Study nickel recycling and leaching of metals from eco-friendly nickel-metal hydride battery by response surface method

A. Vahdattalab[1], A. Khani[1,*] and S. Pirsa[2]

[1]*Department of Chemistry, Miyaneh Branch, Islamic Azad University, Miyaneh, Iran*
[2]*Department of Food Science and Technology, Faculty of Agriculture, Urmia University, Urmia, Iran*
*__Corresponding author__: a.khani59@yahoo.com

ABSTRACT In this research, nickel metal hydride batteries were designed in certain sizes and components. Battery black powder was investigated by X-ray diffraction analyzes and the presence of nickel as the main constituent of black powder was confirmed. The results showed that more than 99 % of the alloy were a nickel. In this study, black powder was leached with sulfuric acid. The influence of parameters such as temperature, sulfuric acid concentration and liquid to solid ratio (L/S: mL/g) on nickel leaching was studied. According to the results, the parameters of sulfuric acid concentration, temperature, liquid to solid ratio and the interaction of acid concentration with itself were important in nickel leaching. Optimal leaching conditions included a temperature of 60 °C, an acid concentration of 1.42 mol/L and a liquid to solid ratio of 10 mL. Under optimal conditions, the leaching efficiency was 81.25 %, which was better compared to the batteries with other models and brands.

KEYWORDS Battery; Nickel; Metal hydride; Leaching; Environmental

1. Introduction

Batteries are electrochemical devices whose convert chemical energy into electrical energy and structurally include anode, cathode, electrolyte, separator, and outer mold. Batteries are divided into two categories based on their chemical composition: wet batteries and dry batteries (Zhang et al., 2013). The electrolyte used in wet batteries is in liquid form, while in dry batteries, it contains gel, paste or other solids. The chemical reactions performed on the original batteries are irreversible, so these batteries are not rechargeable, in other words, they are disposable. In secondary batteries, on the other hand, chemical reactions are reversible and an external energy source can be used to recharge these batteries. Primary batteries include dry carbon-zinc, mercury oxide, silver oxide, silver chloride, and air carbon batteries. Secondary batteries include batteries such as nickel-cadmium, nickel metal hydride, cadmium-silver oxide, lithium ion and lead acid (Xu et al., 2008; Sarakonsri and Kumar, 2010). Primary and secondary batteries (rechargeable) are used in a wide range of fields, including these applications can be used in engines, marine equipment, watches, cameras, calculators, hearing aids, electrical appliances, electronic devices such as computers, and mobile phones. Commonly used batteries today, mainly include zinc-carbon, nickel-cadmium, and nickel metal hydride and lithium-ion batteries (Zhang and Zhang, 2015).

Nickel metal hydride batteries are a rechargeable energy source for use in a wide range of portable devices such as power supplies, mobile phones, cordless phones, camcorders and laptops. Rechargeable nickel metal hydride batteries have a high electrochemical capacity (1.5 to 2 times as much as nickel-cadmium batteries) (Majeau-Bettez et al., 2011). In addition, nickel metal hydride batteries operate effectively in a wide temperature range (from 20-60 °C). Other features of these batteries include their long charge-discharge period (100-1000 cycles). Therefore, the design of new nickel metal hydride batteries seems necessary. Since nickel metal hydride batteries are widely used and considering that the average life of these batteries is 2 years, it can be concluded that a significant amount of these batteries is released into nature every year and are important sources of environmental pollution (Tzanetakis and Scott, 2004). Therefore, recycling of their metal content should be studied to prevent the burial of large amounts of hazardous waste in the environment and to achieve waste minimization goals, and also because of the economic value of metals such as nickel, cobalt and trace elements, efficient recycling processes should be developed. As a result, recycling of this type of waste can be both environmentally and economically beneficial (Georgi-Maschler et al., 2012).

Each battery generally consists of 3 main parts: negative electrode, positive electrode and electrolyte. These 3 main parts of a nickel metal hydride battery are as follows: 1- Negative electrode or negative pole: This pole is made of a nickel alloy with a small amount of other elements such as lanthanum which should be a good adsorbent for hydrogen, because hydrogen as it is an electron donor and by giving an electron it is converted to a hydrogen cation and forms water with a hydroxide anion. 2- Positive electrode or positive pole: This electrode is made of nickel oxyhydroxy (NiOOH) (nickel oxidation number is +3) which is converted to nickel (II) hydroxide ($Ni(OH)_2$) by taking an electron, which in this compound, the oxidation number of nickel is +2. 3- Electrolyte: The electrolyte used in nickel metal hydride batteries contains 20 to 40 % by weight of alkaline hydroxide solution such as potassium hydroxide (KOH) containing other minor

Copyright © 2024 Latin American Applied Research
DOI: 10.52292/j.laar.2024.1235
Received: October 6, 2022.
Accepted: June 27, 2023.
Recommended by José L. Díaz de Tuesta.
This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.

compounds increase battery performance. It is noteworthy that non-woven polyolefin is used to electrically separate the positive and negative poles from each other with the ability to pass electrolyte ions (permeability to ions) (Lee et al., 2010; Dai et al., 2021).

Due to the importance of nickel metal hydride batteries and the need to pay attention to the waste from these batteries in this study, nickel metal hydride batteries were produced with better capabilities than existing commercial batteries, which in addition to the quality of commercial batteries, they have less environmental pollution than commercial batteries. Also, the response surface method (RSM) was used to investigate the leaching phenomenon in the battery, which is another important innovation of this research work.

2. Methods

2.1 Chemicals

The compounds and chemicals used in the design and analysis of nickel metal hydride batteries are as follows. Hydrochloric acid (HCl, 37 %, Merck), nitric acid (HNO_3, 65 %, Scharlau), sodium hydroxide (NaOH, 98 %, Fluka), sulfuric acid (H_2SO_4, 98 %, Merck), sodium carbonate (Na_2CO_3, 99.5 %, Applichem), Nickel Nitrate ($Ni(NO_3)_2{\cdot}6\ H_2O$, 98 %, Hop kin and Williams), Cobalt Nitrate ($Co(NO_3)_2$, 98 %, Fluka), Zinc Nitrate ($Zn(NO_3)_2{\cdot}4\ H_2O$, 98 %, Fluka), manganese nitrate ($Mn(NO_3)_2{\cdot}6\ H_2O$ > 99 %, Merck), water distillation 3 times and blue bond filter paper (Albet). Other materials used in battery design have been used without repurification.

2.2 Equipment and devices

The Shimadzu AA-670G atomic absorption device was used to measure the concentration of analytes by correcting the background of a deuterium lamp and a premixer torch with a gap length of 10 cm. Hollow cathode lamps of nickel, cobalt, zinc, and manganese (Hamamatsu Photonics K.K., Japan) were used as radiation sources. Other devices were used to analyze the designed batteries in the following order. Shimadzu AEL-200 digital scale (Japan) with precision (0.0001 g), pH meter (EUTECh pH 510, Malaysia), water bath for temperature control and regulation (Gran Insruments SB3, England), mechanical stirrer (Type KQPS/29, Griffin & George Limited, Japan), shredder (Electra EK-260 G LTD, Japan), X-ray diffraction (D-5000, Siemens, Germany) (XRD) and magnetic stirrer (Labinco, MODEL: LD-814).

