

Towards Sustainable Waste Management: Optimizing Nitric Acid Leaching for Cadmium Recovery from Spent Alkaline Batteries

Mahmood Mohammed Ali Saleh¹, Mansour A.S. Salem² and Khalil M. A. Qasem³

¹Dept, of Chemistry, Faculty of Education University of Aden, Aden, Yemen

¹Dept, of Chemistry, Faculty of Education University of Aden, Aden, Yemen

¹Dept, of Chemistry, Faculty of Education University of Aden, Aden, Yemen

Abstract:

The improper disposal of batteries, particularly those containing heavy metals, establishes a critical connection between natural resource contamination and accelerated climate change. Carbon emissions from manufacturing new batteries and landfill operations contribute significantly to atmospheric greenhouse gas concentrations. Simultaneously, contamination of soil and water resources by toxic battery components - including cadmium and lead - damages natural ecosystems that function as essential carbon sinks, such as forests and oceans, thereby compromising the Earth's capacity to absorb carbon dioxide. Cadmium is a highly toxic heavy metal, posing significant risks to living organisms even at trace concentrations. In the nickel-cadmium battery industry, cadmium is typically found in association with nickel and cobalt. This study investigates an optimized hydrometallurgical process for recovering cadmium from spent Ni-Cd batteries. Experimental results demonstrated that nitric acid (HNO_3) exhibits significantly superior leaching efficiency compared to sulfuric acid (H_2SO_4). Consequently, the influence of key parameters—including nitric acid volume, molarity, temperature, and leaching time—on cadmium recovery yield was systematically examined. The optimal leaching conditions were determined to be: 70 mL of 5 M nitric acid at a temperature of 70°C for a duration of 180 minutes, using a 2g sample of spent battery material. The solid recovery products were thoroughly characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) to elucidate their phase composition, morphology, and elemental distribution. Furthermore, the chemical composition of the leachates was quantitatively analyzed using atomic absorption spectrometry (AAS) to determine the final cadmium recovery efficiency.

Keywords: Battery Recycling, Cadmium Recovery, Nitric Acid Leaching, Process Optimization, Heavy Metal Pollution.

الملخص:

يُثبت التخلص غير السليم من البطاريات، وخاصةً تلك التي تحتوي على معادن ثقيلة، وجود صلة جوهرية بين تلوث الموارد الطبيعية وتسارع تغير المناخ. تُسهم انبعاثات الكربون الناتجة عن تصنيع البطاريات الجديدة وعمليات طمر النفايات بشكل كبير في تركيزات غازات الاحتباس الحراري في الغلاف الجوي. وفي الوقت نفسه، يُلحق تلوث التربة والموارد المائية بمكونات البطاريات السامة بما في ذلك الكاديوم والرصاص - الضرر بالنظم البيئية الطبيعية التي تعمل كمصارف أساسية للكربون، مثل الغابات والمحيطات، مما يُضعف قدرة الأرض على امتصاص ثاني أكسيد الكربون.

يعدُّ عنصر الكاديوم (Cd) من المعادن الثقيلة عالية السُمِّيَّة، والتي تشكِّل مخاطر جسيمة على الكائنات الحية حتى عند تراكيزها الشديدة الانخفاض. وفي صناعة بطاريات النيكل-كاديوم، يوجد الكاديوم مرافقاً لعنصري النيكل والكوبالت بشكلٍ نمطي.

تستقصي هذه الدراسة عملية استخلاص مائي-معدني مُحَسَّنة لاسترداد الكاديوم من بطاريات النيكل-كاديوم المستهلكة. وأظهرت النتائج التجريبية تفوقاً ملحوظاً لكفاءة استخلاص حمض النيتريك (HNO_3) مقارنة بحمض الكبريتيك (H_2SO_4) وبناءً على ذلك، تم فحص تأثير العوامل الرئيسية والتي تشمل حجم حمض النيتريك، وتركيزه المولي، ودرجة الحرارة، وزمن الاستخلاص على مردود استرداد الكاديوم بشكلٍ منهجي. وتم تحديد الظروف المثلى للاستخلاص على النحو التالي: استخدام 70 مليلتر من حمض النيتريك بتركيز 5 مولار عند درجة حرارة 70 مئوية ولمدة 180 دقيقة، وذلك مع عينة وزنها 2 غرام من مادة البطارية المستهلكة.

