Process intensification for valuable metals leaching from spent NiMH batteries

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ABSTRACT

Acid leaching is an essential unit in hydrometallurgy, yet it is time consuming and requires concentrated acids. Process intensification is examined for the leaching of valuable and rare earth elements (REEs), such as Ni, Co, La, Nd, and Ce, from spent nickel metal hydride (NiMH) batteries using subcritical water extraction (SWE) and microwave-assisted extraction (MAE). Results of SWE revealed that HCl performed better than H_2SO_4 and HNO_3. Leaching efficiency increased as reaction temperature increased from 100 to 150°C, and it increased with HCl concentration. SWE was very effective using 0.5 N HCl, solid concentration of 20 g/L, initial pressure of 9.8 bar, 100°C for 5 min, and leaching efficiency of 99.85% for Ni, 91.72% for Co, 96.26% for La, 85.75% for Nd, and 84.37% for Ce was found, and the total energy consumption was 2,640 kJ. Leaching efficiency of MAE using 0.5 N HCl decreased slightly when heating rate increased from 30 to 70°C/min, and it increased as reaction time increased from 5 to 30 min. Compared with SWE and conventional leaching, MAE was the most energy-efficient, and total of 874.1 kJ was required to reach 85.93% for Ni, 77.60% for Co, 64.04% for La, 75.01% for Nd, and 57.17% for Ce, respectively under experimental conditions of 1 N of HCl, solid concentration of 20 g/L, 100°C for 5 min. Novel acid leaching methods showed promising potential for metals recovery from e-waste.

1. Introduction

Rare earth elements (REEs) are a group of seven chemical elements including yttrium (Y), scandium (Sc) and fifteen lanthanides that are governing the modern lifestyle of people [5]. Fast emerging green technologies, ranging from electric car batteries to solar panels to wind turbines where REEs are widely being used are expected to drive tremendous growth and demands for these metals in near future [4]. Long-term assessment showed that there is a potential imbalance between supply and demand from both the supply and the demand side [34]. Review of potential supply from waste and byproducts revealed that the quantities of REEs contained in secondary sources could meet current global demand even with low extraction yield rates, although related processes are under development [6]. Spent nickel-metal hydride (NiMH) batteries are one of such wastes which may be turned to a potential secondary resource [22]. Along with phosphogypsum, red mud, and coal fly ash with large mass stream, NiMH batteries may also be a promising potential source owing to their high concentrations of REEs [6]. The typical composition of NiMH is 36-42% of Ni, 3-5% of cobalt (Co) and 5-25% REEs [18,23]. However, NiMH batteries are

being gradually substituted by Li-ion batteries and more spent NiMH batteries are expected [27]. The recovery of Ni, Co, and REEs from spent NMH batteries is critical for sustainable utilization of resources.

Total of 95.16% REEs could be extracted from waste NiMH batteries using 20% HCl at 70°C in 100 min [35]. Meshram et al. [25] utilized two-stage leaching for selective extraction from NiMH, and examined effects of temperature, acid concentration and duration. About 99% of Ni could be leached out using 4 M H_2SO_4 at 80°C for 240 min [7]. Shrinking core model could describe the leaching kinetics of base metals using 2 M H_2SO_4 at 348 K and the leaching of rare earth metals was optimized [24]. Simultaneous recovery of valuable metals from spent NiMH and lithium-ion batteries was investigated [18]. Very effective (99%) leaching of rare earth metals from spent AC-NiMH batteries was found using 190 g/L H_2SO_4 at 90°C for 60 min, and recovered metals could be used to synthesize cathodes [37]. A pilot scale hydrometallurgical process for spent car NiMH batteries was optimized [29]. A simple recycling process was proposed on the valorization of waste NiMH batteries [1].

The most common methods used in REEs recovery from e-waste are pyrometallurgical and hydrometallurgical processes. Pyrometallurgical

processes need higher energy input and higher capital cost compared to hydrometallurgical ones [3]. Hydrometallurgical processing for complete recovery of metals has advantages of low energy requirements as well as low greenhouse gases emissions [25]. Various process parameters may affect the process efficiency, such as lixiviant type, concentration of the lixiviant, temperature, pH, and solid to liquid ratio (S/L) [32]. Larsson et al. [12] proposed that the anodic parts of spent NiMH batteries could be completely dissolved with 1 M HCl, H_2SO_4 and HNO_3 (at pH 1.0 and temperature 30°C) within 6 hours. Petranikova et al. [29] reported that 8 M HCl was optimum for the leaching of REEs from cathode and anode mixture. However, there still exist some drawbacks that need to be improved, such as large amount of concentrated acid and long reaction time. Process intensification offers many opportunities as it aims to acquire faster kinetics, substantially decrease size to capacity ratio, energy consumption or waste production, and result in sustainable production [33]. Process intensification was examined for possible application for rare earth elements (REEs) recovery from spent NiMH batteries in the current study, and both subcritical water extraction (SWE) and microwave-assisted extraction (MAE) were utilized.

Subcritical water extraction (SWE) is defined as the condition at temperature between 100°C (the boiling point of water) and 374°C (the critical point of water) and pressure high enough to maintain the liquid state, typically from 10 to 60 bar [2]. Subcritical water decreases solvent viscosity and leads to an enhanced mass transfer, accelerating any mass-transfer-limited chemical reaction [26]. It has been investigated and applied in the extraction of bioactive compounds [36]. It shows potential for large-scale industrial application [10]. The application of SWE for the extraction of valuable metals from electronic waste (e-waste) is still limited. It has been examined on leaching of yttrium (Y) and europium (Eu) from waste cathode-ray tube (CRT) phosphor [16], leaching of lithium (Li), cobalt (Co) and manganese (Mn) from spent Li-ion batteries [15] and the extraction of indium (In) from indium tin oxide (ITO) scraps [31].

Microwave assisted techniques are powerful for process intensification that find wide applications for processing of natural compounds [21]. The general mechanisms of microwave heating are dipolar polarization and ionic migration. It is mainly attributed to the alignment of dipoles or ions in the electric field [11]. Microwave assisted extraction (MAE) has been widely applied for the dissolution of mineral compounds, such as dissolution and recovery of Li and Co from spent $LiCoO_2$ using mild organic acids since it is a simple and rapid [28]. It has been applied for uraninite leaching using dilute H_2SO_4 [20]. Advantages of rapid and selective heating, reduced formation of passivation layer, and induced cracks on mineral surface were found in leaching of manganese from low-grade pyrolusite [17].

A novel study of process intensification using SWE and MAE on valuable metal extraction from spent NiMH batteries was investigated in the current study. The effects of acid type, temperature, acid concentration, solid concentration, and reaction time were studied, and the experimental results were compared to those from conventional acid leaching method. In addition, energy requirement was assessed.