2.3 Design of nickel-metal hydride battery

To make a nickel metal hydride battery from a positive plate containing nickel hydroxide as its main active ingredient, a negative plate composed mainly of hydrogen adsorbent alloys, a separator made of fine fibers, an alkaline electrolyte, a metal chamber and a sealing plate used with a self-closing safety valve. In the cell, nickel hydroxide $Ni(OH)_2$ is oxidized to nickel oxyhydroxide at the positive electrode during charging and converted to nickel hydroxide during discharge. During charging, at the Ni-MH negative electrode, a drop of water produces atomic and adsorbed hydrogen, which diffuses into the intermetallic alloy network and forms the metal hydride. An adverse reaction occurs during discharge.

2.4 Making a capsule layer using $Ni(OH)_2$ and $Co(OH)_2$ powder

Dry nickel hydroxide powder was mixed with cobalt hydroxide in a blender, preferably in a 40:3 ratio of nickel hydroxide to cobalt hydroxide. The dry powders were then heated to about 88 °C. The powders were sprayed with a sufficient amount (100 mL) and concentration of NaOH (4 M) under continuous mixing. The slurry was mixed vigorously (with high shear) for some time at room temperature to form a layer of cobalt hydroxide around the nickel hydroxide particles, the cobalt hydroxide dissolved and deposited on the surface of the nickel hydroxide particles. The coating method is performed in air (atmospheric condition) and leads to partial oxidation of the cobalt hydroxide layer to the conductive state of cobalt oxide hydroxide. Oxygen gas enters the mixing chamber and mixing continues, preferably until all of the cobalt hydroxide in the encapsulated layer is oxidized. The presence of oxygen allows further oxidation of any residual cobalt hydroxide in the encapsulated layer to the cobalt hydroxide state. The material was then separated and washed with water and dried and sieved through a coarse plate such as a mesh plate.

2.5 Preparing the internal contents of the batteries

In this study, nickel metal hydride batteries designed using tools such as saws and scissors were cut lengthwise. Then the metal mold and plastic components of the battery were separated from its internal contents. The designed battery consists of 3 layers consisting of negative electrode, positive electrode and separating layer, the components of which are shown in Fig. 1a. The positive electrode consists of a porous substrate coated with nickel hydroxide and the negative electrode consists of a hydrogen storage alloy on which the material is fixed in a paste. In the next step, the separating layer was separated from the positive and negative electrodes, then the fixed paste was separated on a porous mesh in the negative electrode (Fig. 1b). Positive electrodes and paste from negative electrodes were weighed. Then, in order to remove moisture and volatiles, the positive electrodes and the paste from the negative electrodes were placed in the oven at 110 °C for 4 hours. After drying, the weighing operation was performed again to measure the amount of moisture and volatiles. These materials were then crushed in the mill. The mixture from the milling stage consisted of soft black powder and nickel alloy. In the next step, using a magnetic separator, the nickel alloy was separated from the soft black powder and each was weighed. These two components can be seen in Fig. 1c.

2.6 Quantitative analysis of black powder and nickel alloy using the atomic absorption device

2 g of black battery powder was dissolved in Aqua regia and the amount of nickel in it was determined by atomic

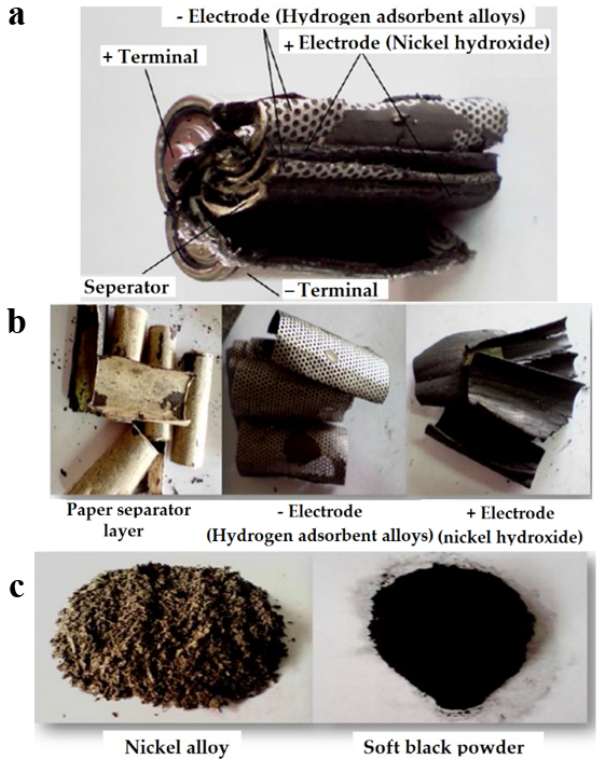

Figure 1: Cut-out battery (a), internal contents of the designed battery used (b) and materials of mechanical and magnetic processing of the designed battery (c).

absorption spectrometry. By dividing the amount obtained for nickel by the amount of powder (2 g), the percentage of nickel in black powder was quantitatively obtained. In the case of nickel alloy, 2 g of it was dissolved in Aqua regia and the amount of nickel in it was obtained by atomic absorption spectrometry. By dividing the amount of nickel obtained by the weight of the alloy dissolved in acid, the purity of the alloy relative to nickel s obtained.

2.7 Leaching test

The leaching test was performed in a reactor consisting of a 250 mL double-bore balloon equipped with a refrigerant and mechanical stirrer. The reactor was placed in a hot water bath equipped with a temperature controller. The system and equipment tested can be seen in Fig. 2. In each experiment, 2 g of the black powder of the battery was leached using sulfuric acid solutions with different concentrations and at different times. In these experiments, stirring was performed using a mechanical stirrer at a constant speed of 210 rpm. The parameters studied in this process were temperature, acid concentration, and liquid to solid ratio. To investigate the leaching operation, mini-tab software and response surface method were used. For this purpose, experiments were designed and modeled and optimal leaching conditions were obtained (Sayilgan et al., 2010).

2.8 Purification

Purification step is the second step of the hydrometallurgical method, which aims to minimize impurities in the solution in order to achieve a solution with the purity

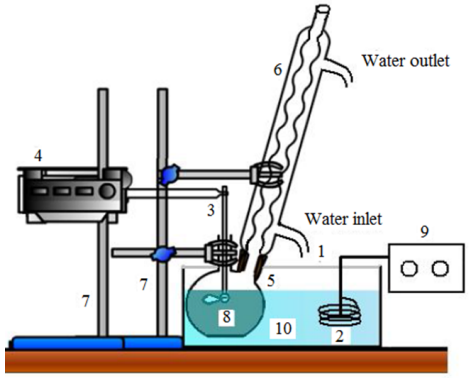

Figure 2: Schematic diagram of the reactor used in the leaching process: 1- Aluminum coating, 2- Magnetic element, 3- Mechanical stirrer, 4- Engine, 5- Reactor, 6- Refrigerant, 7- Base, 8- A mixture of black powder, battery and sulfuric acid, 9- Thermostat, 10- Water bath.

of the desired element. In this study, purification was performed in two ways. In the first case, only sodium carbonate was used. In the second case, a combination of sodium carbonate and sodium hydroxide was used. The precipitation percentage of each ion was calculated from the following equation.

$$Precipitation\,(\%) = \frac{M_{Int}^{2+} - M_{F}^{2+}}{M_{Int}^{2+}} \times 100\ \% \qquad (1)$$

where M_{Int}^{2+} is the amount of metal ions in the initial solution of the battery and M_{F}^{2+} is the amount of metal ions in the solution resulting from the purification step.

