

## **Assessment of Bio-Hydrometallurgical metal recovery from Ni-Cd batteries**

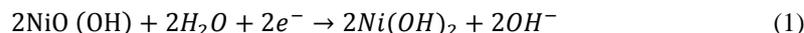
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The use of electrical devices has been increased tremendously around the world. Portable nickel-cadmium (Ni-Cd) batteries have been used in electronic products for many decades and have resulted in the generation of huge amounts of waste batteries. The battery disposal in municipal solid waste has become a serious problem for many countries. A battery can be considered as a recyclable material due to its high metal content and cannot be dumped directly in landfills, both for environmental and economic reasons. Amongst the metals present in Ni-Cd batteries, Cd is a toxic heavy metal harmful to both humans and environment. However, Ni and Co are valuable metals as a result of a decrease in their reserves and consequent increase in trading prices. Their disposal not only causes the loss of valuable metals but also demands the expenses for new material. Consequently, these spent batteries can be used as a secondary source for metals. The recycling of spent batteries is a growing industry. This review assesses the biohydrometallurgical process for recovery of metals from spent Ni-Cd batteries.

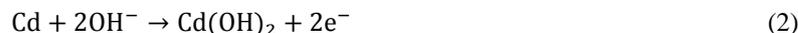
*Keywords:* Ni-Cd battery; Heavy metal pollution; Metal recovery; Bio-hydrometallurgy.

### **1. Introduction**

Batteries act as an efficient and portable power source. Their use has been increased tremendously, due to their versatility, low maintenance, reduced cost and requirements by the electronics industry. They vary in their composition, sizes, and models. In the USA, 3 billion batteries were sold annually.<sup>1</sup> In the year 2000, Europe produced 5 billion units of batteries<sup>1</sup>, of which the nickel-cadmium (Ni-Cd) represents 38%, nickel-metal hydride (Ni-MH) 35% and lithium-ion 18%.<sup>1</sup> Ni-Cd batteries are considered to be the most hazardous one.<sup>1</sup> They are available in different configurations, of which the cylindrical cells are most popular. In Ni-Cd battery, the nickel oxyhydroxide (NiOOH) is the cathodic active material which is converted to nickel hydroxide (Ni(OH)<sub>2</sub>) during discharge of the battery [1], as follows:



The anodic active material contains cadmium metal which is converted to cadmium hydroxide ( $\text{Cd}(\text{OH})_2$ ) on the discharge<sup>2</sup>, as follows:



An electrolyte solution of potassium hydroxide is added enough to wet internal cell components. This electrolyte is usually a mixture of KOH and  $\text{Li}(\text{OH})_2$ . Two types of Ni-Cd batteries are in use, the open, usually used in industrial applications and closed ones generally associated with household devices.

There is a possibility of leaching of metals from spent battery waste making them extremely hazardous to the environment. The safe disposal of this hazardous material is costly due to huge production and, to minimize it, recycling of materials appears to be the most promising solution. This helps in both reduction in production costs and the preservation of raw materials, along with environmental protection. [2, 4, 5]

The hydrometallurgical methods that involve pyrolysis are fast and efficient but are quite expensive and also produce polluting emissions. The hydrometallurgical methods though are cheap and less polluting, are usually not efficient. Biohydrometallurgy could be a sound alternative for recycling of metals from Ni-Cd batteries as they are not only highly efficient and have lower costs but is also an environmentally friendly process. [6, 7]

## **2. Bio-Hydrometallurgical Process for Recycling of Ni-Cd Batteries**

Recently, the biohydrometallurgical processes are not only restricted to mining industries but is also used for recovery of metals from industrial wastes such as battery waste.[7] In a pioneering study, Cerruti et al. (1998) used *T. ferrooxidans* culture to dissolve the nickel–cadmium batteries and to neutralize its electrolyte using sculpture as an energy source.[8] Both direct and indirect leaching mechanisms were considered to study the bioleaching process. Shake flasks experiments with previously adapted *T. ferrooxidans* were carried out to study the direct mechanism. But considering the feasibility of indirect bioleaching process for commercial application, this process was studied using series of two percolators (Fig. 1). 100, 96.5, and 95.0 % recovery of cadmium, nickel and iron were obtained respectively in the time span of 93 days. Authors recommend that this could be the first step in the treatment of nickel–cadmium batteries before recovering metals by physicochemical methodologies.

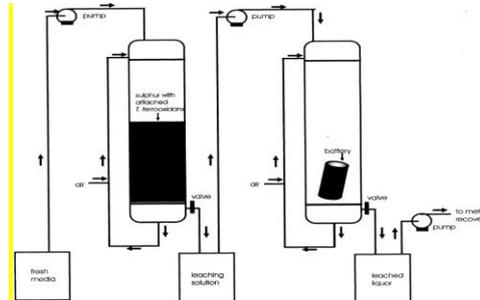


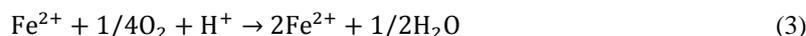
Fig. 1. A schematic representation of the two percolators system used for the dissolution of a spent nickel–cadmium battery.<sup>8</sup>

In another study, Zhu et al. (2003) used indigenous thiobacilli (mixed culture) from the sludge of wastewater treatment plants, for bioleaching of metals from spent Ni-Cd batteries.<sup>9</sup> Elemental sulfur was supplied externally for the growth of indigenous thiobacilli. They constructed bioreactor system in two parts i.e. bioreactor and leaching reactor. They reported that the release of nickel was slower than cadmium. The solubility of cadmium hydroxide is higher than nickel hydroxide. [8, 9]

In continuation to this study, Zhao et al. (2008a) compared the effect of ferrous sulphate and elemental sulfur for bioleaching of metals from Ni-Cd batteries. [10] They used a continuous flow two-step leaching system comprising of an acidifying reactor and a leaching reactor. They demonstrated the production of sulphuric acid or ferric ions using elemental sulphur or ferrous ions as the energy source by the strains of thiobacilli mainly *T. thiooxidans*, and *T. ferrooxidans*. Zhao et al. (2008b) showed that more time was required to achieve the complete leaching of metals from Ni-Cd batteries with the increasing hydraulic retention time [11].

