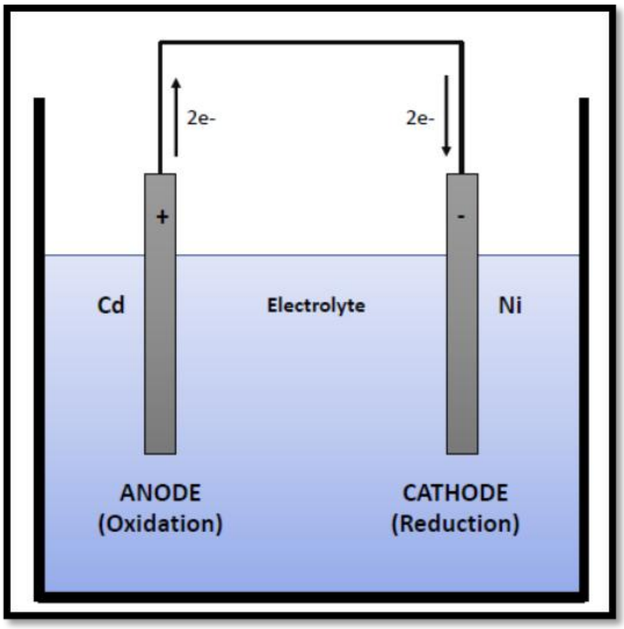

Fig. 1: Ni-Cd Battery Operation Diagram

$$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \quad (1)$$

$$Cd + 2OH^- \leftrightharpoons Cd(OH)_2 + 2e^- \quad (2)$$

III. DISCUSSION

3.1 Recovery of nickel and metals contained in batteries: Hydrometallurgical processes

In recent years, many studies have emerged related to the treatment and recycling of Ni-Cd batteries through hydrometallurgical processes. The advantage of this process is that it can work at low temperature, as the solutions generate little residual gas. The hydrometallurgical process involves a sequence of physical-chemical steps, one of the main steps being the leaching of waste and electrodeposition of a metal, carried out in a sulfuric medium, resulting in an active powder, also called "black mass" [8].

This experiment [8] deals with the separation and recovery of nickel and cadmium, through leaching and electrodeposition. The active powders used in the research were obtained from Ni-Cd batteries that were manually dismantled before the treatment processes. The characterization of the recovered active powder confirmed the presence of metallic hydroxides $Cd(OH)_2$ and $Ni(OH)_2$, as it is a new combination of treatment processes, it was necessary to make several adjustments during the stages, but this treatment proved to be effective and promising for the recovery of nickel and cadmium found in the battery.

Other authors [18] have evaluated the recovery of nickel, cadmium and zinc by hydrometallurgical processes. The authors obtained an overall efficiency of the nickel leaching step of 73% at the anode and 93% at the cathode. It was also possible to identify that pure metallic nickel has a very low recovery percentage, around 26%, but with the addition of hydrogen peroxide (H_2O_2) there is an activation of nickel, increasing the recovery of this metal and reaching approximately 90%. Within this study, very satisfactory results were obtained, using a concentration of 10% of diluted sulfuric acid, the recovery of metals reached 99%, when the temperature varied between 308-328 K.

Another recent study deals with hydrometallurgical processes using a new extractant called Cyphos IL 104 diluted in Toluene during leaching to recover cadmium and nickel. To obtain the active powder, the batteries were manually disassembled. After the leaching process, countercurrent extractions and pickling steps using simple pickling agents, the results were compared and it was possible to identify a recovery of approximately 99% of the metals, being recovered as useful nanometric oxides, which have applications in electronics and as a photocatalyst for pollutant degradation. The authors [10] concluded that Cyphos IL 104 is a promising extractant for this process, as there is economic feasibility and possible commercial use.