2. Experimental methods

2.1. Materials and methods

Spent NMH batteries electrode powder was supplied by Yen-Long Renewable Technology Co., Ltd. When collected, they were discharged, shredded, dried, and separated by a magnetic unit in the recycling plant. The spent NMH batteries powder was separated further by passing through the 140 mesh sieve and only particles smaller than 105 μm were collected for experiments. The sample powder was characterized using X-ray fluorescence (XRF, SEA6000VX, HSFinder), X-ray powder diffraction (XRD, D2 Phaser Bruker) and field-emission scanning electron microscope spectra (FESEM-EDX, JSM-6390LV, JEOL). Total metal content of sample was assessed by aqua regia digestion method

(NIEA S321.63B, Taiwan), and the concentration of metals was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo 7000) at wavelength of Ni (221.647 nm), Co (228.616 nm), lanthanum (La) (333.749 nm), neodymium (Nd) (401.225 nm), cerium (Ce) (535.353 nm), magnesium (Mg) (279.553 nm), potassium (K) (766.490 nm), cadmium (Cd) (214.438 nm), manganese (Mn) (257.610 nm), iron (Fe) (259.940 nm), aluminum (Al) (396.152 nm), and lead (Pb) (220.353 nm). All solid residues from leaching processes were dried at 60°C for 24 h and then assessed by XRD. Standard solutions of La, Nd, Ce, Ni, Co, Mn, Al, and Fe for ICP-OES at 1,000 mg/L in 2-3% HNO_3 with purity >99% were used (Merck). Hydrochloric acid (HCl, 37%) was from Acros, sulfuric acid (H_2SO_4, 95-97%) was from Scharlau, and nitric acid (HNO_3, 65%) was from Panreac. All chemicals were used without further purification.

2.2. Conventional leaching

Conventional extraction of Ni, Co, La, Nd, and Ce under room temperature to 65°C was conducted using a shaker with water bath. Total of 0.2 g of spent NiMH batteries sample was put into each of 100 mL of 1 M HCl solutions to make the solid concentration 20 g/L. Solutions were poured into polypropylene (PP) bottles, pH values measured, the placed in the shaker and reacted for 1, 2, 4, 6, 8, 10, 30, 60, 120, 180, and 240 min under continuous stirring at 100 rpm. When reaction completed, the suspension was filtered by the 0.22 μm membrane (mixed cellulose ester, Advantec), the final pH measured, and the metal concentration in the extractant was analyzed by ICP-OES. The residue was dried at 60°C for 24 h for further analysis.

2.3. Subcritical water extraction (SWE)

The process intensification leaching using SWE was carried out in a bench-scale subcritical water reactor with the output power of 1,760 W [16]. The reactor was made of stainless steel (SS 316) with total volume of 290 mL which can be seen in Fig. 1a. The reactor is equipped with an external electric heater, a pressure gauge, a thermocouple (K-type), and a lid with screws. Magnetic stirrer was used to mix the leaching mixture. Measured amount of spent NiMH batteries powder was mixed with acid solution to make 20 g/L suspension, which was kept in a 50-mL glass chamber and then was placed inside the reactor. Three types of mineral acids, HCl, H_2SO_4, and HNO_3, were used as the leaching agent. After sealing the insulated reactor, N_2 gas was directed into the reactor to pressurize it to initial pressure of 9.8 bar. The reactor was then heated to desired temperatures of 100, 125, and 150°C, respectively. The reaction time ranged from 5 to 30 min, counting when reached the desired temperature. The reactor was cooled to 40-45°C within ca. 10 min. To collect extractant sample, the suspension was filtered through a 0.22 μm membrane and the metal concentration in the filtrate was then analyzed by ICP-OES, and the pH of the filtrate was measured. All experiments were conducted in triplicates and the average value was taken.

2.3. Microwave assisted extraction (MAE)

The microwave digestion system used in the experiments is equipped with controllable microwave power (START D, Milestone Srl) as demonstrated in Fig. 1b. The temperature of the solution in the vessel was measured by a thermocouple inside. Measured amount of spent NiMH batteries powder and acid solution were put into a 50-mL vessel, then placed in the microwave digestion system. In the experiments, HCl solutions of 0.5 and 1.0 N were used. The solid concentration was 20 g/L and the temperature was set at 100°C. The effect of heating rates of 30°C/min, 50°C/min, and 70°C/min to increase the leaching solution temperature from room temperature to 100°C was examined. Once heated to 100°C, the reactor was maintained at 100°C for certain leaching time (5 to 30 min). After being cooled to about 60°C, the suspension was filtered by a 0.22 μm membrane, the metal content in
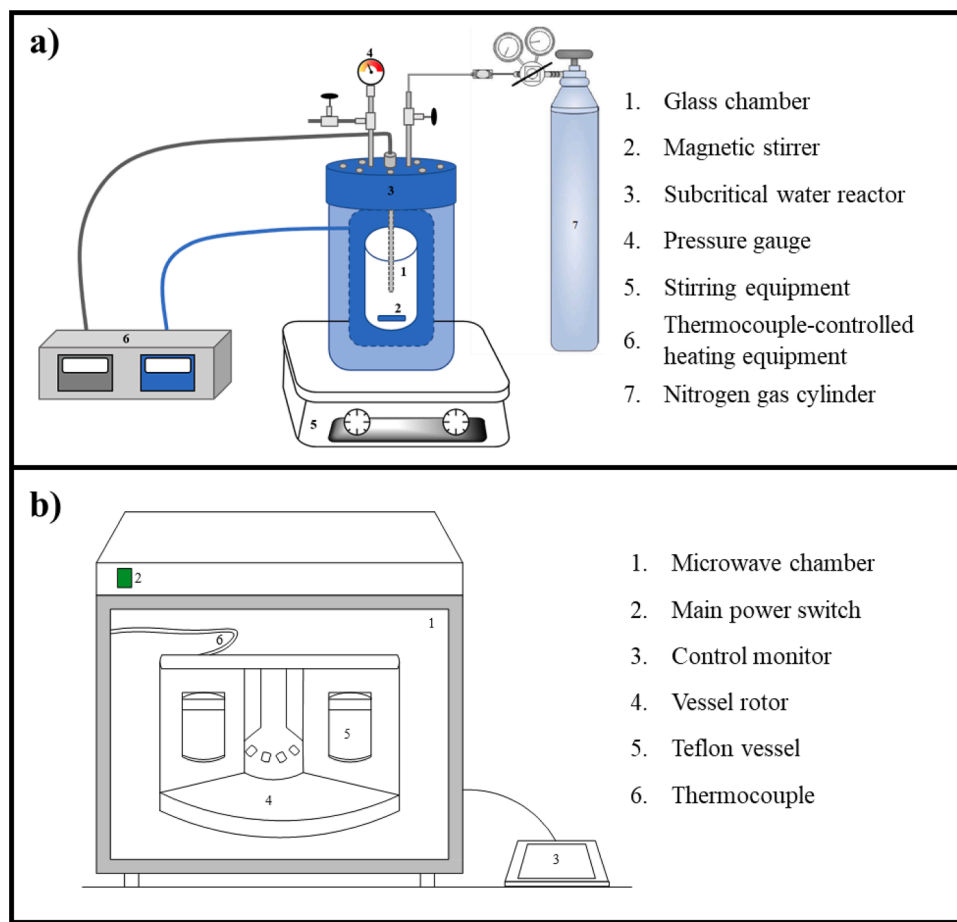
Fig. 1. Process intensification set-up of **a)** subcritical water extraction and **b)** microwave-assisted leaching.

filtrate was analyzed by ICP-OES, and the pH value was measured. All experiments were conducted in triplicates and the average value was taken.