2.9 Purification with sodium carbonate

At this stage, in each experiment, 20 mL of the mother battery solution was placed in an Erlenmeyer flask and each time different volumes of 2 M sodium carbonate were added to the same solutions. The purpose of this step was to remove the impurities in the solution, so that the maximum amount of nickel remained in solution. In each experiment, after adding a certain amount of 2 M sodium carbonate to the Erlenmeyer solution containing the mother battery, the mixture was stirred for 2 hours using a magnetic stirrer at a constant speed of 22 rpm. The resulting solution, which now contains some precipitate, was filtered using a filter. Then, after performing the necessary dilutions, the amount of nickel, cobalt, manganese and zinc ions were measured using an atomic absorption spectrometer. Finally, the graph of the precipitation percentage of nickel, cobalt, manganese and zinc in terms of added volumes of 2 M sodium carbonate was drawn.

2.10 Purification using sodium carbonate and sodium hydroxide

At this stage, in each experiment, 20 mL of mother battery solution was placed in Erlenmeyer and each time sodium carbonate (2 M) was added to the above solutions. In each experiment, after adding of sodium carbonate (2 M), the mixture was stirred for 2 hours using a magnetic stirrer with a constant speed of 22 rpm. The resulting solution,

which now contains some precipitate, was filtered using a filter. The resulting filtrate was used in the next step to continue the purification process. Then different volumes of sodium hydroxide (4 M) were added to the solution obtained from the previous step to continue the purification operation using sodium hydroxide. Other test conditions include the magnetic stirrer speed, the stirring time of the solution, and how the ions are diluted and measured. Finally, the precipitation percentage of nickel, cobalt, manganese and zinc ions was plotted in terms of the volume of sodium hydroxide consumption.

2.11 Recycling of nickel as its hydroxide salt

In this step, the sodium hydroxide agent was used to recover nickel from the rich solution obtained from the purification step. The experiments were performed at different pH (3.5, 7.5, and 11.8) and different times for stirring the solution (10, 40, 90 and 120 minutes). The solution obtained from each experiment was filtered using filter paper. The percentage of nickel precipitated and the appropriate pH and the appropriate stirring time of the solution were calculated in order to achieve the maximum deposition of nickel hydroxide.

2.12 Statistical analysis

In this study, the box behnken design were used for leaching process optimization. In the box behnken design, the process is modeled by adapting a quadratic polynomial to the experimental data (Pirsa et al., 2021; Sharifi and Pirsa, 2021; Jabraili et al., 2021). Table 1 shows the actual levels of factors considered for designing a leaching test. The studied factors were acid concentration (mol/L, liquid to solid ratio (mL/g) and temperature (°C). Design Expert-13 software was used to perform various studies such as analysis of variance, quadratic curve matching and mapping of response procedure curves. 95 % probability level was used for analysis of variance and comparison of means.

Table 1: Design of leaching tests by box behnken design.

Run	Acid concentration (mol/L)	T (°C)	L/S ratio (mL/g)
1	1.5	45	20
2	0.5	30	20
3	0.5	45	10
4	0.5	60	20
5	1.5	45	20
6	1.5	30	30
7	1.5	45	20
8	0.5	45	30
9	1.5	45	20
10	1.5	60	30
11	2.5	60	20
12	2.5	45	30
13	2.5	45	10
14	1.5	30	10
15	2.5	30	20
16	1.5	60	10
17	1.5	45	20

3. Results

The batteries designed in this study consisted of three main components, which are the metal part (including the metal mold and metal mesh of the negative electrode), paper and plastic, and the active materials of the electrodes (positive and negative electrodes and paste from the negative electrodes). Metal accounts for about 20 % of the battery weight (Fig. 3), which can be recycled in the recycling industry, especially in the steel industry. Plastics and paper are also recyclable. Approximately 74 % of the battery weight is related to the active material of the electrodes. In this part of the battery, which contains some moisture and volatile materials, by placing these materials in the oven and by the weight difference of these materials before and after being placed in the oven, the results are given in Fig. 3.

3.1 Analysis of black powder using X-ray diffraction and atomic absorption

X-ray diffraction analysis, spectra shown in Fig. 4. The results indicate that nickel is the main component of black powder, which is in the forms of NiO, NiOOH and $Ni(OH)_2$ forms of it are related to the charge and discharge processes in nickel metal hydride batteries. NiO is also produced due to nickel oxidation due to exposure to air after fission. Studies in the field of nickel metal hydride batteries show that $Ni(OH)_2$, in 2θ of 19°, 34°, 39.5°, 52.5°, 59° and 63°, NiOOH in 2θ of 22°, 36°, 56°, to some extent, 65°, 69° and the NiO peaks at 2θ of 43°, 61°, 76° and 81°. The XRD spectrum output from the designed battery black powder is shown in Fig 4. As can be seen, NiO species in 2θ of 43°, 61°, 76° and 81°, NiOOH species in 2θ of 22°, 36° and approximately 22° and 36° and $Ni(OH)_2$ species, in 2θ of 19°, approximately 39.5°, 52°, 59° and 63° peaks. On the other hand, the presence of peaks in 2θ of 28°, 30°, 42° and 45° confirms the presence of lanthanum and in other words the presence of rare earth elements (Rodrigues and Mansur, 2010).

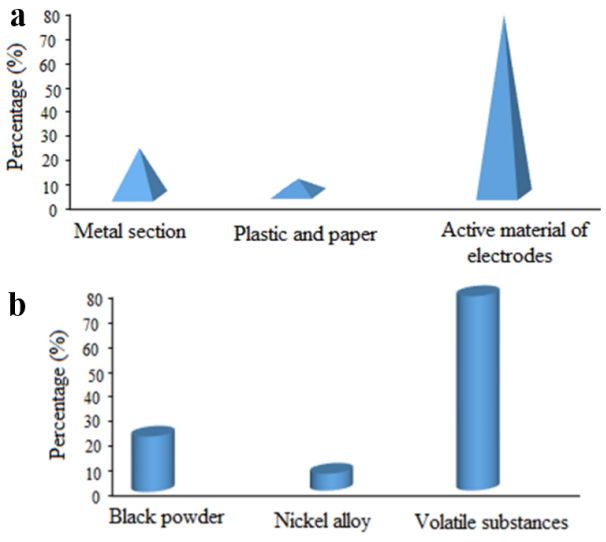

Figure 3: Weight percentage of the main components in the design of nickel metal hydride battery (a) and Weight percentage of active ingredients of electrodes (b).

Table 2: Results of quantitative determination of nickel in black powder and nickel alloy using atomic absorption.

