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Simultaneous recovery of valuable metals from spent mobile phone battery by an acid leaching process

Supasan Sakultung, Kejvalee Pruksathorn and Mali Hunsom†

Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand 10330

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Abstract−This research was carried out to recover some valuable metals from the electrodes of spent mobile phone batteries by leaching process in laboratory scale. Two types of spent mobile phone batteries were employed in this study: nickel-metal hydride (Ni-MH) and lithium-ion (Li-ion) batteries. Effects of parameters including types of acid (H_2SO_4, HNO_3 and HCl), acid concentration (1-6 M), solid-liquid ratio (10-40 g/*l*), leaching time (5-120 min) and leaching temperature (303-363 K) on the leaching percentages of Co and Ni were investigated. The preliminary results indicated that HCl provided higher leaching percentages than that of H_2SO_4 and HNO_3 for both metals at all leaching conditions. At optimum conditions, greater than 92% and 84% of Ni and Co were leached, respectively. Further investigation indicated that the leaching process of both metals was endothermic with the rate law of a second-order reaction and its kinetics was principally controlled by the physical process.

Key words: Spent Battery, Acid Leaching Process, Kinetics Model, Heavy Metal, Saturation Concentration

INTRODUCTION

Industrial development and advancements in communication have greatly increased the demand for cellular or mobile phones, and inevitably increasing the number of waste batteries. In the last seven years, the Li-ion and Li-polymer cell market has increased from 8.4% to 27.3% while the Ni-Cd batteries decreased from 63.8% to 44.4%, and Ni-MH remained practically constant [1]. Presently, Li-ion batteries represent approximately 28% of the rechargeable battery world market and their consumption continues to increase, particularly in small rechargeable cells such as mobile phones. According to the Foundation for Anti Air Pollution and Environmental Protection, the quantity of mobile phones will increase rapidly to more than 20 million in the next 5 years, and this will lead to more than 10 million spent batteries. These spent batteries are Li-ion, Ni-MH, Li-polymer, Ni-Cd, etc. Improper disposal of these batteries could lead to serious problems in the future because they usually contain some heavy metals particularly Ni, Mn, Fe and sometimes Cd or Hg [2]. Currently, a better procedure for disposal of such wastes is the landfill in the deep sea. However, this way can generate various subsequent problems in the future such as the leakage of heavy metals into the environment. Therefore, their recovery and re-use will be an alternative better way from both environmental and economic points of view.

Many different techniques have been introduced to recover and recycle valuable metals such as chemical precipitation, ion exchange process [3], leaching and extraction process [4], adsorption by biosorbents [5,6] and electrochemical methods [7-9]. However, for spent batteries, all previous works started with acid leaching. The best condition for acid leaching was found by using 3 M HCl at high temperature of 368 K and 3-hr leaching time [10]. Zhu et al. [11] used the bio-leaching process to remove Ni and Cd from Ni-Cd batteries. They showed that acid leaching had the most effectiveness at a residence time of the sludge in the bioreactor of 4 days, and the sludge drained from the process could satisfy the requirement of environmental protection agencies with regard to agricultural use. To separate Ni from Cd, a combined process of electrodeposition and chemical precipitation processes was investigated [12]. According to chemical precipitation process, more than 97% of Ni element was recovered from the leaching solution by using NaOH. By using electrodeposition, the appropriate potential for Cd recovery was in the range of −1,100 to −1,120 mV with 70-90% recovery. For Li-ion battery, 10 M NaOH showed the best performance to precipitate Co and Ni from the leaching solution [13,14]. To remove Co and Ni separately, Co was first removed from aqueous solution by solvent extraction process and Ni was then removed as a solid by electrowinning process at a current density of 250 A/m^2 with 87% current efficiency and 2.96 kWh/kg energy consumption [15]. To remove Ni-Co as an alloy form, the electrowinning process was used at current density of 250 A/m^2, pH=4.3 at 323 K [16]. The current efficiency was higher than 91% and good quality alloy was obtained. The removal of Cd from spent Ni-Cd batteries was carried out by using electrodeposition in galvanostatic mode. The result demonstrated that the charge efficiency and deposit morphology depended on the current density, whereas pore size decreased with the increase in current density [17]. Salgado et al. [18] used liquid-liquid extraction to extract Zn and Mn from spent alkaline batteries in bench scale. The results showed that Zn and Mn were easily separated ($\Delta pH_{1/2}\approx 2.0$) using 20% (v/v) Cyanex 272 in Escaid 110 at 323 K.