وتم توصيف نواتج الاسترداد الصلبة بدقة باستخدام تقنيات حيود الأشعة السينية (XRD)، والمجهود الإلكتروني الماسح (SEM)، ومطيافية الطاقة المشتتة للأشعة السينية (EDX) لتوضيح تركيبها الطوري، ومظهرها السطحي، وتوزيع العناصر فيها. تم تحليل التركيب الكيميائي لمستخلصات السوائل كميّاً باستخدام مطيافية الامتصاص الذري (AAS) لتحديد الكفاءة النهائية لاسترداد الكاديوم.

الكلمات المفتاحية: إعادة تدوير البطاريات، استعادة الكاديوم، استخلاص حمض النيتريك، تحسين العمليات، تلوث المعادن الثقيلة.

1. Introduction

Nickel-cadmium (Ni-Cd) batteries represent a significant waste management challenge due to their classification as hazardous materials, primarily attributable to the high concentration of toxic cadmium. Currently, industrial recycling of these batteries relies on pyrometallurgical processes, as exemplified by operations such as SNAM in France, SAFT in Sweden, and INMETCO in the USA, which focus on cadmium distillation (Espinosa *et al.*, 2006). While battery recycling is essential for resource conservation and waste reduction, the specific handling of Ni-Cd waste presents critical environmental and health concerns (Salihah & Hafeeh 2013; Spellman & Frank 2018).

The development of efficient recycling strategies is critically motivated by the severe toxicity of cadmium. This heavy metal is a well-established human carcinogen, classified by the International Agency for Research on Cancer (IARC, 2012) as Group 1: Carcinogenic to humans. Recent evidence consistently links cadmium exposure to an increased risk of lung, prostate (Wang & Wang, 2021), and breast cancers (Oliveira & Souza, 2023), as well as multi-organ toxicity affecting the kidneys and skeletal system through mechanisms like oxidative stress (Rahimzadeh *et al.*, 2022).

Consequently, the recovery of valuable metal content from spent Ni-Cd batteries through environmentally benign processes is not only economically advantageous but also a crucial measure for mitigating environmental pollution (Huang *et al.*, 2009).

Substantial research has been dedicated to the hydrometallurgical recovery of metals from battery waste. Previous studies have demonstrated successful extraction of various metals, including 65% manganese, 99.9% cadmium, 100% zinc, 64% nickel, and 74% cobalt, using leaching agents such as sulfuric acid, hydrochloric acid, and organic complexants (Tanong *et al.*, 2016). Specific methodologies for cadmium recovery include liquid-liquid extraction with ionic liquids (Swain *et al.*, 2016), direct electrodeposition (Hazotte *et al.*, 2016), and solvent extraction using phosphorus-based extractants like Cyanex series reagents (Aline *et al.*, 2012; Reddy *et al.*, 2006). Alternative approaches have also employed ferric sulfate as a leaching medium (Umesh & Hong 2014).

Despite these advancements, the widespread application of Ni-Cd batteries, valued for their high energy density and long cycle life (Freitas *et al.*, 2007; Bale *et al.*, 2009), necessitates continued research into developing simpler, more cost-effective, and highly efficient recovery systems. This study aims to contribute to this goal by systematically evaluating various chemical solvents to identify the most effective agent for cadmium leaching from spent Ni-Cd batteries. The influence of key process parameters—including solvent quantity, molarity, temperature, and recovery time—will be investigated to optimize the leaching efficiency and develop an enhanced hydrometallurgical process for cadmium valorization.

2. Materials and Methods

2.1 Materials and apparatus

The spent Ni–Cd battery powder was obtained from FNO 205L – Hoppecke Solar Batteries which were supplied by Yemen Electrical Power Stations-Hadhramout Valley Station. Sulfuric acid (BDH), hydrochloric acid (BDH), nitric acid (BDH), sodium hydroxide (GCC), potassium hydroxide (GCC), sodium carbonate (GCC), and sodium bicarbonate (GCC) Chemicals, as obtained, were used with no further purification process applied. 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 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). The chemical analysis of leaching samples was carried out using atomic absorption spectrometer (AAS, iC3000- Thermo).