Another approach reported in studies for the recovery of nickel and cadmium from batteries is the steps of selective isolation and hydrothermal synthesis of nickel oxide (NiO) nanocuboids. Nanocuiboids have a more attractive morphology, that is, they have high surface area and high structural stability, in addition to low expansion/contraction when compared to lithium-ion batteries. In this process, after leaching with hydrochloric acid, the material was placed in an autoclave and subjected to the hydrothermal process at a constant temperature of 474 K. After cooling to room temperature, the obtained precipitations were washed repeatedly with distilled water and ethanol, and the dry powder was heated to 450 °C, resulting in the mesoporous nickel oxide (NiO) nanocuboids [3].

From the results of this research [3], it was possible to observe that the leaching process with hydrochloric acid associated with hydrothermal synthesis allows the recovery of about 77% of the nickel from the batteries. The analysis of the material obtained confirmed the high purity and porosity of nickel. The study opens the way for this method to be applied in preparations of other materials from electronic waste.

3.2 Recovery of nickel and metals contained in batteries: Chemical precipitation, Synthesis and Sonochemical process

Some authors [5][11][13][16][17][21][22][25][27] brought in their research the application of the chemical precipitation method for the recovery of nickel, cadmium and zinc from batteries. In all the studies cited, this technique proved to be very efficient and useful for the composition of positive results. Each research has its particularity and different details during the execution, but it is possible to verify that the same technique can be used in different purposes for the use of the recovered material.

Samples of single structure with mixed phase α/β nickel hydroxide partially substituted with aluminum were prepared by chemical precipitation, and compared with samples of pure $\beta\text{-}Ni(OH)_2$. The Al-substituted nickel hydroxide α/β phase had a compact density of 2.02 g/cm^3, a value significantly higher than the α nickel hydroxide, which had a density of 1.70 g/cm^3. When compared with pure $\beta\text{-}Ni(OH)_2$, the mixed phase showed higher electrochemical activity, better electrochemical reversibility, lower electrochemical resistance and higher discharge voltage, making it a promising active material for alkaline secondary batteries [13].

Another method used for sample preparation is the controllable complex precipitation method. The authors [16] used this method to design $Ni(OH)_2/C$ nanocomposites, where $Ni(OH)_2$ nano plates are surrounded and supported by porous carbon. The porous carbon support was synthesized by heat treatment of polyvinylidene chloride. The results showed an increase in the specific surface area of the porous $Ni(OH)_2/C$ nanocomposites, promoting a better electrochemical performance, confirmed by cyclic voltammetry. The increasing intensity of redox peaks, the negative shift of the oxidation peaks and the positive shift of the reduction peaks as the carbon content increases, is attributed to improved reversibility during the charge/discharge process and high electrical conductivity provided by the carbon support. With this new type of composite, it was possible to obtain a specific capacity of 345.2 mAh/g and even after 20,000 cycles its capacity remained at 97% of the initial capacity, which shows significant superiority in aspects of charge/discharge current density, specific capacity and life cycle.

Another study [1] carried out the synthesis of nickel hydroxide by the high-energy ultrasound method (sonochemical), using only oleylamine as a reducing agent, stabilizer and surfactant, and water as a solvent. The difference in the preparation of α-$Ni(OH)_2$ and β-$Ni(OH)_2$ was only the adjustment in the reaction time. Three different nickel hydroxide phases were identified, with well-defined crystalline structures. In addition, the sonochemical method allowed the control of morphology and specific surface area, being able to be used for the preparation of products with different specifications.

In order to obtain new insights regarding the formation of hierarchical nanostructures of Ni(OH)2, The authors [15] carried out several experiments with different sources of nickel, such as nickel chloride (NiCl2), nickel nitrate (Ni(NO3)2) and nickel sulfate (NiSO4) and hexamethylenetetramine (HMT) was used as an alkaline source. The synthesis of the nanostructures occurred through the hydrothermal method. Due to the use of HMT, the predominant phase in the samples was α-Ni(OH)2, although some differences were identified between samples due to different nickel sources. From nickel chloride or nitrate, the microspheres presented a flower shape, consisting of petal-like nanosheets, while the samples prepared with nickel sulfate resulted in two types of Ni(OH)2 structures with different characteristics, one structure was the porous flower-like microspheres and the other was a mesh microsphere. From these results the authors suggested that the combination of alkaline and anion source selections may be useful for the fine control of the structures and morphologies of transition metal hydroxides.