In this study, we attempted to investigate the effects of parameters including types of acid, leaching temperature, acid concentration, solid-liquid ratio and the leaching time on the Ni and Co leaching efficiency. Moreover, the kinetics models of the leaching process of metals were also developed as a function of leaching time and

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†To whom correspondence should be addressed.
E-mail: mali.h@chula.ac.th

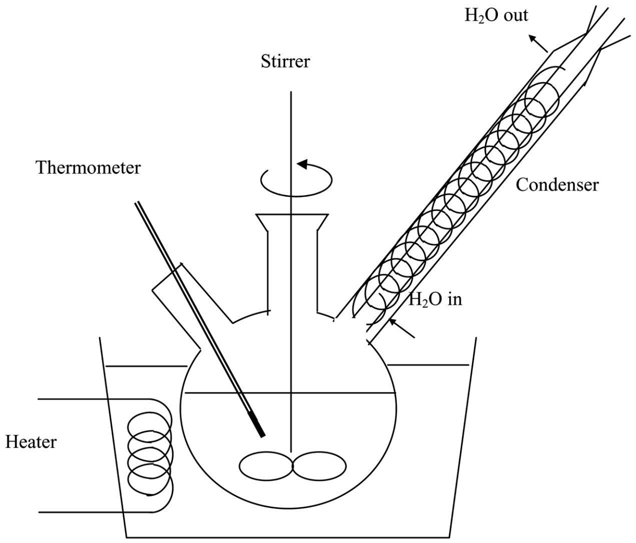

Fig. 1. Scheme of leaching reactor configuration.

leaching temperature.

EXPERIMENTAL

Two types of spent mobile phone batteries consisting of Ni-MH and Li-ion batteries were included in this study. Both were first opened and consequently classified by obvious appearance into four categories including electrode, steel case, plastics case and other components. The electrode component containing valuable metals was employed for further study. It was crushed to obtain a particle size smaller than 2 mm and then dried at 383 K for 2 hr to eliminate free moisture. The metal components in the crushed electrodes were submitted to quantitative analysis by XRF (Siemen SRS3400). Two types of metals in the electrodes of both batteries including Ni and Co were extracted from the crushed electrode particle by acid leaching process.

Fig. 1 displays the configuration of the leaching reactor. It consists of a spherical glass reactor immerged in the water bath. The temperature of the water bath was maintained constant at a preferable value. The condenser was connected at the neck of the glass reactor to condense the generated vapor in the system. The effects of different parameters including types of acid (H_2SO_4, HNO_3 and HCl), acid concentration (1-6 M), leaching time (15-120 min), leaching temperature (303-363 K), and solid-liquid ratio (10-40 g/*l*) on the leaching percentages were investigated in this study. The amounts of metal leached from the electrode particle were traced by using Atomic Absorption Spectroscopy (AVANTA *ε*).

RESULTS AND DISCUSSION

1. Effect of Types of Acid

Eight different conditions were carried out to leach Ni and Co from spent mobile phone batteries (Table 1) by using three types of strong acid, including H_2SO_4, HNO_3 and HCl at a leaching period of 120 min. The initial metal contents in the electrode of the spent mobile phone batteries utilized in this work were Co 30.5%, Ni 31.3%, Cu 5.3%, La 4.7%, Al 2.1% and others 26.1%. Fig. 2 shows the leaching percentages of Ni and Co at different operating conditions. It demonstrated that HCl provided better leaching percentages than that of H_2SO_4 and HNO_3 for both metals at all operating conditions. These results agreed with the results of Zhang et al. [19], which demonstrated that HCl provided higher leaching percentages than that of H_2SO_4 for both Co and Li leaching systems. This is because the