Atomic absorption results	
Percentage of nickel in black powder	Percentage of nickel in nickel alloy
57.16	> 98 %

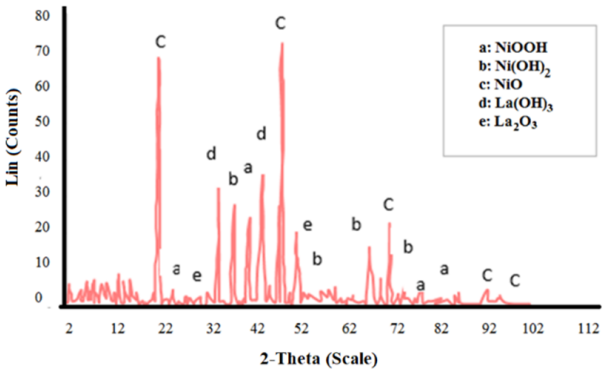

Figure 4: X-ray diffraction spectrum of black battery powder.

The results in Table 2 show the small amounts of nickel in the black powder and nickel alloy obtained using the atomic absorption spectrometer. As can be seen, these results are in complete agreement with the results of XRD analyzes and confirm the presence of nickel as the predominant component in the black powder. Nickel metal is made up of 98 % of the nickel alloy and can be reused to produce these batteries after mechanical and magnetic processing and separation from used batteries.

3.2 Modeling and optimization of nickel leaching process

The leaching process involves the washing of metal-rich materials with acid or base to transfer the metals in it into the aqueous phase. In order to carry out this process, various acids have been used by researchers, including nitric acid, sulfuric acid and hydrochloric acid. Sulfuric acid has been used as a leaching agent by various researchers. Although sulfuric acid such as nitric acid and hydrochloric acid is not a strong and effective acid, but due to low environmental hazards, low corrosion problems, ease of reproduction during electrovining and its cheap price was used in this study as a leaching agent. It is important to note that the following reactions are possible reactions that can occur during the leaching process (Pietrelli et al., 2005; Zhang et al., 1998; Provazi et al., 2011; Cognet et al., 2020; Pospiech and Gega, 2019).

$M(OH)_2 + H_2SO_4 \rightarrow MSO_4 + 2\ H_2O$

$4\ NiOOH + 4\ H_2SO_4 \rightarrow 4\ NiSO_4 + O_2 + H_2O$

$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O$

$Ni + H_2SO_4 + 0.5\ O_2 \rightarrow NiSO_4 + H2O$

$RE + 1.5\ H_2SO_4 + 0.7\ O_2 \rightarrow 0.5\ RE_2(SO_4)_3 + 1.5\ H_2O$

where M is metals such as nickel, cobalt, manganese and zinc and RE is a rare earth element (cerium, lanthanum and neodymium).

Table 3: Summary of fitting the mathematical model.

Fit Statistics	
Std. Dev.	2.050
Mean	81.170
C.V. %	2.530
R^2	0.961
Adjusted R^2	0.937
Predicted R^2	0.836
Adeq Precision	19.818

In this study, one of the most common design methods, the response surface method (box behnken design), was used to optimize the nickel leaching process. The three parameters studied in this process were acid concentration (mol/L), liquid to solid ratio (mL) and temperature (°C) that were selected for design. Based on the array proposed by the box behnken design of the response surface method, 17 leaching experiments were performed, and the nickel content of each solution was measured after performing the necessary dilutions. The values obtained for the leaching percentage were used in 17 experiments as a response variable in the designed experiments. To design the model and also to optimize the test conditions, the values of the response variables were entered into Design Expert 13 software and analyzed using least squares and analysis of variance. The mathematical model of the interaction was obtained to correlate the response variable and the independent variables with the highest R2 in accordance with Table 3. The ANOVA results are shown in Table 4. Then, due to the significant effect of all three factors, modeling was performed based on the model on the interaction and equation 2 of the mathematical model showed the relationship between leaching rate and independent variables. According to the results, it can be concluded that the resulting model can be modeled with acceptable accuracy of experimental results and used to predict the percentage of leaching within the modeled range.

$$R = 52.26 + 8.77C + 0.21T + 0.43L/S + 0.03C \times T + 0.04C \times L/S - 0.006T \times L/S \quad (2)$$

Figure 5 shows the experimental response diagram against the predictions predicted by the model, diagrams related to the evaluation of model fit through residues, the normal distribution curve of residues, residual values versus predicted values and residual histogram residual values versus data order. The results show that considering the value of R^2 equal to 0.94, only 4.1 % of the changes in the response rate cannot be explained by the model. In addition to the tests performed, the fit of the model was assessed by evaluating the residues (differences between experimental and predicted data). In the residual thermal distribution curve, the distribution of points on the straight line indicates the normal distribution of the residues and means that the results are realistic. As can be seen in Fig. 5, the linearity of the normal distribution curve and the randomness of the distribution of the residual values indicate the fit of the model.

Table 4: Regression constants and results of analysis of variance obtained from analysis of experimental test results.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1044.73	6	174.12	41.3	<0.0001	significant
A-C	976.82	1	976.82	231.72	<0.0001	
B-T	30.3	1	30.3	7.19	0.023	
C-L/S Ratio	32.12	1	32.12	7.62	0.0201	
AB	0.9025	1	0.9025	0.2141	0.6535	
AC	0.7225	1	0.7225	0.1714	0.6876	
BC	3.86	1	3.86	0.9159	0.3611	
Residual	42.16	10	4.22			
Lack of Fit	41	6	6.83	23.62	0.0544	not significant
Pure Error	1.16	4	0.2893			
Cor Total	1086.89	16				