A study [9] proposed the synthesis of $Ni(OH)_2$ nanosheets modified with nitrogen-doped carbon points (NCD), aiming to further improve the energy storage performance of $Ni(OH)_2$ for practical applications. With the correct (unspecified) addition of NCD it is possible to obtain an optimization of specific electrochemical capacitance of the nanocomposites $Ni(OH)_2$/NCD. When compared with pure $Ni(OH)_2$, the nanocomposites showed smaller size and thinner thickness. The assembled super capacitor containing $Ni(OH)_2$/CD nanocomposites as positive electrode and three-dimensional graphene as negative electrode demonstrated high energy density, and the authors concluded that nitrogen-doped carbon dots played a very important role as a structure steering agent, in adjusting the size and thickness of $Ni(OH)_2$, being promising electrode materials for high performance.

A composite electrode in 3D format was developed, containing $Ni(OH)_2$/carbon nanotubes (CNT)/carbon fiber (CF), for the purpose of treating wastewater containing urea. The methods of electrophoretic code position and hydrothermal treatment were adopted to combine the advantages of each chosen component. The prepared electrode demonstrated favorable electrocatalytic activity and this positive point can be attributed to the 3D conductive structure and modification with CNT, because in this pre-treatment there is an increase in the number of groups containing oxygen, this causes the attraction of Ni^{+2} to the CF substrate to be more accelerated in the synthesis process. The $Ni(OH)_2$ catalyst is composed of the single phase of α-$Ni(OH)_2$ and its crystallinity was improved with increasing hydrothermal reaction time. The $Ni(OH)_2$/CNT/CF composite electrode exhibited a higher urea oxidation reaction current and a lower oxidation potential, that is, a lower electrode over potential. In addition, the composite electrode showed a lower charge transfer resistance, and this characteristic can be attributed to the increase of the surface area of the reaction and electrical conduction of the electrode due to the CNT. The phase transformation of $Ni(OH)_2$ into NiOOH can activate the oxidation of urea more easily, thus helping to decrease pollution and H_2 production during the treatment of urea-containing wastewater [14].

Nickel hydroxide has two polymorphs, known as α-$Ni(OH)_2$ and β-$Ni(OH)_2$ phases. However, the commercialization of the α-$Ni(OH)_2$ phase is limited due to problems of structural instability and low conductivity, being easily converted into another phase during some procedure. Due to this, the influence of sodium carbonate on structural stability and crystalline phase for nickel hydroxide doping was studied [26]. They were prepared by means of ultrasound-assisted precipitation. Four series of nickel hydroxide with different amounts of sodium carbonate were synthesized. The nickel source for this study was $Ni(NO_3)_2 \cdot 6H_2O$ and the metal ion sources for doping were $Al(NO_3)_3 \cdot 9H_2O$/ $Co(NO_3)_2 \cdot 6H_2O$/ $YbN_3O_9 \cdot 5H_2O$. After the first evaluation, the samples underwent the aging process to evaluate the stability of α-$Ni(OH)_2$. It can be seen that there was a process of recrystallization during the aging treatment, and that sodium carbonate had different positive effects, proving to be useful for the formation and maintenance of the structural stability of α-$Ni(OH)_2$.

IV. CONCLUSION

Through this, it is possible to verify that currently there are several studies that allow the recycling and recovery of nickel and metals that make up used batteries. Some of this research demonstrate that by employing some additives, doping alloys or nickel support materials, the results obtained are even more satisfactory indices and high percentages of recovery and use. Some of these studies still bring the areas where reused materials can be better applied, thus having the best possible performance. It is still difficult to define just one type of treatment or chemical process, as each of them brings a different benefit that contributes to the recovery and reuse of nickel. The main objective was to compile studies that deal with the recovery of nickel, cadmium and zinc for possible reuse in several areas, thus having a database for future research and future laboratory tests in this area.

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