Table 1. Conditions of acid leaching process

Condition	Temperature (K)	Acid concentration (M)	Solid-liquid ratio (g/*l*)	Time (min)
[1]	313	1	10	120
[2]	353	1	10	120
[3]	313	5	10	120
[4]	353	5	10	120
[5]	313	1	40	120
[6]	353	1	40	120
[7]	313	5	40	120
[8]	353	5	40	120

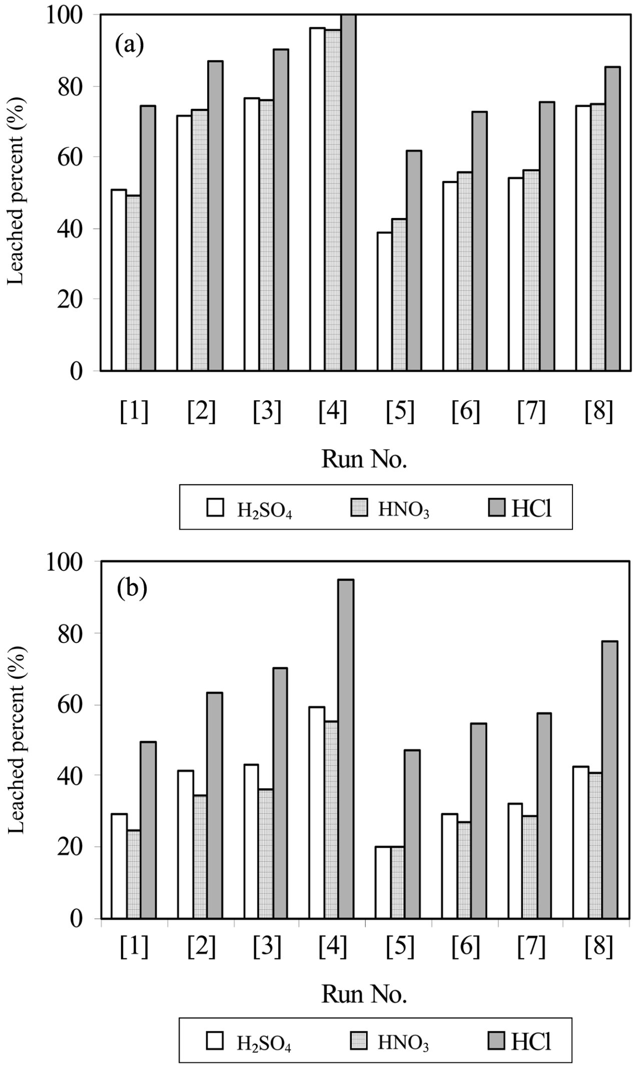

Fig. 2. Leaching percentages of Ni (a) and Co (b) by using H_2SO_4, HNO_3 and HCl at various conditions.

value of the dissociation constant (K_a) of HCl is higher than that of H_2SO_4 and HNO_3. Namely, dissociation constants of HCl, H_2SO_4 and HNO_3 are 10^6, 10^3 and 28, respectively [20].

Comparing the effectiveness of H_2SO_4 with HNO_3 demonstrated that both types of acid provided nearly similar leaching percentages for Ni. However, for Co, H_2SO_4 can achieve higher percentages than HNO_3. In addition, the leaching percentages of Ni were greater than that of Co at approximately 2-fold for all conditions. This is because both metals in electrodes of batteries are generally presented in different forms of ionic compounds. When the leaching process was carried out, a different amount of protons generated from the acid dissociation was required to attach the ionic bonding of these compounds according to Eqs. (1)-(4). From these equations, it can be seen that the Ni leaching process requires a smaller quantity of protons than the Co leaching process. In other words, the leaching percentages of Ni will be equal or higher than that of Co when the same operating conditions are carried out. According to the above results, for simultaneous removal of both metals, the HCl was selected for further study.