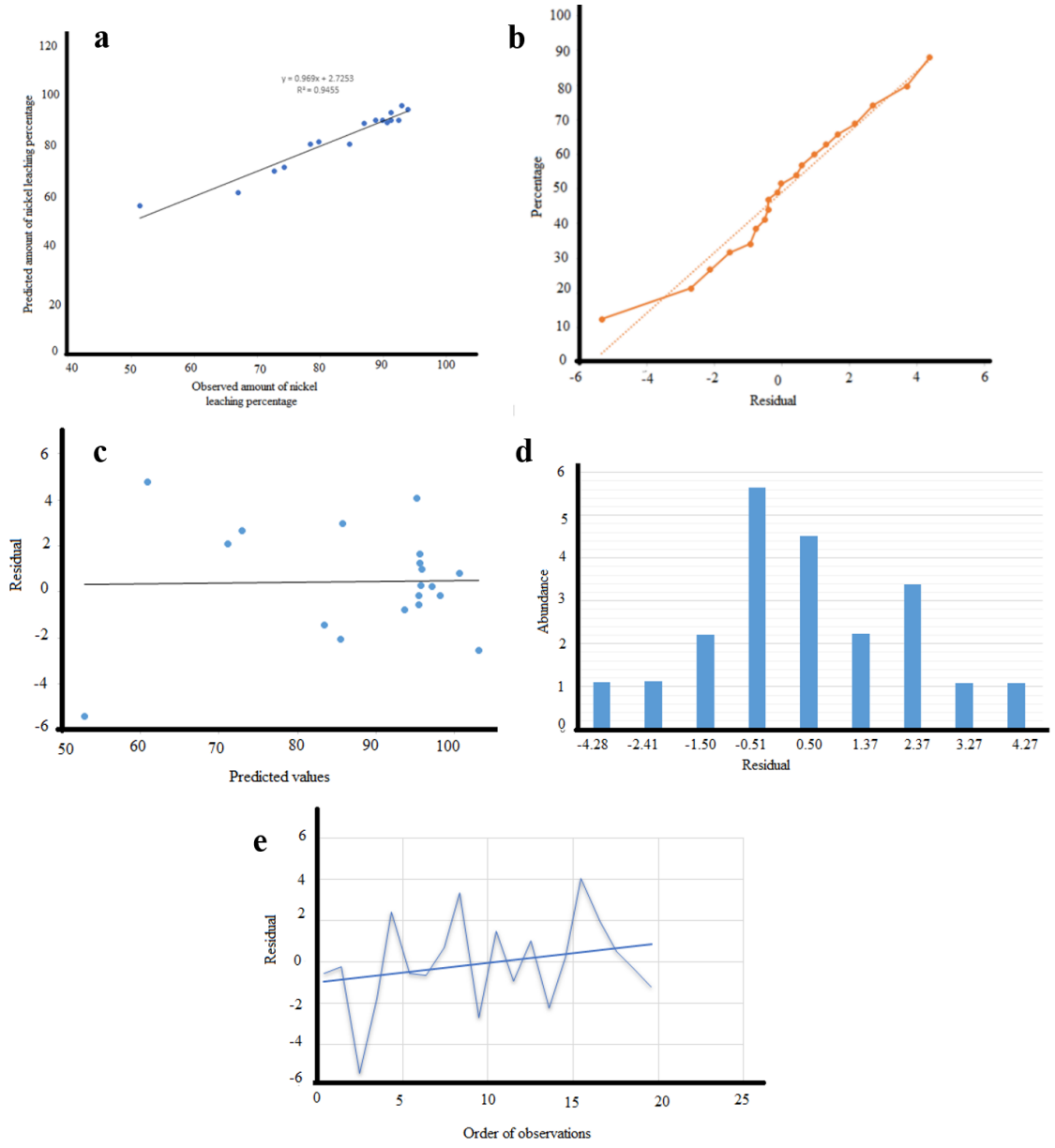

Figure 5: Experimental response diagram against the predictions predicted by model (a), diagrams related to the evaluation of model fit through residues (difference between experimental and predicted grains) (b), normal distribution curve of residues (c), residual values versus predicted values (d) and residual histogram residual values versus data order (e).

3.3 Simultaneous effect of factors on nickel extraction

Contour plots have been used to investigate the dependence of the response to variables. These curves provide a geometric picture of the response function and make it possible to accurately understand the direct and interactive effects of variables. In these two-dimensional curves, the changes of the response are plotted in terms of two variables, while the other variables are kept constant at their zero level.

The simultaneous effect of temperature and liquid to solid ratio on the percentage of nickel leaching at the constant acid concentration in the form of two-dimensional diagrams (contour diagrams) is shown in Fig. 6. As can be seen from the results of ANOVA analysis (Table 4), the effect of the interaction between temperature and liquid to solid ratio is not systematic. That is, each of these two factors does not have a significant effect on the role of the other factor on the percentage of nickel leaching. Figure 6 shows that with increasing temperature, the percentage of nickel leaching increases, which may be due to the increase in solvent viscosity and ion mobility, and thus increase the probability of effective collision between the solid phase and the liquid phase. This figure shows that in all liquid-to-solid ratios, the percentage of leaching increases with increasing temperature. This diagram also shows that in ohmic temperatures, with increasing the ratio of liquid to solid, it increases to about 30 % of the leaching ratio, but from the ratio of 30 onwards, a slight decrease in the percentage of leaching is observed that probably is due to soluble conditions and interactions. Similar results have been observed in previous work. For example, Pietrelli et al. (2005) developed a hydrometallurgical method for recycling zinc and manganese from used alkaline batteries. In this study, leaching process with sulfuric acid performed in the leaching process, experiments were performed to investigate the effect of liquid to solid ratio at 55 °C and sulfuric acid 0.4 %. The results showed that the liquid-to-solid ratio of 30 g/mL increases the leaching efficiency of zinc metal, but at higher ratios the leaching efficiency decreases and takes a downward trend. However, these researchers have not reported any reason to justify the observed trend.

Figure 6 also shows the simultaneous effect of temperature and acid concentration on the percentage of nickel leaching in two-dimensional diagrams. Based on the significant results (Table 4), the effect of interaction between temperature and acid concentration on the percentage of nickel leaching is not significant, i.e. each of the two factors of temperature and acid concentration has no significant effect on the role of the other factor in the nickel leaching process.

The diagram in Fig. 6 also shows that the effect of different concentrations of acid on the leaching percentage is different. By increasing the acid concentration to about 1.3 mol/L at constant temperature, the leaching rate increases by 3 %, but by increasing the acid concentration to concentrations of more than 1.3 mol/L, the leaching percentage decreases. Similar results have been observed

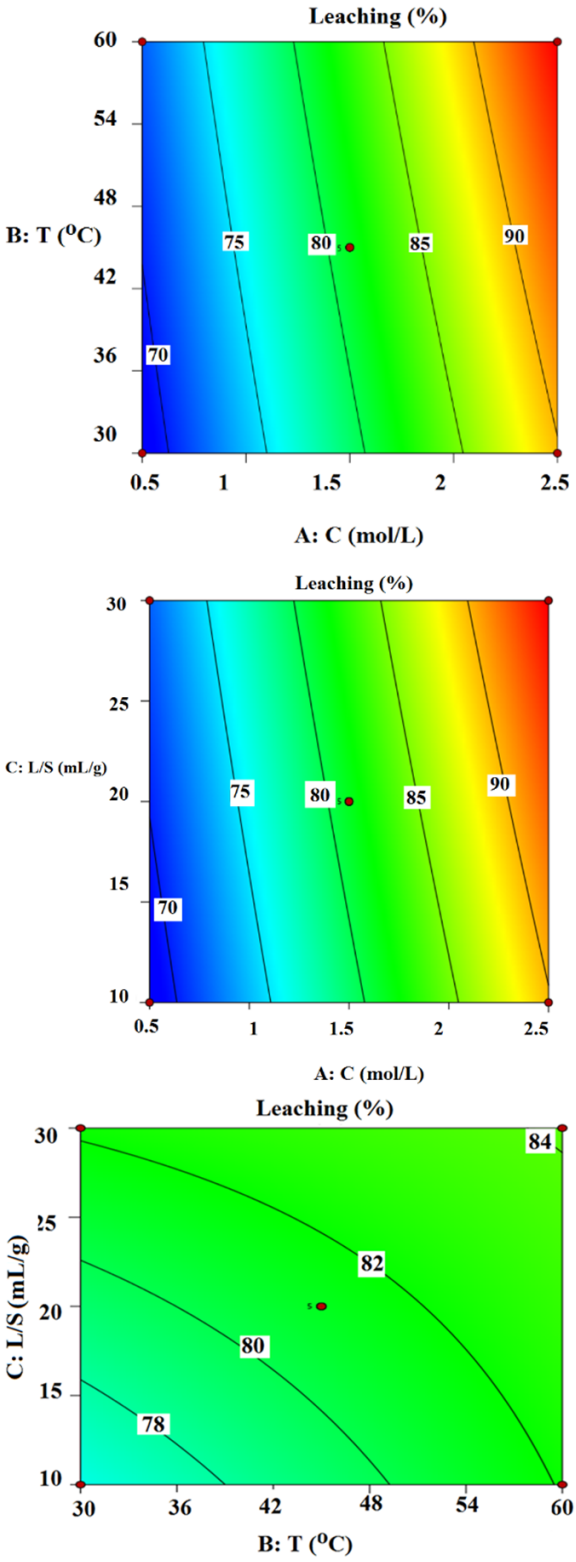

Figure 6: Simultaneous effect of factors affecting the amount of nickel extraction in the leaching process.

in previous research (Misra and Pandey, 2005).