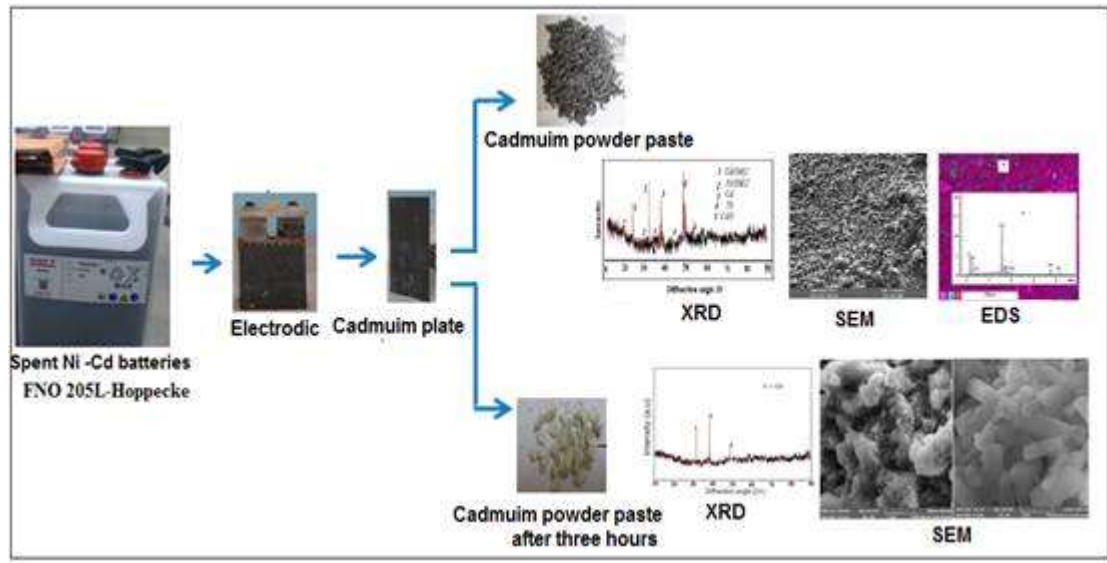


Figure 1. Schematic illustration of the chemical recycling of Cadmium from the Negative electrode of spent Nickel-Cadmium batteries.

2.2. Preparation of Acid and Bases Solutions

All acid and base solutions were prepared in 1 L volumetric flasks. Stock solutions of sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) were systematically diluted to achieve concentrations ranging from 2 to 6 M, following standard dilution principles. Similarly, basic solutions of sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate (NaHCO_3), and sodium carbonate (Na_2CO_3) were prepared at a standardized concentration of 2 M. This consistent methodology ensured accurate and reproducible solution concentrations for all subsequent experimental procedures.

2.2 Material Recovery Procedure

Spent Ni-Cd batteries were manually dismantled to separate their components. The electrode assemblies were carefully excised from their supporting panels. The cadmium anode plates underwent sequential cleaning with tap water followed by distilled water, then were sectioned into fine fragments and pulverized using a mortar and pestle.

The resulting anode powder was subjected to systematic leaching treatments using various acid and base solutions. Following each leaching process, the mixtures were filtered, and the obtained leachates were evaporated to dryness. The recovered cadmium content was quantitatively determined using atomic absorption spectrometry (AAS), with recovery efficiency calculated based on leachate concentration measurements. Figure 1 presents a schematic overview of the battery dismantling process and material identification stages throughout the chemical treatment sequence.

3. Results and Discussion

3.1 Anode Material Characterization

The chemical composition of the Ni-Cd battery anode was determined through AAS, EDS, and XRD analyses following digestion in HNO_3 , H_2SO_4 , and HCl . Figure 2a displays the SEM micrograph of the anode powder, revealing a predominantly loose particulate morphology with limited aggregation. This structural observation suggests effective material solubility, consistent with established dissolution mechanisms reported in literature (Nogueira *et al.*, 2004; Randhawa *et al.*, 2015).