$$NiOOH\,(s)+2H^+\,(aq)\rightarrow Ni^{2+}\,(aq)+3/2H_2+O_2 \quad (1)$$

$$Ni(OH)_2\,(s)+2H^+\,(aq)\rightarrow Ni^{2+}\,(aq)+2H_2O \quad (2)$$

$$LiCoO_2\,(s)+3H^+\,(aq)\rightarrow Co^{2+}\,(aq)+Li^++3/2H_2+O_2 \quad (3)$$

$$CoO_2\,(s)+2H^+\,(aq)\rightarrow Co^{2+}\,(aq)+H_2+O_2 \quad (4)$$

2. Effect of Acid Concentration

The effect of HCl concentration was explored in the range of 1-6 M at a leaching temperature of 353 K, solid-liquid ratio of 10 g/*l* and leaching time of 120 min. The results demonstrated that the leaching percentages of both metals increased with the increase of acid concentration (Fig. 3) which is similar to the results of Lee et al. [21]. Namely, by using 1 M HCl, the leaching percentages of Ni and Co were approximately 86.7% and 63.4%, respectively. Increasing the acid concentration up to 5 M could promote the leaching percentage of Ni to greater than 99.9% and that of Co up to 95%.

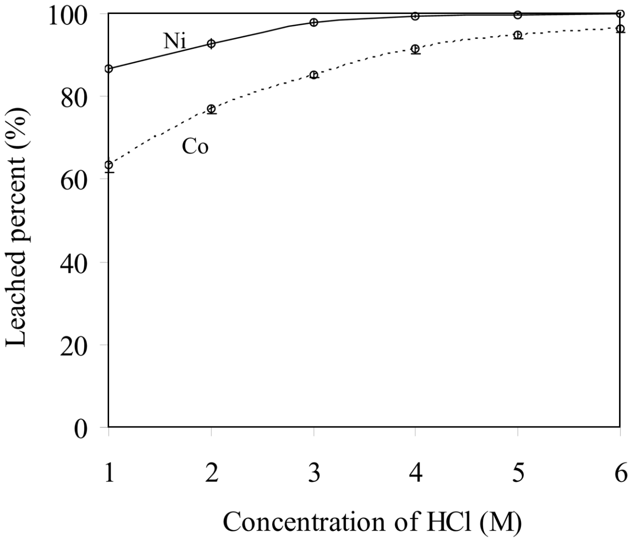

Fig. 3. Leaching percentages of Ni and Co as a function of acid concentrations.

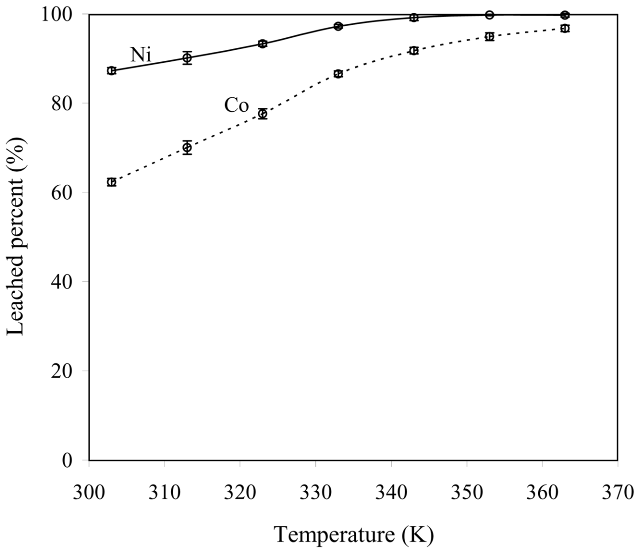

Fig. 4. Leaching percentages of Ni and Co as a function of leaching temperature.

This can be explained that the increased acid concentration leads to the increase of the amount of proton attaching to the metal compounds in the leaching system. In addition, the strong acidic condition can achieve fast kinetics of the metal leaching process. However, further increase of the acid concentration up to 6 M can achieve complete leaching only for Ni and but not for Co. This might be attributed to the limitation of Co equilibrium, which will be further investigated. According to the results in this part, the optimum acid concentration employed to leach both metals simultaneously was found to be at 5 M.