3. Results and discussions

3.1. Characterization of spent NiMH batteries powder

The results of XRF analysis of spent NiMH batteries powder are listed in Table 1. The major elements were Ni (56.52%), Mn (8.67%), Zn (7.25%), La (6.74%), Co (6.39%), and K (4.27%). There were other REEs detected in the sample, including Ce (2.49%), Nd (1.58%), Y (0.19%), Dy (0.16%), Pr (0.07%), and Te (0.04%). The spent NiMH batteries powder had irregular shape and non-uniform particle size as demonstrated in Fig. 2, while EDX analysis indicated that the sample powder contained C, O, K, Mn, Zn, Zr, Cd, Ni, Co, La, Nd, and Ce. The XRD patterns of the powder from spent NiMH batteries are shown in Fig. 3a. The crystalline phases were identified by semi-quantitative software DIFFRAC.EVA V.3.1. The crystalline phases of nickel hydroxide (Ni(OH)$_2$), nickel (Ni), cerium nickel (Ce$_2$Ni$_7$), lanthanum nickel (LaNi$_5$),

lanthanum oxide (La$_2$O$_3$), neodymium nickelate (Nd$_2$NiO$_4$), cobalt hydroxide (Co(OH)$_2$), and cobalt oxide (CoO) were identified. The most intense peak in the XRD patterns was found at 19.238°, which corresponds to Ni(OH)$_2$ and Co(OH)$_2$. The results revealed that the sample powder was the mixture of anode and cathode of spent NiMH batteries [12].

The metal contents of spent NiMH batteries were analyzed by using aqua-regia digestion method. These experiments were repeated for 6 times, and the average chemical compositions are shown in Table 2. The dissolution of the sample was around 98% and the spent NiMH batteries powder consisted mainly of Ni (383.88 mg/g), La (78.56 mg/g), Mn (64.25 mg/g), Co (48.3 mg/g), K (44.46 mg/g), Zn (36.33 mg/g), Al (35.08 mg/g), Ce (33.03 mg/g), Cd (21.13 mg/g), Nd (20.03 mg/g), and C (26.35 mg/g), with trace amount of other elements, including Fe (6.71 mg/g), Li (2.42 mg/g), Pb (1.67 mg/g), and Mg (1.50 mg/g). Considering the values and contents, the current study would focus on certain metals in the spent NMH batteries powder, including Ni, Co, La, Ce, and Nd. The residue from aqua regia digestion was dried at 60°C for 24 h and characterized by XRD analysis as shown in Fig. 3b. The results showed that only graphite (C) was found, which implied that all of the metallic compounds of the sample were dissolved completely during aqua regia digestion. The amount of the residue was about 26.35 ± 0.65 mg/g. The leaching efficiency or extraction efficiency of each metal was calculated using the equation as follows:

$$\text{Leaching efficiency}(\%) = \frac{\text{amount of metal leached by acid}}{\text{amount of metal dissolved in aqua regia}} \times 100\%$$

Table 1
The elemental composition of spent NiMH batteries analyzed by XRF.

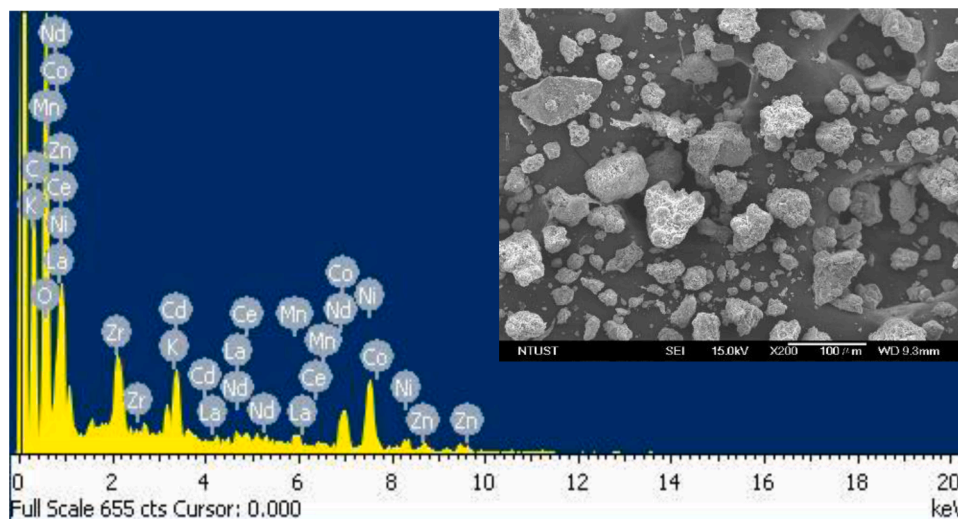| Element	Ni	Mn	Zn	La	Co	K	Ce	Cd
wt. (%)	56.52	8.67	7.25	6.74	6.30	4.27	2.49	2.07
Element	Nd	Cl	Fe	Mg	Al	P	Si	Y
wt. (%)	1.58	1.17	0.99	0.38	0.30	0.21	0.20	0.19
Element	Ca	Dy	S	Pr	Zr	Sn	Te	Pb
wt. (%)	0.17	0.16	0.09	0.07	0.06	0.05	0.04	0.03

Fig. 2. FESEM image and EDX results of spent NiMH batteries powder.
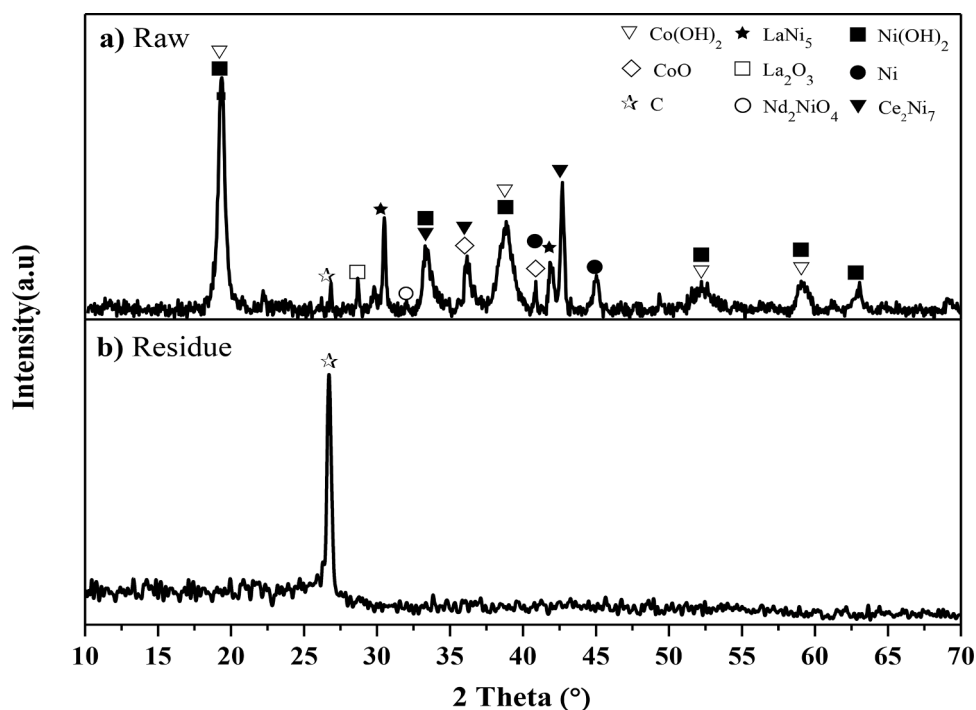

Fig. 3. XRD patterns of **a)** raw sample powder form spent NiMH batteries and **b)** residue after aqua regia digestion.