X-ray diffraction analysis (Fig. 2b) confirmed the presence of metallic Cd (JCPDS: 04-0850), $\text{Cd}(\text{OH})_2$ (JCPDS: 31-0228), CdO_2 (JCPDS: 27-0956), and metallic Ni (JCPDS: 04-0850) in the anode material. The elemental composition determined by AAS and EDS (Table 1) revealed nickel and cadmium as the predominant constituents, with minor amounts of Si, Co, and K. Notably, the cadmium content in the present sample exceeded values typically reported in literature for spent Ni-Cd batteries (Nogueira *et al.*, 2004; Randhawa *et al.*, 2015; Nogueira & Margarido; Pietrelli *et al.*, 2005).

EDS spectral analysis (Fig. 2c, 2d) further identified carbon and cobalt as additional components, consistent with their known role as conductive additives in electrode formulation (Nogueira *et al.*, 2004; Randhawa *et al.*, 2015). The detected oxygen signature correlates with the observed cadmium and cobalt oxides, while potassium is likely derived from residual KOH electrolyte adsorbed on the material surface.

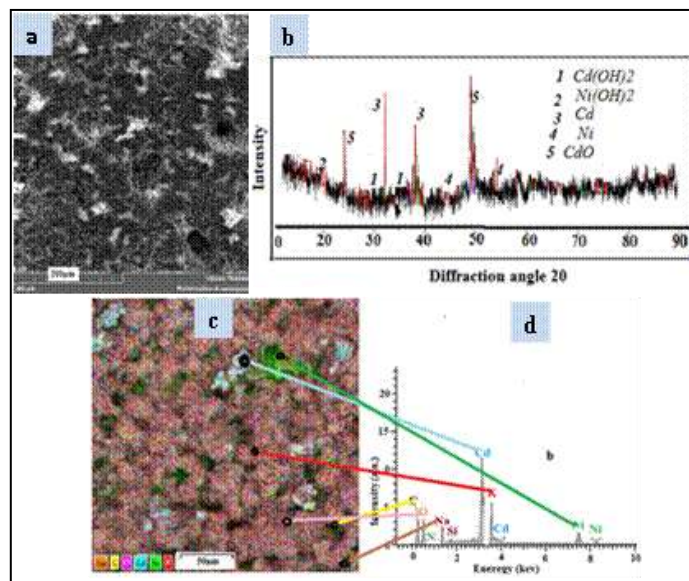


Figure 2. (a) Scanning electron micrograph, (b) XRD , (c) and (d) Energy dispersive X-ray (EDX) spectrum for powder obtained from the negative electrode of spent Ni–Cd battery batteries.

Table 1. Chemical composition of spent Ni-Cd battery powder of the negative electrode and leached residue.

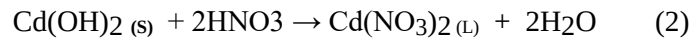
Element	Chemical composition Spent Ni–Cd battery powder	Leached residue (Wt.%)
Cd	49.0	99.0
Ni	3.4	Not found
Si	1.6	0.04
K	11.1	Not found
Co	2.2	Not found

3.2. Leaching Studies

3.2.1. Cadmium Recovery Efficiency of Various Leachants.

The leaching efficiency of different acidic and basic solutions (Na_2CO_3 , KOH, NaHCO_3 , NaOH, HCl, HNO_3 , H_2SO_4) was evaluated under standardized conditions: 2 M concentration, 15 mL solvent volume, 2.5 g anode material, 25°C, and 60-minute duration. As shown in Figure 3a, acidic solutions demonstrated superior cadmium recovery compared to basic solutions. Nitric acid (HNO_3) achieved the highest

recovery yield, while sodium carbonate exhibited the lowest efficiency. The dissolution mechanisms for different phases in acidic media were simulated using the reaction module in FACTS age 6.1 (Nogueira *et al.*, 2004; Bale *et al.*, 2009).