3. Effect of Leaching Temperature

Fig. 4 shows the alternation of the leaching percentages of Ni and Co as a function of leaching temperature in the range of 303-363 K by using the acid concentration of 5 M, solid-liquid ratio of 10 g/*l*, and leaching time of 120 min. The results revealed that the leaching percentages strongly depended on the leaching temperature. That is, both Ni and Co were leached at approximately 87.3% and 62.3% by using the leaching temperature of 303 K. Increasing leaching temperature up to 353 K led to the rise of the leaching percentages up to 100% for Ni and greater than 95% for Co. This is because the metal leaching process is the endothermic reaction. The reaction can move forward at high operating temperature. In addition, increasing leaching temperature led to the increase of the kinetics energy of acid molecules attached to the metals compounds. The higher the temperature, the higher the kinetic energy of acid molecules was achieved. Nevertheless, further increasing leaching temperature greater than 363 K cannot improve the leaching percentages of Co. This might be due to its kinetics limitation. Comparing the leaching percentages of Ni with Co, it seems that Co leaching was more affected by temperature than Ni leaching. This might be attributed to the effect of electronic properties of metals such as the electronegativities or binding energy or the effect of different form of ionic compounds presented in the system. Therefore, to extract both Ni and Co simultaneously, the optimum leaching temperature was found to be at 353 K.

4. Effect of Solid-liquid Ratio

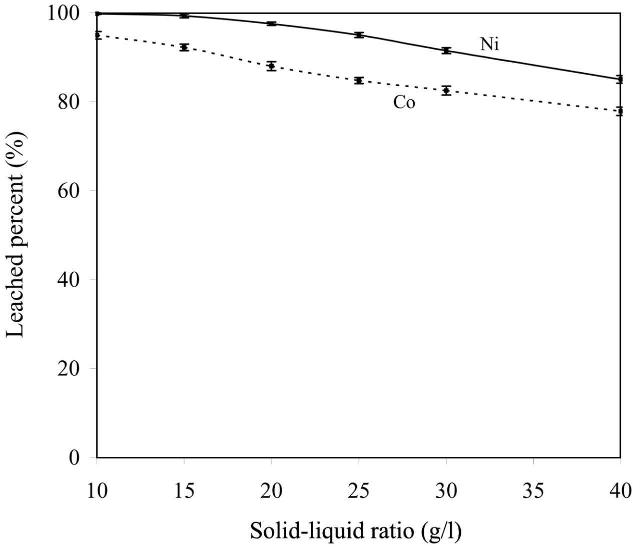

Fig. 5. Leaching percentages of Ni and Co as a function of solid-liquid ratio.

Optimum ratio of the crushed spent electrode to the quantity of HCl was determined in terms of the solid-liquid ratio in the range of 10-40 g/*l* by employing HCl at a concentration of 5 M, leaching temperature of 353 K and leaching time of 120 min. Fig. 5 exhibits that the leaching percentages of both metals decreased when the solid-liquid ratio was increased similar to the previous work [22]. This is because, at high solid-liquid ratio, the amount of protons is not adequate to react with metal compounds completely. Furthermore, raising the solid-liquid ratio above 15 g/*l* resulted in a sharper decrease of leaching percentages of both metals relative to the case below 15 g/*l*. Therefore, the optimum solid-liquid ratio for leaching both metals simultaneously was selected at 15 g/*l*, which led to leaching percentages of Ni and Co greater than 99.3% and 92.2% of Ni and Co, respectively.

5. Effect of Leaching Time

The effect of leaching time on the leaching percentages of both metals was carried out in the range of 15-120 min by employing 5 M HCl and 15 g/*l* solid-liquid ratio at a leaching temperature of 353 K. The results indicated that the leaching percentages of both metals increased sharply from the initial time to approximately 15 min. Afterwards, they increased slightly until 60 min and reached their plateaus when the leaching time was greater than 60 min, as plotted in Fig. 6. This is probably due to the leaching process reaching equilibrium. Therefore, it can be said that the optimum leaching time for Ni and Co was obtained at 60 min. At this condition, the leaching percentages were approximately 83.3%, 86.2%, 92.9%, and 97.9% for Ni, and 59.1%, 67.3%, 83.9%, and 89.1% for Co at temperature of 303, 313, 333 and 353 K, respectively.

