Optimization of nitric acid properties for chemical recycling of cadmium from spent Ni-Cd batteries

M M Saleh¹, Salim F. Bamsaoud²* and H M Barfed¹

¹ Department of Chemistry, College of Science, Hadhramout University, Mukalla, Yemen.
² Department of Physics, College of Sciences, Hadhramout University, Mukalla, Yemen.

* Corresponding author: saalem88@hu.edu.ye

Abstract. Cadmium is poisonous to living species even at low doses. In the cadmium-nickel battery industry, cadmium is commonly associated with nickel and cobalt. In this paper, the experimental results revealed that in recovering cadmium from spent nickel-cadmium batteries, sulfuric acid was much less potent than nitric acid. The effect of nitric acid quantity, molarity, temperature, and recovery time are studied to improve the process of recovering cadmium from spent Nickel-Cadmium batteries. The optimum values of nitric acid quantity, molarity, temperature, recovery time, and wasted material are 70 ml, 5 M, 70°C, 180 min, and 2g respectively. The recovered materials were investigated using an x-ray diffractometer (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDX). An atomic absorption spectrometer (AAS) was used to analyze the chemical composition of the leached samples.

1. Introduction

Ni–Cd batteries are currently being recycled by dedicated pyrometallurgical processes (SNAM in France, SAFT in Sweden and INMETCO in the USA) focused on cadmium distillation [1]. Recycling refers to the process by which waste or residues of used materials, such as empty bottles, plastic bags, damaged equipment, etc., are collected in order to become involved in the new safe products industry [2]. The scientific analysis of this phenomenon, however, has revealed that what is an advantage to the life of the city has become a serious issue and a form of environmental pollution [3]. In previous studies, researchers have done a wonderful job of extracting 65% of manganese, 99.9% of cadmium, 100% of zinc, and 64% of nickel, and 74% of cobalt from wasted batteries [4]. Using hydrometallurgical, sulfuric acid, hydrochloric acid, oxalic acid, sodium hydroxide, acetic acid, EDTA, and ammonium chloride, the recovered precious metals from a different mix of consumed batteries could be recovered.

The manufacture of rechargeable nickel-cadmium batteries originated in Europe and the United States in 1950. These batteries are used in applications that require high energy capacity, long life, and high discharge speeds [23]. For these reasons, the extensive use of Ni-Cd batteries increases the environmental pollution and the wasted heavy metals nickel and cadmium become real danger. Because of the high content of toxic cadmium in spent nickel-cadmium batteries, they are known as hazardous waste. Cadmium is a toxic transition metal that has piqued the interest of scientists due to its broad variety of dangerous, long-term occupational and environmental hazards [5]. With a systemic or direct contact, cadmium may induce prostatic proliferative lesions, including adenocarcinomas. [7-
Also cadmium is clearly a potent, multi-tissue animal carcinogen [11, 12]. So researchers are interested in recycling of metal value using environmentally friendly process which is the best option to obtain economical advantage and prevent environmental pollution [24].

Researchers reported different methods used to extracted cadmium. Swain et al [13] used liquid–liquid extraction of cadmium (II) from sulfate medium. They used phosphonium and ammonium based ionic liquids diluted in kerosene. Hazotte et al recover cadmium directly from Ni-Cd spent batteries by electrolysis (electro assisted) and electrolysis (electrodeposition) in one cell [14]. Also Hydrometallurgical route in the recycling of metals was using Aline team to recover nickel, cobalt, and cadmium from spent Ni-Cd batteries. They recovered Co (II) and Cd (II) by solvent extraction [15]. Umesh et al. [16] showed a new process in which ferric sulfate was used to recycle heavy metals from spent Ni-Cd batteries. Reddy et al. reported different methods to extract cadmium (II), cobalt (II) and nickel(II) from sulphate leach liquor of spent Ni-Cd batteries [17]. They used phosphorus based extractants such as TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302 and Cyanex 301 diluted in kerosene. Many experts have worked tirelessly to address environmental issues by the careful management of discarded batteries and at the same time the recycling of precious metals. However, the extensive use of Ni-Cd metals in applications due to their high energy density, long life [18] requires a great deal of research in the recovery process in order to obtain a simple, cheaper and highly effective system.