Table 2
Metal compositions of spent NiMH batteries from aqua regia digestion.

Metal	Content (mg/g)	Metal	Content (mg/g)	Metal	Content (mg/g)
Ni	383.88 ± 1.62	Zn	36.33 ± 0.33	Fe	6.71 ± 0.04
La	78.58 ± 0.55	Al	35.08 ± 1.00	Li	2.42 ± 0.08
Mn	64.25 ± 1.33	Ce	33.03 ± 0.05	Pb	1.67 ± 0.01
Co	48.39 ± 0.80	Cd	21.13 ± 0.04	Mg	1.50 ± 0.01
K	44.46 ± 0.04	Nd	20.02 ± 0.16		

3.2 Subcritical water extraction (SWE)

3.2.1 Effect of acid type

The effect of acid type on the leaching of Ni, Co, La, Nd and Ce was firstly investigated by using three mineral acids, HCl, H_2SO_4 and HNO_3.

The SWE experiments were conducted at identical extraction conditions using 0.25 N of acid, solid concentration of 20 g/L, 100°C, 9.8 bar of initial pressure, 30 min of reaction time, and 300 rpm stirring speed. The final pH of extractants using HCl, H_2SO_4 and HNO_3 was 5.31 ± 0.05, 5.93 ± 0.05, 5.86 ± 0.05, respectively. Apparently, the acid strength was not enough to dissolve all metals from the sample judging from the final pH. The amount of acid consumed per gram electrode material dissolved can be estimated assuming that metals are present in the form of oxides, hydroxides and metals even though there is some uncertainty due to heterogeneities in the samples [12]. However, it is noted that target metals are REEs, Ni, and Co, thus it is not necessary to dissolve all metals. Experimental results are shown in Fig. 4. It was observed that H_2SO_4 showed the best extraction ability for Ni with efficiency of 51.37%, while HNO_3 was effective at extracting La with efficiency of 66.18%. However, HCl was the best extraction agent among the three
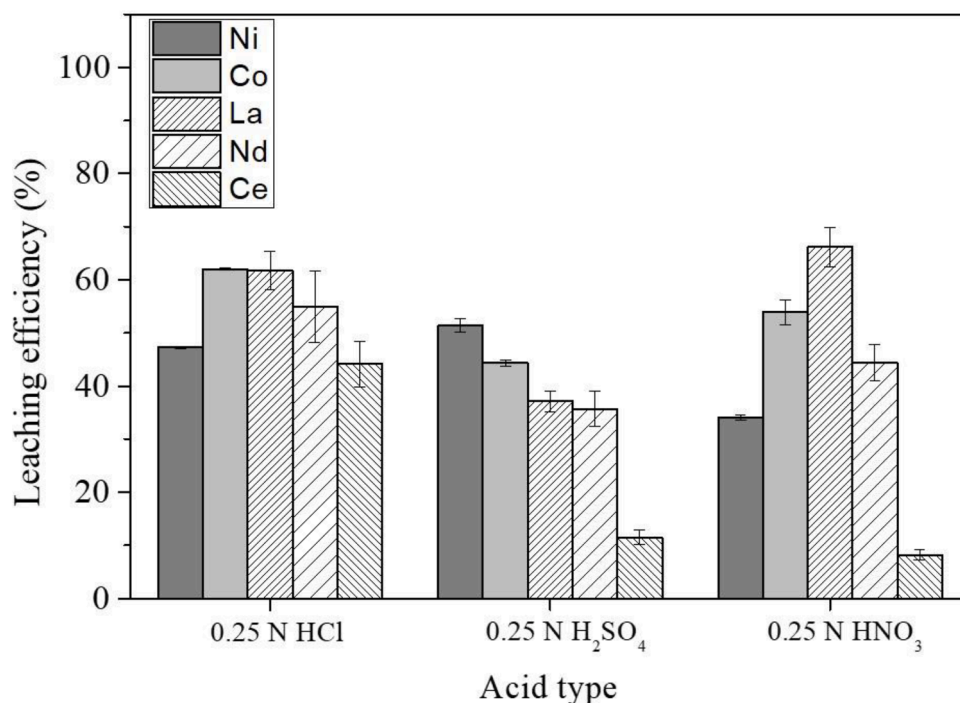
Fig. 4. Effect of acid type on leaching efficiency in SWE using 0.25 N of acid, solid concentration of 20 g/L, 100°C, 9.8 bar of initial pressure, and 30 min of reaction time.

acids in SWE considering that the leaching efficiency of Ni, Co, La, Nd, and Ce by using HCl was 47.24%, 62.05%, 61.76%, 54.95%, 44.13%, respectively. It is mainly because of different acid strength. The dissociation constant (pK_a) value of HCl, H_2SO_4 and HNO_3 is -7.0, -3.0 and -1.3, respectively, which implies that the strength of the acids is in the order of HCl > H_2SO_4 > HNO_3. Similar results were found when three mineral acids were applied for the extraction of In from indium tin oxide (ITO) scraps [31]. Therefore, HCl was used for further experiments.