6. Kinetics Model of Metal Leaching Process

Regarding the kinetics of the leaching process, it was found that the metal concentration in the bulk liquid solution initially increased very fast, and then slowly reached a saturation value. This phenomenon suggested that the kinetics model of the leaching process might be represented by the second-order rate law expression as follows [21,23]. The integrated rate law of the Eq. (5) by using the boundary conditions t=0 to t and C_t=0 to C_t, was obtained in linear form as expressed by Eq. (6). According to Eq. (6), plotting the value of t/C_t versus t will provide a straight line with the slope of 1/C_s and the intercept of 1/kC_s^2. The metal concentration at each period was obtained by the rearrangement of Eq. (6) as expressed by Eq. (7).

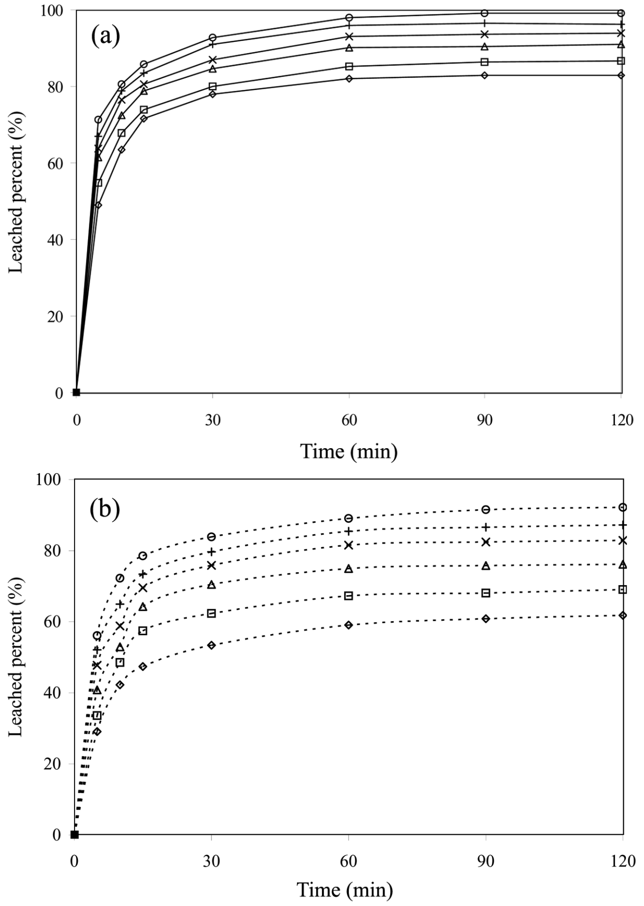

Fig. 6. Leaching percentages of Ni (a) and Co (b) as a function of leaching time at 303 K (◇); 313 K (□); 323 K (△); 333 K (×); 343 K (+) and 353 K (○).

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \tag{5}$$

$$\frac{t}{C_t} = \frac{1}{kC_s^2} + \frac{t}{C_s} \tag{6}$$

$$C_t = \frac{t}{\frac{1}{kC_s^2} + \frac{t}{C_s}} \tag{7}$$

Fig. 7 displays the series plots of t/C_t as a function of leaching time during transient region (0-60 min) at various leaching temperatures of the Ni and Co leaching processes by using HCl. Very good agreement between the second-order leaching model and the experimental results was obtained with a coefficient of determination, R^2, of 0.9999. This can be confirmed as there were two phenomena during the leaching process: initially there was intense dissolution and scrubbing in which the maximum leaching occurred, and consequently, a much slower stage was obtained which corresponded to the external diffusion related to the soluble remainder.