The recovery percentage was calculated as follows [24]:

$$\text{Recovery (\%)} = \frac{\text{metal in solution (mg)}}{\text{metal in sample (mg)}} \times 100 \dots \dots \dots (4)$$

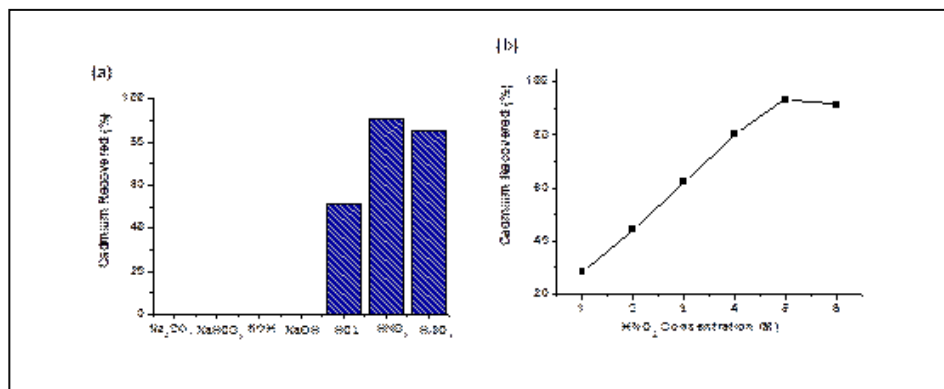


Figure 3. (a) The cadmium recovery (%) using different chemical solutions for 2.5 g paste, (b) effect of HNO₃ concentration on recovering process.

3.2.2. Effect of Nitric Acid Concentration

Building upon the superior performance of nitric acid identified in the previous section, its concentration was systematically varied from 1 to 6 M to quantify its effect on leaching efficiency. Figure 3b demonstrates a positive correlation between acid concentration and cadmium recovery, with yield increasing progressively up to a maximum of 93.31% at 5 M concentration. Beyond this point, the recovery rate plateaued, indicating approach to saturation at 6 M. These findings align with trends reported in comparable hydrometallurgical studies (Nogueira *et al.*, 2004; Bale *et al.*, 2009), confirming 5 M HNO₃ as the optimal concentration for maximal cadmium extraction under the investigated conditions.

3.2.3 Effect of Cadmium Paste Mass

The influence of cadmium paste mass on leaching efficiency was investigated using 5 M nitric acid with varying solid masses (1-3 g). Figure 4a illustrates the recovery percentages, revealing an optimal cadmium recovery at 2 g of paste mass. Beyond this mass, a decline in recovery efficiency was observed, with the 3 g sample yielding the lowest extraction rate. Consequently, 2 g was established as the optimal paste mass, representing the threshold for maximizing cadmium recovery under the specified leaching conditions.