In this work, various chemical solvents are used to identify the best solvent that could boost the efficiency of re-covered cadmium from a waste Ni-Cd battery. To improve the efficiency of the chemical process of recovering cadmium from spent Nic-el-Cadmium batteries, different variables such as solvent quantity, molarity, temperature, and recovery time will be studied.

2. Materials and Methods

2.1. Materials and apparatus

In this work the spent Ni-Cd battery powder was obtained from FNO 205L – Hoppecke Solar Batteries. The batteries were supplied by Yemen Electrical Power Stations-Hadramout Valley Station. Various chemicals, with no further purifications process, were used such as Sulfuric acid (BDH), hydrochloric acid (BDH), nitric acid (BDH), sodium hydroxide (GCC), potassium hydroxide (GCC), sodium carbonate (GCC), and sodium bicarbonate (GCC). Since the characterization of the metal content produced can provide valuable knowledge for the implementation of successful recycling processes, the chemical composition of spent Ni-Cd battery powder has been investigated using XRD. The XRD pattern was recorded using (Bruker D8 Discover) instrument and a copper source at 40 kV and 40 mA was used. Morphology of the sample and leach residues were investigated using (SEM, TESCAN Ultra-High Resolution). This Scanning electron microscope (20 kV) is also equipped with an X-ray, energy dispersive spectroscope (EDS). An atomic absorption spectrometer (AAS, iC3000- Thermo), was used to analyze the chemical composition of the leaching samples.
2.2. Preparation of Acid and Bases Solutions
All solutions were prepared in volumetric flask of 1 L. The acid and base solutions were gradually diluted using dilution law. Sulfuric acid, nitric acid, and hydrochloric acid concentrations ranged from 2 to 6 M. The sodium hydroxide, potassium hydroxide, sodium bicarbonate, and sodium carbonate were prepared with the concentration of 2 M.

2.3. Procedure recovery of materials
All the constituents of spent Ni-Cd batteries were manually isolated. The electrodes were released by cutting from the supporting panels. The anode cadmium plate was cleaned using tap water and distilled water several times. Before crushed out using mortar and pestle, the cleaned plate was cut into tiny pieces. The chemical treatments of the anode powder was firstly leached using different basic and acidic solutions. The leach solutions were filtered, and the leachate was dried and removed to measure the quantity of cadmium recovered. The cadmium concentrations were measured using AAS. Based on their leach liquor concentrations, the cadmium recoveries were estimated. The dismantled Ni-Cd waste battery diagram and the substance identification before and during the chemical phase are shown in Figure 1.

3. Results and Discussion
3.1. Anode Characterization
After the required solubilization in an HNO₃ and H₂SO₄ HCl, the chemical composition of the Ni-Cd anode was identified using AAS, EDS, and XRD. Figure 2a presents the SEM image of the anode part. The picture shows the surface morphology of the anode powder. It can be seen that most of the particles are loosely bonded and a comparably small number of particles are aggregated. The well-used solubility approach is demonstrated by these observations [19, 20].
Figure 2. Characterizations of negative electrode powder derived from a spent Ni–Cd battery: (a) SEM, (b) XRD, (c), and (d) EDX.

The XRD pattern (Figure 2b), confirms the presence of Cd (JCPDS file: 04-0850), and Cd (OH)$_2$ (JCPDS file: 31-0228), CdO$_2$ (JCPDS file: 27-0956) and Ni (JCPDS file: 04-0850). The chemical compositions of the anodic materials of spent battery powder were determined by AAS, XRD and EDS are given in Table 1. The table indicates that the main components are nickel and cadmium. There were other elements such as Si, Co and C in limited quantities. It would be worthy to note that cadmium content in the present sample is quite higher than what other researchers reported for spent Ni–Cd batteries. This result is consistent with other literature data [19-22]. Figure 2c and 2d show the EDS spectrum of the anode material. The EDS data indicates that the main ingredients of the anode are nickel, cadmium, carbon, cobalt, and silicon. The presence of potassium in the anode may come from the KOH electrolyte which was detected on the surface of the material. EDS data show also a presence of carbon (C) and cobalt (Co) elements. They are well known in use as additives to improve the electrical conductivity of the negative electrode [19,20]. Therefore, the presence of oxygen, which showed by EDS, could probably due to the Cd and Co oxides.