3.2.2 Effect of temperature

The effects of temperature on leaching efficiency of Ni, Co, La, Nd, and Ce from spent NiMH batteries are shown in Fig. 5. The SWE process was carried out under 100, 125, and 150°C, respectively, at identical conditions of 0.25 N of HCl, solid concentration of 20 g/L, initial pressure of 9.8 bar, 30 min of reaction time and stirring speed at 300 rpm. The leaching efficiency increased with increasing temperature as it increased from 47.24% to 50.27% of Ni, from 62.05% to 74.36% of Co, from 65.43% to 81.44% of La, from 54.95% to 65.85% of Nd, and from
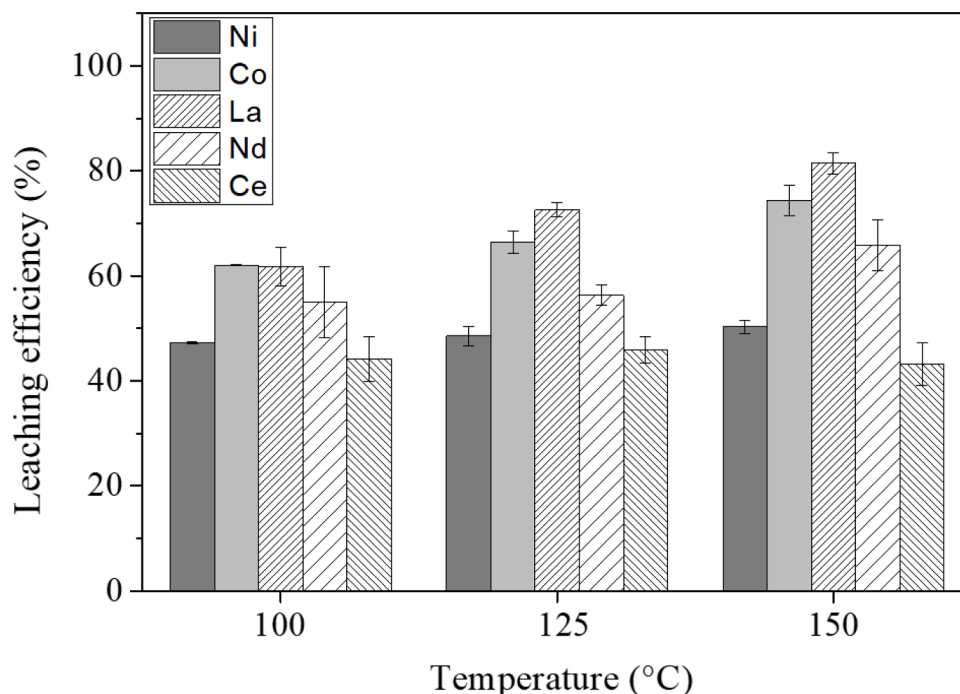

Fig. 5. Effect of temperature on leaching efficiency in SWE using 0.25 N of acid, solid concentration of 20 g/L, 9.8 bar of initial pressure, and 30 min of reaction time.

44.13% to 43.12% of Ce as the reaction temperature increased from 100 to 150°C. In general, extraction efficiency of metals from spent NiMH batteries increased as temperature increased [24,35,37]. It has been indicated that SWE condition was in the temperature range between 100°C and 374°C where the concentrations of hydronium (H_3O^+) and hydroxide (OH^-) are greatly influenced by the self-ionization of water molecules, and resulted in enhanced mass transfer, higher solubility, and higher diffusivity [26]. When temperature increased, the dielectric constant, viscosity and surface tension of water decreased, which lead to increased diffusivity of metals and enhanced heat and mass transfer efficiency [36]. However, there was no significant improvement for Ce with increasing temperature. It was probably because it already reached its equilibrium state within 30 min of reaction time under 0.25 N HCl, and all acidity was consumed. It could also be related to the fact that Ce only existed as cerium nickel (Ce_2Ni_7), the alloy that is more difficult to be leached out. When utilizing SWE, the extraction efficiency of Y and Eu from waste CRT phosphor increased significantly as temperature increased from 100 to 125°C using 0.75 M of H_2SO_4 [16]. The extraction efficiency of indium (In) from waste ITO by SWE increased with increasing temperature as well [31].

3.2.3 Effect of solid concentration

To study the effect of solid concentration on leaching efficiency of Ni, Co, La, Nd, and Ce from spent NiMH batteries powder, solid concentrations of 10, 20, 40 g/L were used in the experiment and the results are shown in Fig. 6. The leaching process was conducted using 0.25 N of HCl, 100°C, initial pressure of 9.8 bar, 30 min of reaction time, and stirring speed at 30 rpm. When solid concentration increased from 10 g/L to 40 g/L, the leaching efficiency decreased from 100% to 16.73% for Ni, 100% to 35.01% for Co, 97.47% to 29.51% for La, 98.40% to 33.80% for Nd, and 65.50% to 5.73% for Ce. Apparently, the leaching efficiency decreased as solid concentration increased.

3.2.4 Effect of acid concentration

To study the effect of acid concentration on leaching efficiency of Ni, Co, La, Nd, and Ce from spent NiMH batteries powder, HCl solutions of various concentration (0.1, 0.25, 0.5, and 1.0 N) were used and the results are depicted in Fig. 7. The leaching process was conducted at solid concentration of 20 g/L, 100°C, initial pressure 9.8 bar, 30 min of reaction time, and 300 rpm of stirring speed. When using 0.1 N of HCl at final pH of 5.71, and the efficiency was limited, and only 12.24% of Ni, 28.10% of Co, 17.10% of La, 9.37% of Nd, and 1.29% of Ce were extracted. When HCl concentration increased to 0.25 N with final pH of 5.31, the leaching efficiency of Ni, Co, La, Nd and Ce increased to 47.24%, 62.05%, 65.43%, 54.95%, and 44.13%, respectively. As HCl concentration increased to 0.5 N with final pH of 1.22, the leaching efficiency of Ni, Co, La, Nd, and Ce remarkably increased to 100.73%, 99.28%, 97.02%, 96.12% and 91.71%, respectively. As HCl concentration further increased to 1.0 N with final pH 0.47, the leaching efficiency of Ni, Co, La, Nd and Ce was all ca. 100%. It was apparent that the leaching efficiency increased as acid concentration increased. The pH value also determining in the dissolution of Ni, Co and REEs, since acidity of leaching solution induces high dissolution of those metals [25, 37].

3.3 Microwave assisted extraction (MAE)

3.3.1 Effect of heating rate

The effects of heating rate (30, 50, 70°C/min) of MAE on leaching efficiency of Ni, Co, La, Nd, and Ce from spent NiMH batteries powder were studied, and results are shown in Fig. 8. The leaching process was conducted using 0.5 N of HCl, solid concentration of 20 g/L, 100°C, and reaction time of 5 min. Experimental results revealed that as heating rate increased from 30 to 70°C/min, leaching efficiency slightly reduced from 65.98% to 60.70% for Ni, 57.66 % to 53.47% for Co, 51.20% to 48.56% for La, 49.12% to 47.08% for Nd, and 45.36% to 42.54% for Ce. It is noted that as heating rate increased from 30 to 50, 70°C/min, the corresponding heating time shortened from 2.5 to 1.5, 1.07 min, respectively. That was probably the reason why leaching efficiency decreased slightly with increasing heating rate [14]. However, the effect of heating rate was not very significant, hence, the heating rate of 70°C/min was recommended for more rapid and efficient heating process.