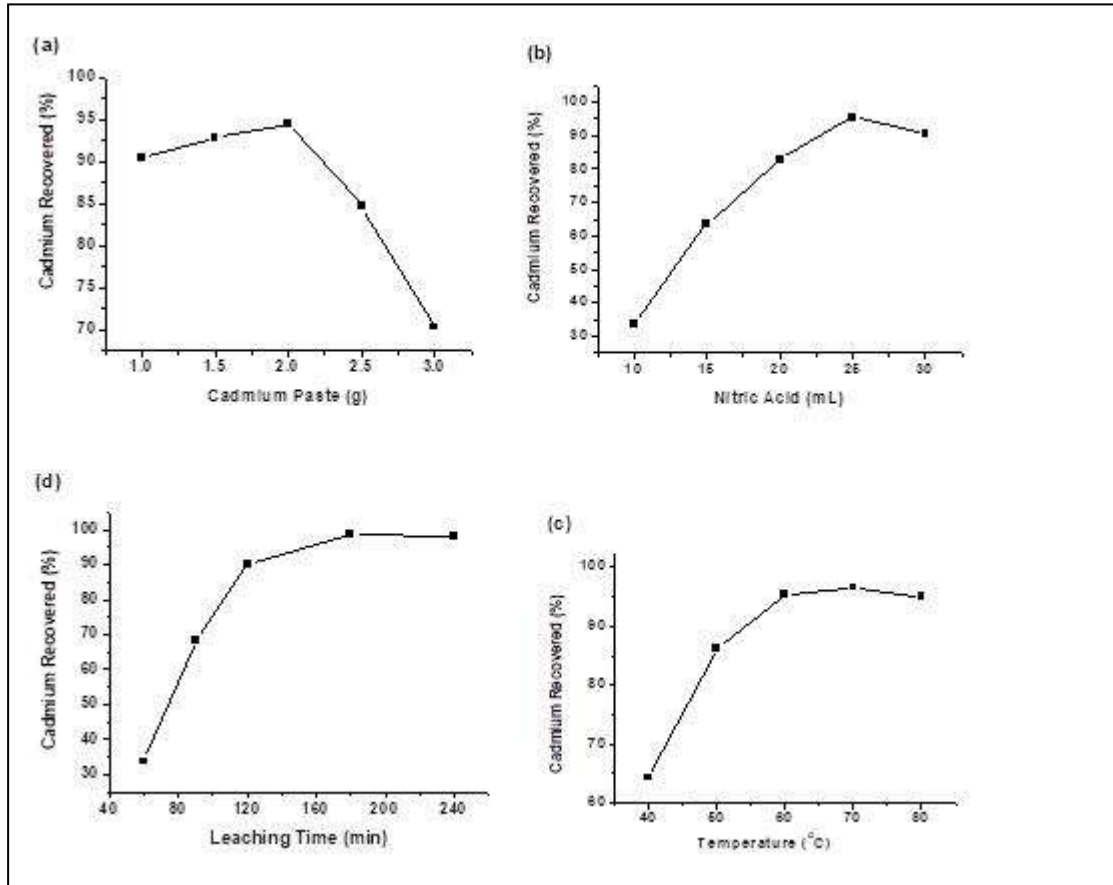


Figure 4. percentage of the extracted cadmium against (a) the crushed plate quantity (b) solvent quantity (c) temperature and (d) time of the extraction process.

3.2.4 Effect of Nitric Acid Volume.

Following the determination of optimal concentration (5 M) and paste mass (2 g), the effect of nitric acid volume on cadmium recovery was investigated. Various volumes (10-30 mL) of 5 M HNO_3 were reacted with 2 g of cadmium paste. As shown in Figure 4b, cadmium recovery efficiency increased with acid volume, reaching a maximum of 95.32% at 25 mL. Beyond this optimal volume, a 5% decrease in recovery was observed at 30 mL, establishing 25 mL as the optimum nitric acid volume for maximal cadmium extraction efficiency (Randhawa *et al.*, 2015).

3.2.5 Effect of Leaching Temperature.

The influence of temperature on leaching efficiency was investigated by conducting experiments at temperatures ranging from 30 to 80°C, maintaining constant optimal parameters of 25 mL 5 M HNO_3 and 2 g cadmium paste. As shown in Figure 4d, cadmium recovery exhibited a positive temperature dependence, increasing progressively to reach a maximum yield of 96.5% at 70°C. Notably, the recovery rate demonstrated negligible enhancement beyond 60°C, indicating system saturation. This temperature-dependent behavior aligns with established reaction kinetics and is consistent with previous studies on hydrometallurgical extraction (Randhawa *et al.*, 2015; Abdel-Aal *et al.*, 2004; Al-Mansi & Monem 2002).

3.2.6 Effect of Leaching Time.

The influence of leaching duration on cadmium recovery was investigated over intervals of 60-240 minutes under optimal conditions (25 mL of 5 M HNO₃, 2 g cadmium paste). As shown in Figure 4c, recovery efficiency increased with time, reaching a maximum of 98.52% at 180 minutes. Further extension to 240 minutes resulted in saturation, indicating completion of the extraction process (Randhawa *et al.*, 2015).

Phase analysis of leaching residues by XRD (Figure 5a-b) confirmed progressive dissolution of cadmium compounds. After 120 minutes, minor CdO₂ phases persisted (JCPDS: 27-0956) (Zhang *et al.*, 2022), while the 180-minute sample exhibited complete conversion to metallic cadmium. Corresponding SEM micrographs (Figure 5c-d) revealed significant morphological evolution, with 120-minute samples showing finer particulate structures that coalesced into larger, porous aggregates by 180 minutes. This microstructural transformation correlates with the progressive dissolution of mesh-like cadmium formations and exposure of underlying pitted connective structures.