Table 1. The chemical contents of the leached residue and the spent Ni-Cd battery powder.

| Element | Chemical composition | Leached residue (Wt.%)|
|---------|----------------------|-----------------------|
| Cd      | 49.0                 | 99.0                  |
| Ni      | 3.4                  | Not found             |
| Si      | 1.6                  | 0.04                  |
| K       | 11.1                 | Not found             |
| Co      | 2.2                  | Not found             |
3.2. Leaching Studies

3.2.1. Cadmium Recovery Using Different Solutions

To evaluate the efficacy of solutions in cadmium recovery process, different acidic and basic solutions (Na$_2$CO$_3$, KOH, NaHCO$_3$, NaOH, HCl, HNO$_3$, H$_2$SO$_4$) were used. The use of acidic and basic solutions to dissolve the electrode materials were calibrated to have a concentration of 2 M. The anode sample (2.5 g) of was soaked in 15 ml of the above-mentioned solvents in order to extract cadmium. The solvent volume, temperature, recovery time and cadmium past were controlled to be 15 mL, 25°C, 60 min and 2.5 g respectively. The results of the recovered cadmium percentage are shown in Figure 3a. The results reveals that the recovered cadmium was found to be higher for acidic solution and lower for basic solution under the same conditions. The highest values of the recovered cadmium (%) were observed for the nitric acid (HNO$_3$). Moreover, the lowest amount of recovered cadmium (%) was recorded for the used sodium carbonate solution. The reactions mentioned below can be used to account for the dissolution of the above phases in various acidic leach liquors, as determined by the FACT Sage 6.1 reaction module. [19, 23]:

\[
\begin{align*}
\text{Cd(OH)}_2(s) + 2\text{HCl}(l) &\rightarrow \text{CdCl}_2(l) + 2\text{H}_2\text{O}(g) \\
\text{Cd(OH)}_2(s) + 2\text{HNO}_3(l) &\rightarrow \text{Cd(NO}_3)_2(l) + 2\text{H}_2\text{O}(g) \\
\text{Cd(OH)}_2(s) + \text{H}_2\text{SO}_4(l) &\rightarrow \text{CdSO}_4(l) + 2\text{H}_2\text{O}(g)
\end{align*}
\]

The percentage of regeneration was estimated as follows [24]:

\[
\text{Recovery (\%)} = \frac{\text{metal in solution (mg)}}{\text{metal in sample (mg)}} \times 100
\]

Figure 3. (a) The cadmium recovery (%) using different chemical solutions for 2.5 g paste, (b) effect of HNO$_3$ concentration on recovering process.

3.2.2. Effect of Acid Concentration

Due to the fact that nitric acid results in the highest amount of cadmium, its concentrations (1, 2, 3, 4, 5, and 6 M) were investigated in recovering the acid concentration in recovering process. Figure 3b illustrates the effect of nitric acid concentrations on the quantity of cadmium during the recovering process. The figure revealed that the leaching yields increase gradually with increase in acid concentration. The quantity of the extracted cadmium reaches the highest percentage of (93.31%) for 5 M concentration and got nearly saturated when acid concentration is 6 M. The results achieved in this research have been compared with other studies reported [19, 23].

3.2.3. Effect of The Cadmium Paste

The third factor which could contribute in enhancing the recovering process of cadmium is the cadmium paste. The concentrated nitric acid (5 M) was combined with various cadmium pastes (1, 1.5, 2, 2.5, and 3) and the weight of the extracted cadmium was measured. The calculated percentages of the extracted cadmium are shown in Fig 4a. It is noticed that the highest recovered cadmium percentage was obtained when the weight of the dough is (2 g) and the lowest quantity of the recovered cadmium was noticed.
when the weight of the dough is (3 g), the weight of the sample was adopted at (2 g) as the best weight because the difference in the quantity of cadmium recovered is less than the amount of cadmium recovered when using the weight of the dough (3 g).

**Figure 4.** Percentage of the extracted cadmium against (a) the crushed plate quantity (b) solvent quantity (c) temperature and (d) time of the extraction process.

**3.2.4. Effect of Nitric Acid Volume**

After the study of the optimum concentration of nitric acid (5 M) and the cadmium paste (2 g), further experiments were performed to determine the influence of the amount of nitric acid on the cadmium recovering process. A different quantity (10, 15, 20, 25, and 30 mL) of nitric acid (5 M) were mixed with 2 g of cadmium paste. The values of nitric acid volume against the recovered cadmium are plotted in Figure 4b, showing that the percentage of the recovered cadmium is increasing with increasing the acid volume and the highest cadmium recovered (95.32%) is noticed for the volume of (25 mL) [20]. With further increase of nitric acid volume (30 mL) the recovered cadmium decreases by (5%) from the highest value. So, the volume of 25 mL considered as the optimum volume.