3.3.2 Effect of reaction time

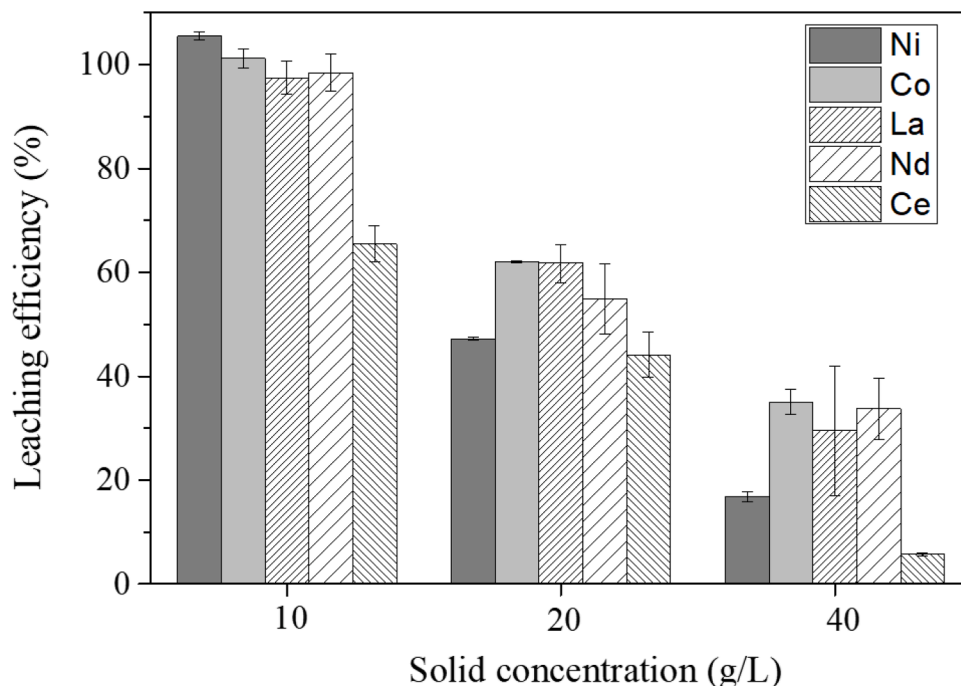To study the effect of reaction time of MAE on leaching efficiency of

Fig. 6. Effect of solid concentration on leaching efficiency in SWE using 0.25 N of HCl, initial pressure of 9.8 bar, and 30 min of reaction time.
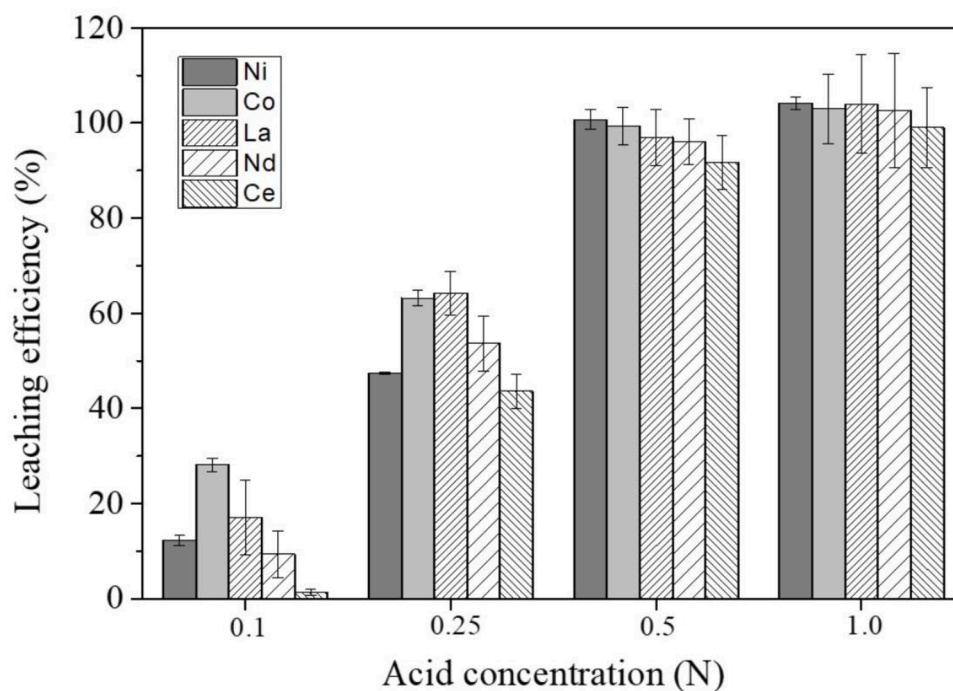
Fig. 7. Effect of HCl concentration on leaching efficiency in SWE at solid concentration of 20 g/L, 100°C, initial pressure 9.8 bar, 30 min of reaction time.
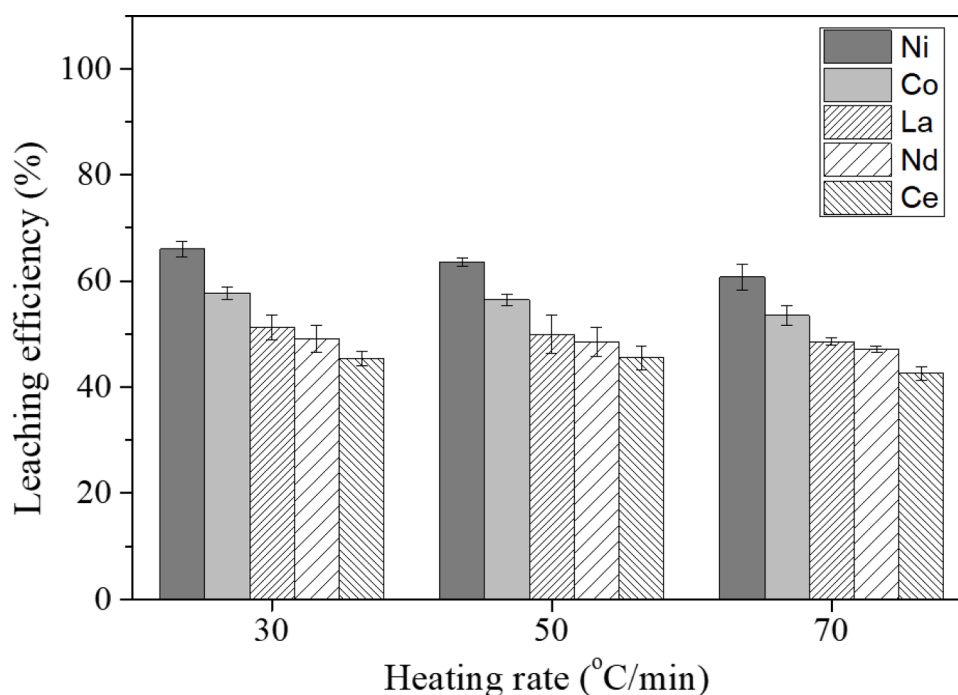

Fig. 8. Effect of heating rate on leaching efficiency of MAE using 0.5 N of HCl, solid concentration of 20 g/L, 100°C, and reaction time of 5 min.