Velgosova et al. (2010) used the pure culture of *Acidithiobacillusferrooxidans* and a mixed culture of *Acidithiobacillusferrooxidans*, *Acidithiobacillusthiooxidans* for studying various factors influencing the bioleaching of metals from spent Ni-Cd batteries.<sup>2</sup> Results indicated that the efficiency of leaching process increased by selecting appropriate parameters. Also, the pre-treatment of battery parts such as grinding, lead to better leaching performance. Results showed that complete Ni hydroxide leaching was observed using *Acidithiobacillusferrooxidans*, however, a negligible leaching of the metallic Ni was observed. 100% Cd bioleaching was observed from anode and cathode powders. 100% Cd bioleaching was observed using Fe ions. They proposed mechanisms for Cd bioleaching from spent battery waste. During bioleaching process, the bacteria use Fe (II) ions as an energy

source. The Fe (II) ions get oxidized into Fe (III) ions which act as strong oxidizing agents causing the solubilization of Cd (3), (4).



The bacteria produce sulphuric acid using sulfur as an energy source which plays the major role in dissolving Cd from spent Ni-Cd batteries.



The view was supported by another study of Bajestani et al. (2014)[12], who used the Box–Behnken design of response surface methodology to study the bioleaching of metals from spent Ni-Cd battery. Effects of particle size, initial pH, and initial  $\text{Fe}^{3+}$  concentration on the recovery efficiency of nickel, cadmium, and cobalt were studied. In practice, the separation of solid waste into individual battery type and materials of cathode and anode will be time-consuming and difficult. Therefore, it is necessary to find out the efficiency of bioleaching process for such kind of a waste. To achieve this, two types of battery wastes were mixed together to get a uniform composition of the waste material to be treated. The NiMH battery waste was mixed with Ni-Cd battery waste and the bioleaching process for the mixed anode and cathode materials were studied. This effort will be helpful for developing an industrial process. [13]The Box- Behnken design model predicted recovery of 85.6% Ni, 66.1% Cd, and 90.6% Co under optimized conditions. The authors confirmed these results using an experiment at optimum condition, which resulted in 87%, 67%, and 93.7% recovery of Ni, Cd, and Co, respectively. [12]

All these studies used *Acidithiobacilli* bacteria. Fungal recovery of metals from battery waste has not been tried in recent past due to the long processing time, the requirement of constant nutrients supply for their growth and their handling. However, fungi have several advantages over bacterial bioleaching including their ability to grow at high pH, making them more effective for bioleaching of alkaline materials. Recently, Kim et al. (2016) used several species of *Aspergillus* for metal bioleaching from spent batteries using malt extract and sucrose as a nutrient source. [13]

A comparison of various methods is shown in Table 1.

Table 1 Comparison for metal extraction from spent Ni-Cd battery

Micro-organisms used	Medium for metal recovery	Time for metal recovery (Days)	Removal of metal (%)	Reference
<i>Thiobacillusferrooxidans</i>	Iron-free 9 K medium with sulphur	93	Cd (100), Ni (96.5) and Fe (95.0)	8
Indigenous thiobacilli in sewage sludge	Sewage sludge with elemental sulphur	50	Cd (100), Ni (75.6)	9
Indigenous thiobacilli in sewage sludge	Sewage sludge with ferrous sulphate and elemental sulfur	16	Cd (100) and Ni (100)	10
Indigenous thiobacilli in sewage sludge	Sewage sludge with elemental sulphur	40	Cd (100) and Ni (100)	11
<i>At. ferrooxidans</i> <i>At. thiooxidans</i>	9 K medium	28	Cd (84)	2
<i>Acidithiobacillusferrooxidans</i>	9 K medium	28	Anode powder: Ni (5.5) and Cd (98) Cathode powder: Ni (45) and Cd (100)	14
<i>Acidithiobacillusferrooxidans</i>	9 K medium	--	Ni (87), Cd (67), and Co (93.7)	12
<i>A. niger</i> KUC5254 and <i>A. tubingenis</i> KUC5037	--	4	Ni, Cd, and Zn > (90)	13
<i>A. japonicus</i> KUC5035	Malt extract (ME) and sucrose media	8	Ni, Cd, and Zn (80) and Co (90)	13

### 3. Conclusion

The increasing use of electrical devices is resulting in an increase in the use of batteries. This is generating a huge amount of metal-containing waste that is entering the municipal waste. This issue is not only associated with environmental concerns but also for the raw material consumptions. These problems associated with spent batteries put forth a need for the collection of spent batteries, their recycling, and recovery of metals. The spent batteries can act as secondary metals ore. The requirements for establishing a metal recovery process are the economic recovery of metals along with ease of operation, selectivity, efficacy and environmental friendliness. The bio-hydrometallurgical processes seem to be more environmental-benign compared to hydrometallurgical methods. The bio-hydrometallurgical processes require longer processing time which limits their application on a large scale. But this approach has several advantages including, lower operational difficulties, easy storage, and transportation. Such technologies are required also for other components of batteries such as plastic, paper, steel, etc. Future developments

in the biohydrometallurgical process could lead to its application at industrial and commercial level.

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