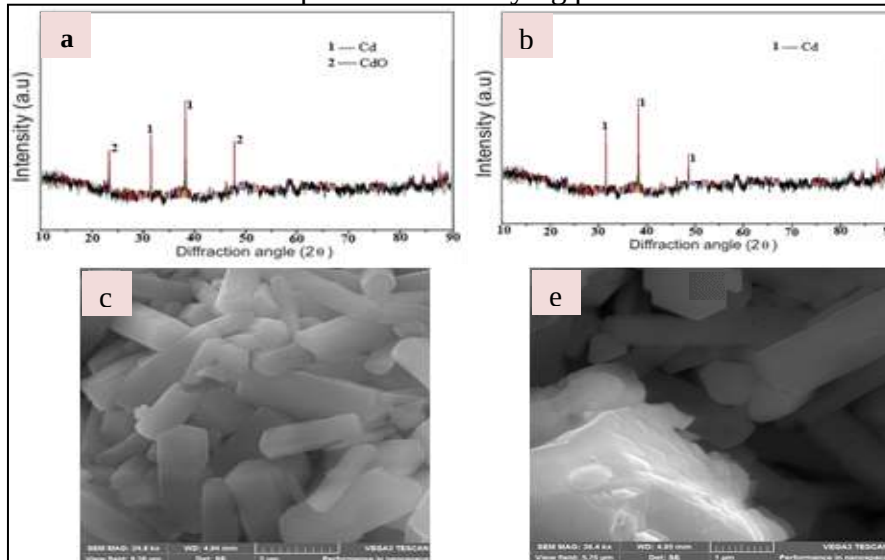


Figure 5. X-ray diffraction pattern and SEM for samples leached for (a and c) 120 min and (b and e) 180 min.

4. Conclusions

This study demonstrates an effective hydrometallurgical process for cadmium recovery from spent Ni-Cd battery anodes using nitric acid leaching. The optimized parameters—5 M HNO₃ concentration, 70°C temperature, and 180-minute duration—achieved a remarkable cadmium recovery efficiency of 98.52%. Systematic characterization via SEM and XRD revealed progressive morphological transformations consistent with the shrinking core model, confirming the dissolution mechanism. The principal innovation of this work lies in achieving near-complete cadmium recovery (~99%) using moderate-temperature acid leaching, presenting an efficient and potentially scalable alternative to conventional pyrometallurgical methods for heavy metal reclamation from hazardous battery waste.

5. Acknowledgments

The authors extend their sincere appreciation to the Surface Science Laboratory at the Chemistry Department of Kabardino-Balkarian State University (KBSUN), Nalchik, Russia, for performing sample characterization and

analysis. Gratitude is also expressed to Hadhramout University, College of Science, for providing the research facilities essential for the completion of this study.