**3.2.5 Effect of Acid Temperature**

As a chemical reality, the temperature has a great influence on many chemical reactions. In this analysis, the temperature of the system (cadmium paste and nitric acid) was increased from 30 to 80°C to determine the optimal temperature at which the leaching process is completely faster with highest yield. The 25 mL nitric acid (5 M) and 2.5 cadmium paste reaction experiments were performed separately at various temperatures (30, 40, 50, 60, 70, and 80 °C). This experiment findings are illustrated in Figure 4d. Similar to the reaction time tests (Figure 4c), the cadmium yield increases as the temperature increases, and a small
change in the cadmium yield was found at a temperature of (60°C). The optimum amount of cadmium extraction is 96.5% at 70°C. With further rise in temperature, no change in the volume of cadmium was detected and the yield saturates at 60°C [20,25,26].

3.2.6 Effect of Recovering Time
A long or short period is one of the variables that may influence the process of metal recovery. To determine the required time to get the highest recovered cadmium from 2.5 cadmium paste using the 25 mL of nitric acid with 5 M concentration, experiments were performed at different periods of time ranging from (60, 90, 120, 180, and 240 min). The results are shown in Figure 4c, indicating that with increasing process time the percentage of the recovered cadmium increases to reach 98.52% on 180 min. With further increasing time the percentage is almost getting saturated. [20]

To identify the phases, the final leaching residue obtained at different times was identified by X-ray and which is presented in Figure 5 (a and b). The lack of related peaks in Figures 5a and 5b indicates that leaching in nitric acid dissolves all the cadmium phases, i.e. CdCO$_3$ and Ni(OH)$_2$, as well as Cd(OH)$_2$. The XRD data of the sample having leaching time of 120 min (Figure 5a) shows very low intensity peaks which are attributed to CdO$_2$ (JCPDS file: 27-0956) [27]. The XRD data of the sample having leaching time of 180 min (Figure 5b) shows only peaks related to Cd metal and no peaks related to CdO$_2$. The SEM images of the samples leached at 120 and 180 min are illustrated in Figure 5c and 5d. The microscope images (SEM) show that the morphology of the leaching residues has improved drastically. The SEM shows that the sample with leaching time of 120 min have particles with lower size than the sample prepared in 180 min. As particle size increases, there can be major improvements in the ruggedness and size of the pores in the collected samples. The SEM shows nearly particles with cylindrical type structure formed of small particles that disintegrate along the progress of leaching. The cadmium that contains powdery mass (mash-like formations) gradually vanished while at the last stages of the leaching, the pitted connecting wires comprising Cd have predominated.

![Figure 5. X-ray diffraction pattern and SEM for samples leached for (a and c) 120 min and (b and e) 180 min.](image)

4. Conclusions
Using various acidic solutions, the chemical recycling of anode materials from spent Ni-Cd batteries was investigated. The following assumptions were formulated based on the findings achieved from the present work: The paper shows that the leaching with the nitric acid leaching in HNO$_3$ will achieve a high level of cadmium recoveries. Cadmium recovery was significantly affected by nitric acid concentrations and the
optimized concentration of nitric acid is 5M. The cadmium leaching recovered substantially by a temperature of 96.5% within 180 min at 70°C. The cadmium regeneration was increased to 98.52% after three hours of leaching time. The SEM and XRD analytics showed a gradual shift in the morphology of particles and size during leaching that confirmed the use of the shrinking core model for the leaching data. An innovative aspect of this investigation was the high cadmium recovery by leaching of Ni particles and size during leaching three hours of leaching time. The SEM and XRD analytics showed a gradual shift in the morphology of optimized concentration of nitric acid is 5M. The cadmium leaching recover

Acknowledgments
The authors would like to thank Surface Science Laboratory Chemistry Department-Kabardino-Balkaria State University Nalchik Russia (KBSUNR) for currying out sample characterizations. Also, the authors would like to thank Hadramout University, College of Science for providing research facilities to complete this work.

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