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Reaction kinetics modeling for lithium and cobalt recovery from spent lithium-ion batteries using acetic acid

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Abstract: Lithium and cobalt recovery from spent lithium-ion batteries (LIBs) is a major focus because of their increased production and usage. The conventional method for recycling spent LIBs using inorganic acids produces harmful byproducts. In this work, the leaching agent was substituted with a less expensive and more environmentally friendly alternative—acetic acid—and a mathematical model was developed to describe the kinetics of the recovery process. The variables used were the pH value, temperature, H_2O_2 concentration, and the solid-to-liquid (S/L) ratio. The mathematical model used was the shrinking core model, which was modified to accommodate an equilibrium reaction. The experimental results show that the rate of recovery of Li and Co over time was only affected by temperature. The leaching behaviors of Li and Co were found to oppose each other. An increase in temperature resulted in increased recovery of Li but decreased recovery of Co because of the product-favoring endothermic reaction of Li and the reactant-favoring exothermic reaction of Co. The product of Li has a lower entropy value than the reactant as a free-moving ion, whereas the product of Co leaching has a higher entropy value as a stiff crystal complex. Thus, temperature conditioning is a pivotal factor in the leaching of spent LIBs.

Keywords: spent libs; lithium; cobalt; kinetics; modeling; recovery; equilibrium

1. Introduction

The recovery of valuable metals from spent lithium-ion batteries (LIBs) becomes a more prominent issue every year. Because LIBs have high value as secondary rechargeable batteries, their application in devices ranging from small gadgets such as mobile phones and tablets to large devices such as electric cars has increased over time. With increasing production and waste of LIBs, their recycling and reuse via highly efficient and environmentally friendly processes have become an active research area [1–8].

In the process of recycling LIBs, the most efficient method currently used is hydrometallurgy because it yields highly pure recycled metals, consumes little energy, and emits small amounts of gases [9]. The main process of hydrometallurgy is leaching, where acid is used as a leaching agent to extract metals from the cathode waste of LIBs. Conventionally, the acids used as the leaching agents are inorganic acids such as H_2SO_4, HCl, and HNO_3 [10–12]. However, the use of inorganic acids in the leaching process produces harmful byproducts. To solve this problem, researchers have investigated the use of organic acids as substitute leaching agents with much success. Examples of viable substitutes include malic acid, aspartic acid, oxalic acid, and citric acid [2,13–14].

This study aims to justify the use of acetic acid as an inexpensive and environmentally friendly leaching agent substitute. Acetic acid has been demonstrated to leach heavy metals such as Pb, Cd, Zn, Cr, and Cu over a wide pH range. In this research, using acetic acid to leach Li and Co from spent LIBs is justified [15–16].

The formulation of a mathematical model to better elucidate the kinetics of the leaching process of Li and Co from spent LIBs using acetic acid will be carried out using a solid–liquid reaction model. A solid–liquid reaction generally follows the kinetics described in the conventional shrinking core model developed by Yagi and Kunii in 1955 [17]. In the shrinking core model, the rate-controlling step of the

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reaction can be one of the following:

(a) Diffusion of reactant from the liquid body through the film surrounding the solid particle;

(b) Diffusion of reactant through the ash layer to the surface of the unreacted core;

(c) Reaction at the surface of the unreacted core;

(d) Diffusion of product through the ash layer to the outer surface of the particle; or

(e) Diffusion of product through the film surrounding the particle to the liquid body.

This kinetic model is accurate for most of the solid particle reactions in real life and has been the basis of calculation for solid–liquid reaction kinetics [18–19].

Although the conventional shrinking core model has been proven accurate, in some cases, the model needs to be further modified to increase its accuracy for certain types of leaching reactions [20]. Some examples of leaching reactions modeled using modified shrinking core models are the leaching of gold from gold ore, the leaching of manganese ore, uranium carbonate reactor leaching, and the leaching of nickel from nickel laterite [21–25]. Therefore, in the present work, modification of the shrinking core model is necessary to increase its accuracy.

2. Experimental

2.1. Materials and reagents

Spent LIBs were collected from a local vendor in D.I. Yogyakarta, Indonesia, and were separated from their plastic cases. They were then discharged using salt water for one day. Pliers were used to open the iron cases of the LIBs and remove their cathodes; their binders were then removed manually. Each cathode was scratched from the surface of the aluminum current collector using a spatula. The obtained powders were then heated to 700°C at a speed of 5°C/min, where they were calcined for 4 h to remove the residual carbon. The calcined samples were analyzed using energy-dispersive X-ray spectroscopy (EDX; EDX-8100, Shimadzu, Japan) and inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 8300, Perkin Elmer, USA).