Ni, Co, La, Nd, and Ce from spent NiMH batteries powder, reaction from 5 to 30 min were chosen, and the results are shown in Fig. 9. The leaching process was conducted at 1.0 N of HCl, solid concentration of 20 g/L, 100°C, and 70°C/min. When the reaction time was prolonged from 5 to 10 min, and 30 min, the leaching efficiency increased from 85.93% to 92.81%, and 95.82% for Ni, 77.60% to 88.41%, and 89.76% for Co, 64.04% to 75.24%, and 76.45% for La, 75.01% to 84.75%, and 80.92% for Nd, and 57.17% to 64.39%, and 64.28% for Ce, respectively. Similar findings on leaching efficiency of uranite from a low grade ore increased with microwave power, reaction temperature, and the

reaction kinetics followed shrinking core model [20]. Similar Microwave heating time affected leaching efficiency of REEs from mixed concentrate through both micro-fracturing of particles and excessive sintering by thermal stress and there existed optimum heating time [8].

3.4. Conventional leaching

The experiments for conventional leaching were conducted using 1 N of HCl solution of 20 g/L solid concentration at three different reaction temperature (25, 45, 65°C), and different reaction time (1, 2, 4, 6, 8, 10,
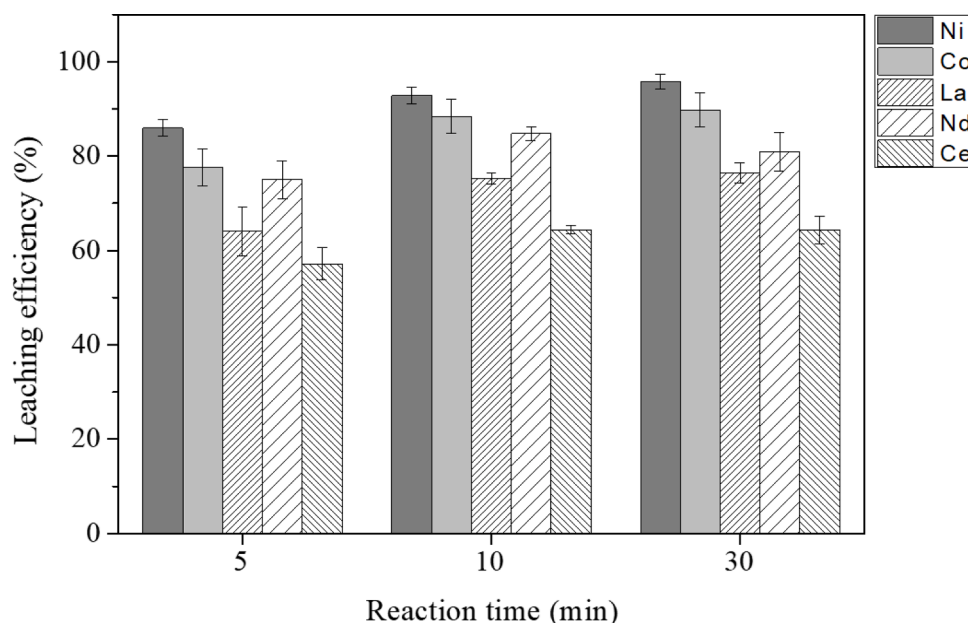
Fig. 9. Effect of reaction time on leaching efficiency of MAE using 1.0 N of HCl, solid concentration of 20 g/L, 100°C, and 70°C/min.

20, 30, 60, 90, 120 min). The leaching efficiency of Ni, Co, La, Nd and Ce from spent NiMH batteries powder at various temperatures are shown in Fig. S1. The leaching efficiency increased with increasing temperature, and the time to reach steady state decreased with increasing temperature. The leaching efficiency for 60 min reaction time at 25°C for Ni, Co, La, Nd, and Ce was 66.63%, 77.53%, 93.92%, 95.57%, and 89.16%, respectively, and the leaching efficiency for Ni, Co, La, Nd, and Ce partly increased to 102.32%, 97.54%, 100.69%, 100.48%, and 92.49%, respectively, at 60°C. In addition, reaction kinetics could be described by the pseudo-second-order model and kinetic parameters are listed in Table S1. The activation energy was assessed by plotting ln k versus 1000/T as shown (Fig. S2). The activation energy (Ea) of Ni, Co, La, Nd, and Ce leaching was 34.9 kJ/mol, 25.5 kJ/mol, 20.7 kJ/mol, 23.3 kJ/mol, and 15.6 kJ/mol, respectively. Since the activation energy was lower than 40 kJ/mol, it implied that the leaching processes were diffusion-controlled [13].

3.5. Comparison and assessment of three methods

The total energy consumption and leaching efficiency by using SWE, MAE, and conventional leaching are estimated and compared as showed in Table 3. The calculation of energy consumption of each leaching method was provided in Table S2. The output power was obtained from specification of each instrument and equipment, and the power was the average value since the power supply to the equipment may not be constant throughout the leaching experiment. Among the three leaching methods, conventional leaching required the longest reaction time and the highest energy consumption. The experimental condition of using 1 N of HCl, solid concentration of 20 g/L, 45°C, and reaction time of 60 min required total of 7,140 kJ to reach 102.02% for Ni, 94.61% for Co, 99.14% for La, 99.48% for Nd, and 96.43% for Ce, respectively. When increasing the reaction temperature to 60°C and reducing the reaction time to 30 min, the total energy consumption was estimated to be 6,003 kJ, and the leaching efficiency was 102.85% for Ni, 94.13% for Co, 95.57% for La, 94.74% for Nd, and 87.95% for Ce, respectively.

When using SWE under the conditions of 0.5 N of HCl, solid concentration of 20 g/L, 100°C, reaction time of 5 min, the leaching efficiency was 99.85% for Ni, 91.72% for Co, 96.26% for La, 85.75% for Nd, and 84.37% for Ce, respectively, and the total energy consumption was 2,640 kJ. When increasing reaction time to 30 min, leaching efficiency improved to 100.73% for Ni, 99.28% for Co, 97.02% for La, 96.12% for

Table 3
Comparison among conventional leaching, SWE and MAE with competitive leaching efficiency.

Parameter	Conventional leaching		SWE		MAE	
Solid concentration (g/L)	20	20	20	20	20	20
Acid concentration (N)	1.0	1.0	0.5	0.5	1.0	1.0
Temperature (°C)	45	65	100	100	100	100
Heating rate (°C/min)	1.09	1.10	3.75	3.75	70	70
Heating time (min)	18.3	36.2	20	20	1.07	1.07
Reaction time (min)	60	30	5	30	5	10
Cooling time (min)	0	0	10	10	0	0
Pressure (kg/cm^2)	1	1	10	10	ND	ND
Energy consumption (kJ)	7,140	6,003	2,640	5,280	874.1	1,594.1
Ni leached (%)	97.03	99.56	99.85	100.73	85.93	92.81
Co leached (%)	94.61	94.13	91.72	99.28	77.60	88.41
La leached (%)	99.14	95.57	96.26	97.02	64.04	75.24
Nd leached (%)	99.48	94.74	85.75	96.12	75.01	84.75
Ce leached (%)	96.43	87.95	84.37	91.71	57.17	64.39

ND: not detected

Nd, and 91.71% for Ce, respectively, and the total energy consumption increased two-fold, which was 5,280 kJ. The SWE is effective, energy efficient, and the most chemical-efficient method since 0.5 N HCl was used. Among the three methods, MAE was the most energy-efficient. Total of 874.1 kJ was required to reach 85.93% for Ni, 77.60% for Co, 64.04% for La, 75.01% for Nd, and 57.17% for Ce, respectively under experimental conditions of 1 N of HCl, solid concentration of 20 g/L, 100°C, and reaction time of 5 min. When extending the reaction time from 5 min to 30 min, the total energy consumption increased to 4,474.1 kJ, and the leaching efficiency became 95.82% for Ni, 89.76% for Co, 76.45% for La, 80.92% for Nd, and 64.28% for Ce, respectively. MAE has been regarded as a promising method for leaching because of its low energy consumption. This study showed that process intensification (SWE and MAE) for valuable metals leaching from NiMH batteries is effective and efficient.