Fig. 8(a) shows the relationship between the saturation concen-

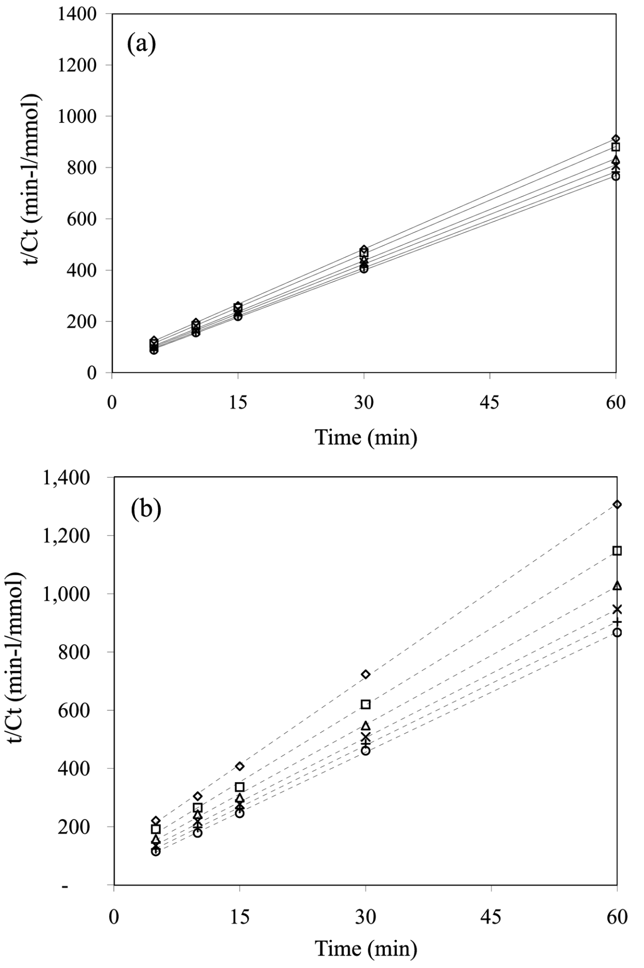

Fig. 7. Second-order leaching kinetics of Ni (a) and Co (b) as a function of leaching time at 303 K (◇); 313 K (□); 323 K (△); 333 K (×); 343 K (+) and 353 K (○).

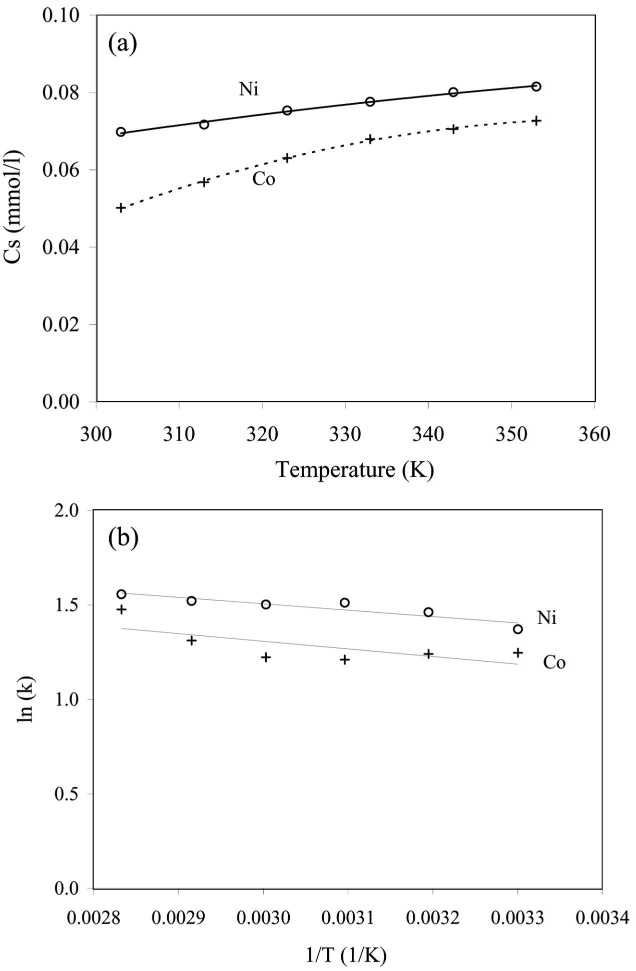

Fig. 8. Effect of the leaching temperature on the kinetics rate constant (a) and saturation concentrations (b).