6. References

- Abdel-Aal, E. A., & Rashad, M. M. (2004). Kinetic study on the leaching of spent nickel oxide catalyst with sulfuric acid. *Hydrometallurgy*, 74(3-4), 189–194.
- Al-Mansi, N. M., & Monem, N. A. (2002). Recovery of nickel oxide from spent catalyst. *Waste Management*, 22(1), 85–90.
- Bale, C. W., Bélisle, E., Chartrand, P., Decterov, S. A., Eriksson, G., Hack, K., Jung, I.-H., Kang, Y.-B., Melançon, J., Pelton, A. D., Robelin, C., & Petersen, S. (2009). FactSage thermochemical software and databases — recent developments. *Calphad*, 33(2), 295–311.
- Espinosa, D. C. R., & Tenório, J. A. S. (2006). Recycling of nickel–cadmium batteries using coal as reducing agent. *Journal of Power Sources*, 157(2), 600–604.
- Freitas, M. B. J. G., Penha, T. R., & Sirtoli, S. (2007). Chemical and electrochemical recycling of the negative electrodes from spent Ni–Cd batteries. *Journal of Power Sources*, 163(2), 1114–1119.
- Goering, P. L., Waalkes, M. P., & Klaassen, C. D. (1994). Toxicology of metals, biochemical effects. In R. A. Goyer & M. G. Cherian (Eds.), *Handbook of Experimental Pharmacology: Vol. 115. Toxicology of Metals* (pp. 189–214). Springer.
- Hafeeh, S. (2013). *The environmental and economic importance of recycling solid waste in industrial establishments and its relationship to sustainable development, a field study at the level of the metal conversion company* [Master's thesis, University of Khamis Meliana].
- Hazotte, C., Leclerc, N., Meux, E., & Lapique, F. (2016). Direct recovery of cadmium and nickel from Ni-Cd spent batteries by electro-assisted leaching and electrodeposition in a single-cell process. *Hydrometallurgy*, 165, 94–103.
- Hoffmann, L., Putzke, H. P., Kampehl, H. J., Russbült, R., Gase, P., Simon, C., Erdmann, T., & Huckstorf, C. (1985). [Article title]. *Journal of Cancer Research and Clinical Oncology*, 109, 193–199.
- Huang, K., Li, J., & Xu, Z. (2009). A novel process for recovering valuable metals from waste nickel–cadmium batteries. *Environmental Science & Technology*, 43(23), 8974–8978.
- International Agency for Research on Cancer. (2012). Cadmium and cadmium compounds. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 100C: Arsenic, Metals, Fibres, and Dusts*. IARC Press.
- K., T., L., C., G., M., & J. F., B. (2016). Recovery of metals from a mixture of various spent batteries by a hydrometallurgical process. *Journal of Environmental Management*, 181, 95–107.
- Li, J., Zhang, Y., Wang, L., & Chen, W. (2022). Insight into the leaching kinetics of cadmium from hazardous leaching residue: Mechanisms and phase transformations. *Journal of Hazardous Materials*, 424(Part C), 127582.

- Nogueira, C. A., & Margarido, F. (2004). Leaching behavior of electrode materials of spent nickel–cadmium batteries in sulphuric acid media. *Hydrometallurgy*, 72(1-2), 111–118.
- Nogueira, C. A., & Margarido, F. (2007). Chemical and physical characterization of electrode materials of spent sealed Ni–Cd batteries. *Waste Management*, 27(11), 1570–1579.
- Oliveira, M. M., & Souza, V. C. (2023). Cadmium as a breast carcinogen: A systematic review and meta-analysis. *Environmental Research*, 216(Pt 3), 114696.
- Pietrelli, L., Bellomo, B., Fontana, D., & Montoreali, M. R. (2005). Characterization and leaching of NiCd and NiMH spent batteries for the recovery of metals. *Waste Management*, 25(2), 221–226.
- Rahimzadeh, M. R., Rahimzadeh, M. R., Kazemi, S., & Moghadamnia, A. A. (2022). Cadmium toxicity and treatment: An update. *Caspian Journal of Internal Medicine*, 13(2), 367–373.
- Randhawa, N. S., & Kumar, K. G. (2015). Leaching kinetics of spent nickel–cadmium battery in sulphuric acid. *Hydrometallurgy*, 158, 1–5.
- Reddy, B. R., Priya, D. N., & Park, K. H. (2006). Separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquors of spent Ni–Cd batteries using phosphorus based extractants. *Separation and Purification Technology*, 50(2), 161–166.
- Spellman, F. R. (2018). *The science of environmental pollution* (3rd ed.). CRC Press.
- Ștefănuț, M. N., Căta, A., & Sfirloagă, P. (2008). Electrochemical recovery of nickel and cadmium from spent Ni–Cd batteries. *Chemical Bulletin of "POLITEHNICA" University of Timișoara, Romania*, 53(67), 1-2.
- Swain, S. S., Nayak, B., Devi, N., Das, S., & Swain, N. (2016). Liquid–liquid extraction of cadmium (II) from sulfate medium using phosphonium and ammonium based ionic liquids diluted in kerosene. *Hydrometallurgy*, 165, 1–25.
- Umesh, U. J., & Hong, H. (2014). Removal of nickel and cadmium from battery waste by a chemical method using ferric sulphate. *Environmental Technology*, 35(10), 1263–1268.
- Wang, M., & Wang, Z. (2021). Cadmium and its epigenetic effects on prostate cancer. *Journal of Toxicology and Environmental Health, Part B*, 24(5), 215–235.