In a study by Li et al. (2010) examined the recycling of cobalt and lithium from lithium-ion batteries. In the mentioned study, the leaching process was performed using malic acid. The results of the study of acid concentration in the leaching process were that initially with increasing

the concentration of acid to 1.5 mol/L, the leaching efficiency increases, but from a concentration of 1.5 mol/L, the leaching efficiency decreases (Li et al., 2010). In another similar study, (Al-Mansi and Abdel Monem, 2002) examined the recycling of nickel from using catalysts. Leaching was performed using sulfuric acid. In this study, the effect of acid concentration on leaching was investigated and the results showed that the percentage of nickel leaching increases with increasing acid concentration to a certain amount, and then with further increase in acid concentration, the leaching is reduced. The observed trend may be due to a decrease in ion activity due to an increase in acid concentration. Which leads to slowing down the transfer of nickel from the solid phase to the liquid phase and as a result the percentage of nickel leaching decreases, but on the other hand, as shown in the diagram, with increasing temperature and increasing the acid concentration, the percentage of leaching increases. It can be said that at temperatures above 35 °C, an increase in temperature probably compensates for the decrease in ion activity due to the increase in acid concentration. According to the diagrams in Fig. 6, at all concentrations, the percentage of nickel leaching increases with increasing temperature. As the temperature increases, the viscosity of the solvent decreases, thus creasing the mobility of the ions, which can lead to an increase in the effective collisions between the solid and liquid phases, which ultimately leads to an increase in the leaching percentage. However, the increase in leaching percentage due to temperature change is less than the increase in leaching percentage due to change in acid concentration.

3.4 Optimal conditions of nickel leaching process

The statistical method of desirability function was used to obtain the optimal leaching condition. Figure 7A shows the optimal leaching conditions. Based on the results of Fig. 7A, the following condition was obtained: temperature equal to 60 °C, acid concentration 1.42 mol/L and liquid to solid ratio equal to 10 mL. Under optimal conditions, the leaching efficiency was 81.25 %. To verify the predicted value, 2 g of battery powder with optimal values of the parameters mentioned above was leached and the amount of nickel in the leaching solution was measured. The other conditions used in these experiments were the same and in the following order: the amount of black powder 2 g, reaction time 120 minutes and stirrer speed 210 rpm. The mean value was 81.25 % for the percentage of leaching under optimal conditions with 3 repetitions of the experiment, also the relative standard deviation (RSD) was 4.75 %. The obtained value shows a good agreement with the value predicted by the model (Fig. 7B). It should be mentioned that under optimal conditions, the leaching efficiency was 81.25 %, which was better compared to the production batteries with other models and companies.

3.5 Purification with sodium carbonate and with a combination of sodium carbonate and sodium hydroxide

Figure 8 shows the curves of percentage precipitation of elements in the presence of 2 M sodium carbonate solution (A) and precipitation percentage of elements in the presence of 4 M sodium hydroxide solution added to the solution purified with 2 M sodium carbonate solution (B). Table 5 shows the results of purification with sodium carbonate solution (2 M) and a combined solution of sodium carbonate solution (2 M) and sodium hydroxide solution (4 M). According to what can be seen, up to 4 mL of 2 M sodium carbonate, the amount of nickel precipitation is very small (1.09 %), while elements such as cobalt, manganese and zinc are partially precipitated and separated from the solution phase. As can be seen in Table 5, the removal percentages of cobalt, manganese and zinc from the solution are 24.25, 10.02 and 15.41 percent, respectively. According to the productivity of metal carbonates, it is expected to precipitate the remaining ions such as manganese, cobalt and zinc during the purification step with sodium carbonate before nickel ion. However, because the amount of nickel ions in solution is very high compared to other ions, some nickel ions are precipitated at the same

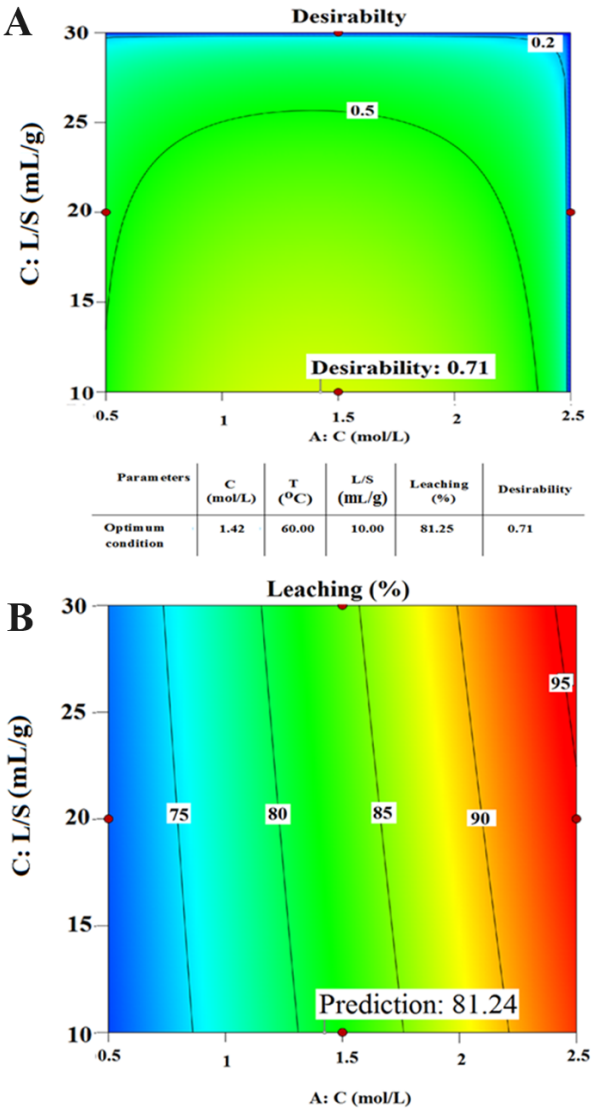

Figure 7: Optimal leaching conditions (A) and confirmation of the efficiency of the proposed model for predicting leaching values (B).

time as these ions. Fig. 8A shows a curve of the precipitation of ions in solution in terms of the added volume of sodium carbonate solution (2 M). As mentioned in the previous sections, the purpose of the purification step is to remove impurities from the solution in the battery designed to increase the nickel concentration for recycling. By adding 4 mL of sodium carbonate (2 M) to a 20 mL of nickel-containing solution, the pH of the solution reached about 1.2, and after filtration, the material remaining on the paper filter was a white precipitate, which confirmed the deposition of rare earth elements (Li et al., 2009). At this pH the amount of nickel remaining in the solution was about 99 %.