trations of both metals against the leaching temperature. The plots demonstrate that similar trends of both saturation concentration curves were obtained; namely, the saturation concentration of both metals increased with the leaching temperature. The occurrence of this phenomenon might be due to the thermodynamic equilibrium since the solid solubility usually increases with the temperature [24]. However, the saturation concentration of Ni was greater than that of Co approximately 1.1-1.4 times. According to these results, the best fit between the saturation concentration of both metals and the leaching temperature can be expressed by Eqs. (8)-(9) with a coefficient of determination of 0.9930 and 0.9991, respectively.

$$C_{s,Ni}=-1.23\times10^{-6}T^2+1.06\times10^{-3}T-0.137 \tag{8}$$

$$C_{s,Co}=-6.56\times10^{-6}T^2+4.76\times10^{-3}T-0.789 \tag{9}$$

Fig. 8(b) displays the values of the natural logarithmic value of second-order leaching rate constants (ln k) of the leaching process of both metals as a function of reciprocal absolute leaching temperature (1/T). It can be seen that there was a linear relationship between them with a coefficient of determination of 0.8416 and 0.8161 for nickel and cobalt, respectively. It can be emphasized that the leaching process of both metals from the spent mobile phone batteries was the endothermic reaction. The activation energy of the leaching process of both metals was also calculated according to the Arrhenius equation [25]. Eqs. (10) and (11) show the relationships of the kinetics rate constants against the leaching temperature in Arrhenius form. They demonstrate that the values of the activation energy of both metals were 2.823 and 3.348 kJ/mole, which were lower than 20 kJ/mole. Since, in general, the activation energy of a physical process is less than 20 kJ/mole, whereas that of a chemical process exceeds 40 kJ/mol [21], it can be suggested that the physical process or diffusion process controlled the leaching rates of both metals. In addition, the lower activation energy of Ni agreed with the fact that the leaching of Ni occurred faster than that of Co.

$$k_{Ni}=12.493\exp\left(-\frac{2.823}{RT}\right) \tag{10}$$

$$k_{Co}=12.375\exp\left(-\frac{3.348}{RT}\right) \tag{11}$$

The rate law equations for the second-order leaching process of both Ni and Co were obtained by substituting the values of C_s and k from Eqs. (8)-(11) into Eq. (7) which provided the fact that higher leaching temperature will produce a more efficient leaching process.

CONCLUSIONS

Valuable metals including Ni and Co were extracted from the electrodes of spent mobile phone batteries by using the acid leaching process. For eight different leaching conditions, HCl provided the best metal removal percentages for all conditions. The metals recovery percentages increased with the increases of acid concentration, leaching temperature, solid-liquid concentration and leaching time. The optimum leaching condition was obtained at acid concentration of 5 M, leaching temperature of 353 K, solid-liquid ratio of 15 g/*l* and leaching time of 60 min. According to this condition, greater than 92% and 84% of Ni and Co were leached, respectively. The kinetics model of the leaching process of both metals was also explored. It was found that the leaching process of both metals was a second-order reaction with respect to the metal concentration gradient in the solution, and the leaching process was an endothermic reaction. The saturation concentration and kinetics rate constant of both metals were in direct proportion to the operating temperature. The values of the activation energy of Ni and Co were 2.823 kJ/mol and 3.348 kJ/mol, which indicated that the leaching process was controlled by a diffusion process. Furthermore, the saturation concentration, the initial leaching rate and the generalized predictive models of both metals were also evaluated with the second-order leaching rate equation.

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NOMENCLATURE

C_s : saturation concentration of metal [mmol/*l*]
$C_{s,Ni}$: saturation concentration of nickel [mmol/*l*]
$C_{s,Co}$: saturation concentration of cobalt [mmol/*l*]
C_t : metal concentration at time t [mmol/*l*]
k : second-order leaching rate constant [*l*/mmol-min]
k_{Ni} : second-order leaching rate constant of nickel [*l*/mmol-min]
k_{Co} : second-order leaching rate constant of cobalt [*l*/mmol-min]
R : gas constant [kJ/mol·K]
t : leaching time [min]
T : absolute temperature [K]

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