3.6. Leaching residue

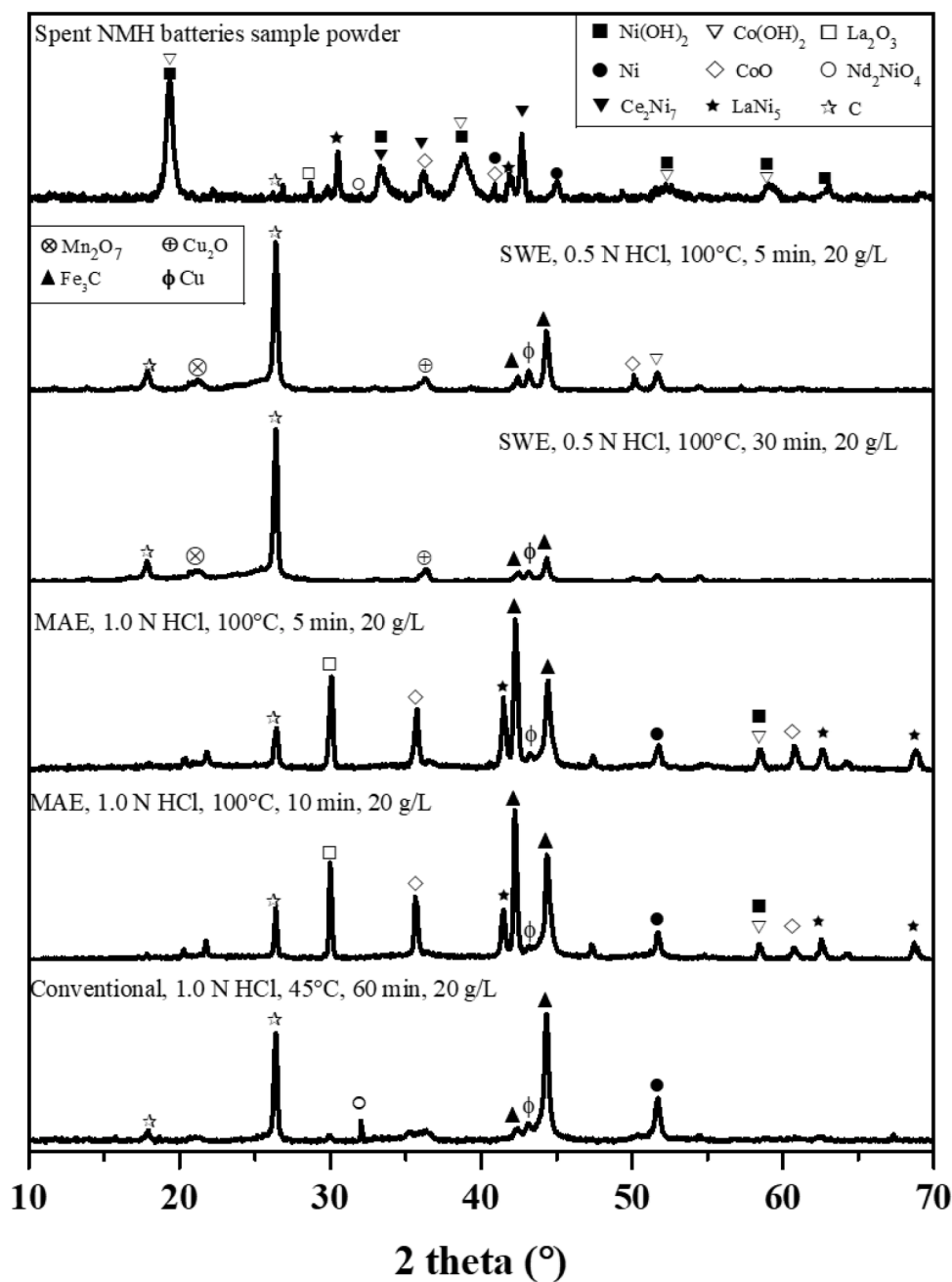The XRD assessment of leaching residues are shown in Fig. 10. In the

Fig. 10. XRD spectra of leaching residues of spent NiMH batteries powder.

SWE residues, the most intense peak was graphite (C), and there were small peaks that correspond to Ce_2Ni_7 and $Co(OH)_2$. As the reaction time increased from 5 min to 30 min, the small peaks diminished. Besides, in the residue of conventional leaching, the peak of Ce_2Ni_7 remained, which implied that it was difficult to dissolve that rendered leaching efficiency of Ce lower than other elements. In the MAE residues, there were various peaks existing, which indicated that the residue from MAE contained various elements, and the leaching efficiency of using MAE was the lowest.

4. Conclusions

Leaching of Ni, Co, La, Nd, and Ce from spent NiMH batteries was investigated by using SWE, MAE, and conventional leaching. Major findings of the current study can be summarized with followings:

1. In SWE system, the leaching efficiency of Ni, Co, La, Nd, and Ce increased with increasing HCl concentration, reaction temperature, and reaction time, while decreased with increasing solid concentration. It was very effective using 0.5 N HCl, solid concentration of 20 g/L, initial pressure of 9.8 bar, 100°C for 5 min, and leaching efficiency of 99.85% for Ni, 91.72% for Co, 96.26% for La, 85.75% for Nd, and 84.37% for Ce was found,

2. In MAE system, the leaching efficiency of Ni, Co, La, Nd, and Ce increased with increasing HCl concentration and reaction time, but decreased with increasing heating rate. The leaching efficiency was 95.82% for Ni, 89.76% for Co, 76.45% for La, 80.92% for Nd, and 64.28% for Ce, respectively, at 1.0 N of HCl, solid concentration of 20 g/L, 100°C, and 70°C/min.

3. In conventional leaching, pseudo-first-order model could describe the leaching rate better than pseudo-second-order model. The

activation energy (Ea) for Ni, Co, La, Nd, Ce was 34.8, 25.5, 20.7, 23.3, and 15.6 kJ/mol, respectively, when using 1.0 N of HCl.

4 The SWE is effective, energy efficient, and the most chemical-efficient method when compared with MAE and conventional leaching. Among the three methods, MAE was the most energy-efficient. However, the leaching efficiency was slightly lower.

5 Process intensification using novel leaching methods for spent NiMH batteries is full of potential.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2021.108507.

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