Due to the fact that by adding volumes of more than 4 mL, a significant percentage of nickel precipitates from the solution, so the volume of 4 mL of 2 M sodium carbonate at this stage were considered as a suitable volume for purification. The solution obtained from this step was used to recycle nickel as its salt in the next step. Fig. 8B shows the precipitation of ions in the previously purified solution (purified by 2 M sodium carbonate) in terms of the added volume of sodium hydroxide (4 M). In fact, in this part, a combination of two precipitating agents was used to perform the purification operation. In the first step, sodium carbonate was used (exactly according to the explanations mentioned in the previous section), then sodium hydroxide (4 M) was added to the resulting solution to continue the purification process. As shown in Fig. 8B, the addition of 1.5 mL of sodium hydroxide (4 M) removes a small amount of nickel and some cobalt, manganese and zinc.

Table 5 shows that at the end of purification 1.45 % of nickel, 22.31 % of cobalt, 10.08 % of manganese and 15.34 % of recycling zinc were removed from the solution and 98.5 % of nickel remains in the solution. The solution obtained in this step was used to recycle nickel as its salt in the next step.

3.6 Recycling of nickel in the form of hydroxide salt and sodium carbonate

After purification and filtration, a nickel-rich solution was obtained on each of the solutions obtained from the previous steps. The purpose of this step is to transfer nickel ions from the liquid phase to the solid phase by means of precipitation by sodium hydroxide so that the maximum amount of nickel precipitates from the soluble phase. Prior to precipitation, the onset pH of nickel hydroxide precipitation was calculated. The starting pH of the solution for the 0.257 M nickel solution was 6.66. The pH of nickel hydroxide precipitation was 7.66. Experimental data showed that the pH of the nickel hydroxide precipitation is higher than the pH calculated in theory. The similar results have been reported by Sun et al. (2016) studies. The precipitation of nickel as its hydroxide salt was performed at different pH and by applying different stirring times of the solution. Thus, the pH was adjusted to about 7.5, 8.5 and 11.3 and at times were 10, 40, 90, and 120 minutes.

The curve of nickel hydroxide salt recovery percentage in terms of the stirring times of the solution is shown in

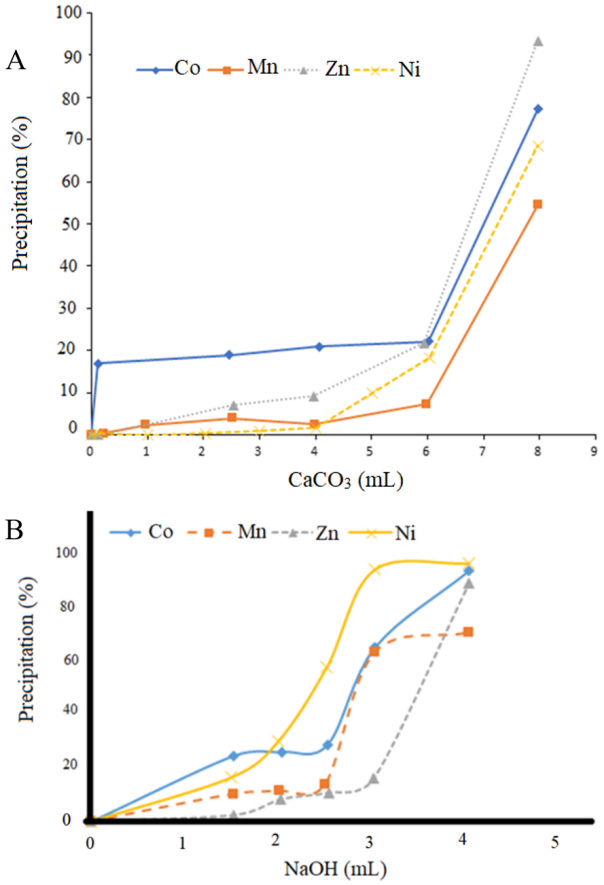

Figure 8: Curves of precipitation of elements in the presence of sodium carbonate solution (2 M) (A) and in the presence of a combined solution of sodium carbonate (2 M) and sodium hydroxide (4 M) (B).

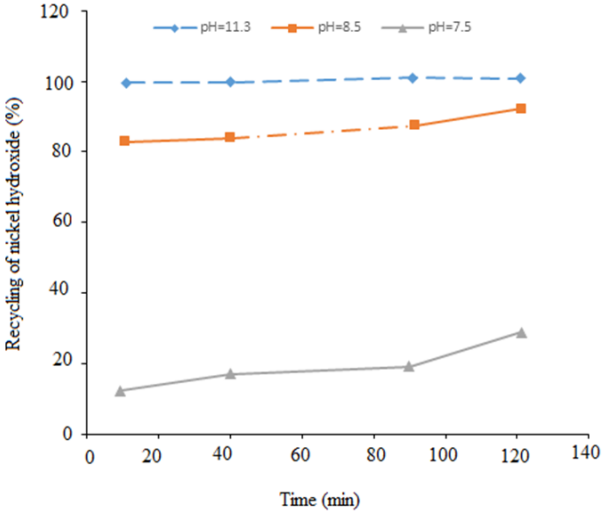

Figure 9: Nickel hydroxide recycled by sodium carbonate (2 M) at different pH (At ambient temperature and stirring speed of 22 rpm).

Fig. 9 at different pH. According to the Fig. 9 at pH = 7.5, the percentage of nickel recycled in the solution reaches 10.61 % in 10 minutes to 25.11 % in 120 minutes. At pH = 8.5 and with increasing alkalinity and OH concen-

Table 5: Purification with sodium carbonate (2 M), and combination of sodium carbonate (2 M) and sodium hydroxide (4 M).

Element type	Initial ion concentration (ppm)	Purification with sodium carbonate solution (2 M)		Purification with sodium carbonate solution (2 M) and sodium hydroxide (2 M)	
		Ion concentration after purification (ppm)	Ion removing (%)	Ion concentration after purification (ppm)	Ion removing (%)
Ni	15330.5	15081.86	1.32	15081.33	1.45
Co	2451.31	1642.32	24.25	1916.84	22.31
Mn	612.2	571.20	10.02	5716.34	10.08
Zn	235.7	211.46	15.41	205.13	15.34

Table 6: Nickel recycling, in the form of nickel hydroxide.

pH	Stirring (minute)	Concentration of nickel (ppm) in the solution obtained by purification with Na_2CO_3 solution (2 M)	Concentration of nickel(ppm) in solution after adding 4 M NaOH solution	Nickel recycling (%)
7.5	10	1541.58	1324.15	10.61
7.5	40	1513.54	1251.90	16.24
7.5	90	1514.23	1215.11	18.51
7.5	120	15143.10	11021.6	25.11
8.5	10	15138.51	1264.98	72.54
8.5	40	15143.54	2251.61	83.10
8.5	90	15134.14	1884.12	82.51
8.5	120	15147.60	1357.76	91.87
11.3	10	15146.61	37.32	99.41
11.3	40	15143.60	15.13	99.89
11.3	90	15138.60	2.03	99.98
11.3	120	15142.59	19.54	99.87

tration in solution, the amount of nickel precipitation also increases significantly. As shown in the Fig. 9, the amount of nickel recycled at this pH reaches 72.54 % in 10 minutes. However, by giving more time, the recycling rate eventually reaches 91.87 % in 120 minutes. At pH = 11.3, it precipitates the maximum amount of nickel ions in the solution. In a way that in 10 minutes more than 99 % of nickel ions in the solution precipitate. These results are generally shown in Table 6. On the other hand, as shown in Fig. 9, changing the time from 10 to 120 minutes has little effect on increasing the percentage of nickel recovery. Therefore, nickel was recovered from solution at pH = 11.3 and lasted for 10 minutes using a magnetic stirrer with a constant speed of 22 rpm.

4. Conclusions

In this study, a battery based on nickel metal hydride was designed in certain dimensions and components and the necessary quantitative and qualitative tests were performed on it. 74.11 % by weight of these designed batteries were the active materials. After mechanical and magnetic processing, it was found that 86.99 % of the active material of the electrodes were black powder and 23.11 % were nickel alloy. By performing quantitative analyzes, the percentage of nickel purity in nickel alloy was more than 99 %, which shows a higher percentage compared to similar products with different brands. The resulting black powder was leached in the next step. In this study, response surface method was used to optimize the leaching process. Optimal values were determined for the selected variables. At the optimum leaching, acid concentration was 1.15 mol/L, temperature was 23.8 °C and liquid to solid ratio was 23.4 mL/g. The maximum predicted value for leaching efficiency was 90.99 %. In the next step, sodium carbonate and a combination of sodium carbonate and sodium hydroxide were used for purification. In the next step, the nickel-rich solution obtained from the purified step was used to recycle nickel in the form of nickel hydroxide powder. Analyzes performed on powders prepared from solutions obtained from the purification process showed that more than 83 % of the rare earth elements were removed during the purification process. About 99 % of the nickel ions present in the initial solution during purification with sodium carbonate (2 M) and 98.5 % of the nickel ions present in the initial solution during purification by a combination of sodium carbonate (2 M) and sodium hydroxide (4 M) remained in solution. In the recycling stage, 99.99 % of the nickel ions in the solutions obtained from the purification steps were recycled, which was a better recycling percentage

compared to batteries with different brands. Because the return of cobalt, manganese, zinc to nature or the environment by other batteries was higher than the designed battery and the recycling percentage of nickel ions was lower. Therefore, the designed battery has both higher nickel recyclability and less pollution and can be used as an environmentally friendly and economical battery.

References

Al-Mansi, N. and Abdel Monem, N. (2002). Recovery of nickel oxide from spent catalyst. *Waste Manag.*, 22(1):85–90.

Cognet, M., Condomines, J., Cambedouzou, J., Madhavi, S., Carboni, M., and Meyer, D. (2020). An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks. *J. Hazard. Mater.*, 385:121603.

Dai, H., Jiang, B., Hu, X., Lin, X., Wei, X., and Pecht, M. (2021). Advanced battery management strategies for a sustainable energy future: Multilayer design concepts and research trends. *Renew. Sustain. Energy Rev.*, 138:110480.

Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., and Rutz, M. (2012). Development of a recycling process for Li-ion batteries. *J. Power Sources*, 207:173–182.

Jabraili, A., Pirsa, S., Pirouzifard, M. K., and Amiri, S. (2021). Biodegradable nanocomposite film based on gluten/silica/calcium chloride: Physicochemical properties and bioactive compounds extraction capacity. *J. Polym. Environ.*, 29(8):2557–2571.

Lee, S. S., Kim, T. H., Hu, S. J., Cai, W. W., and Abell, J. A. (2010). Joining technologies for automotive lithium-ion battery manufacturing: A review. In *ASME 2010 Int. Manuf. Sci. Eng. Conf. Vol. 1*, pages 541–549. ASMEDC.

Li, L., Ge, J., Wu, F., Chen, R., Chen, S., and Wu, B. (2010). Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.*, 176(1-3):288–293.

Li, L., Xu, S., Ju, Z., and Wu, F. (2009). Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical $Ni(OH)_2$. *Hydrometallurgy*, 100(1-2):41–46.

Majeau-Bettez, G., Hawkins, T. R., and Strømman, A. H. (2011). Life cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. *Environ. Sci. Technol.*, 45(10):4548–4554.

Misra, V. and Pandey, S. (2005). Hazardous waste, impact on health and environment for development of better waste management strategies in future in India. *Environ. Int.*, 31(3):417–431.

Pietrelli, L., Bellomo, B., Fontana, D., and Montereali, M. (2005). Characterization and leaching of NiCd and NiMH spent batteries for the recovery of metals. *Waste Manag.*, 25(2):221–226.

Pirsa, S., Banafshechin, E., Amiri, S., Rahimirad, A., and Ghafarzadeh, J. (2021). Detection of fraud of palm, sunflower, and corn oil in butter using HPLC profile of tocopherols and tocotrienols by response surface method. *J. Iran. Chem. Soc.*, 18(5):1167–1177.

Pospiech, B. and Gega, J. (2019). Solvent extraction of metal ions from sulfate solutions obtained in leaching of spent Ni-MH batteries. *New Trends Prod. Eng.*, 2(2):214–221.

Provazi, K., Campos, B. A., Espinosa, D. C. R., and Tenório, J. A. S. (2011). Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques. *Waste Manag.*, 31(1):59–64.

Rodrigues, L. E. O. C. and Mansur, M. B. (2010). Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. *J. Power Sources*, 195(11):3735–3741.

Sarakonsri, T. and Kumar, R. V. (2010). Primary Batteries. In Aifantis, K. E., Hackney, S. A., and Kumar, R. V., editors, *High Energy Density Lithium Batter.*, chapter 2, pages 27–52. Wiley.

Sayilgan, E., Kukrer, T., Yigit, N., Civelekoglu, G., and Kitis, M. (2010). Acidic leaching and precipitation of zinc and manganese from spent battery powders using various reductants. *J. Hazard. Mater.*, 173(1-3):137–143.

Sharifi, K. A. and Pirsa, S. (2021). Biodegradable film of black mulberry pulp pectin/chlorophyll of black mulberry leaf encapsulated with carboxymethylcellulose/silica nanoparticles: Investigation of physicochemical and antimicrobial properties. *Mater. Chem. Phys.*, 267:124580.

Sun, X., Duffort, V., and Nazar, L. F. (2016). Prussian blue Mg-Li hybrid batteries. *Adv. Sci.*, 3(8).

Tzanetakis, N. and Scott, K. (2004). Recycling of nickel–metal hydride batteries. I: Dissolution and solvent extraction of metals. *J. Chem. Technol. Biotechnol.*, 79(9):919–926.

Xu, J., Thomas, H., Francis, R. W., Lum, K. R., Wang, J., and Liang, B. (2008). A review of processes and technologies for the recycling of lithium-ion secondary batteries. *J. Power Sources*, 177(2):512–527.

Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T. M., and Inoue, K. (1998). Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries. *Hydrometallurgy*, 50(1):61–75.

Zhang, T., He, Y., Ge, L., Fu, R., Zhang, X., and Huang, Y. (2013). Characteristics of wet and dry crushing methods in the recycling process of spent lithium-ion batteries. *J. Power Sources*, 240:766–771.

Zhang, Z. and Zhang, S. S. (2015). *Rechargeable batteries. Materials, Technologies and New Trends*. Green Energy and Technology. Springer International Publishing, Cham.