2.2. Metal leaching

The leaching reagent was prepared by mixing glacial acetic acid (100vol%) and pro-analytical H_2O_2 (30vol%), both of which were produced by Merck Inc. The leaching process was conducted in a three-necked flask by mixing 5 g of calcined cathode powder with 500 mL of acetic acid solution with a concentration of 2.8 M (pH 2.09) containing 2vol% of H_2O_2. The sample was then heated using a mantle heater equipped with a reflux condenser and with a stirrer operated at a speed of 400 r/min. Samples were collected at 0, 1, 5, 10, 15, 30, 60, and 120 min during the experiment. The pH value of the acid solution, temperature, H_2O_2 concentration, and the solid-to-liquid (S/L) ratio of the cathode powder to the leaching solution during the leaching process were varied to examine the kinetics of the leaching reaction.

2.3. ICP-AES analysis

The sample preparation was carried out by diluting 0.25 mL of the leachate to 25 mL (100× dilution) using distilled water. The sample was then filtered using a 0.22-μm membrane filter to separate any suspended solid in the filtrate. The filtrate was then analyzed using ICP-AES (Optima 8300, Perkin Elmer, USA) to find the amount of Li and Co recovered by leaching.

2.4. Data analysis and calculation

The data analysis and calculation for this experiment were performed via MATLAB. The method used was minimization of sum of square error (SSE) using Jacobian matrices (lsqnonlin) as the basis of the equation solver.

2.5. Mathematical model

In the leaching of LIB cathodes using acetic acid, the reaction of acetic acid with transition metals such as Co^{2+} ions forms metal complexes [26]. The metal complex product formed from the reaction of Co^{2+} ions and acetate ligands is $Co(CH_3COO)_2·4H_2O$ with an octahedral coordination structure [27–28]. The formation of octahedral metal complexes has been proven to mimic an equilibrium reaction [29]; thus, the complete reaction in the leaching process can be described as

$$LiCoO_{2(s)} \rightleftharpoons Li^+_{(aq)} + Co^{3+}_{(aq)} + 2O^{2-}_{(aq)} \tag{1}$$

$$\begin{aligned} &CoCo^{3+}_{(aq)} + 2OCo^{2-}_{(aq)} + H_2O_{2(aq)} + 2H^+ \rightarrow \\ &\quad Co^{2+}_{(aq)} + 2H_2O_{(l)} + O_{2(g)} + e^- \end{aligned} \tag{2}$$

$$Co^{2+}_{(aq)} + 2CH_3COO^-_{(aq)} \rightleftharpoons [Co(CH_3COO)_2]_{(aq)} \tag{3}$$

In describing the kinetic reaction, the mathematical model used is the equilibrium-based shrinking core model. The model is based on the following assumptions:

(1) The reactant was stirred at a speed that prevented film formation;

(2) The pretreatment already eliminated any inert material that can form an ash layer;

(3) The particles used in the reaction were fine particles with uniform particle distribution;

(4) The reaction was pseudo-homogeneous because of the uniform particle size and good particle dispersion.

2.5.1. Equilibrium reaction rate

The equation for calculating the reaction rate was derived from Eqs. (1) and (3). These reactions are simplified to

$$\text{Reactant} \rightleftharpoons \text{Product} + \text{Side product} \tag{4}$$

where the product of reaction (1) is Li^+ and the product of reaction (3) is $Co(CH_3COO)_2$.

The rate of equilibrium reaction in this experiment can be split into two parts:

(1) Rate of forward reaction. On the basis of the simplified reaction, the rate of forward reaction in this experiment can be defined as

$$-r_{Rf} = k_f C_R^m = k_f (C_{R0} - C_{R0} X_R)^m \tag{5}$$

$$-r_{Rf} = k_f C_{R0}^m (1 - X_R)^m \tag{6}$$

For one mole of reactant, $C_{R0} = 1$ mol/L; thus,

$$-r_{Rf} = k_f (1 - X_R)^m \tag{7}$$

where $-r_{Rf}$ is the rate of forward reaction, s^{-1}; C_R is the reactant concentration, mol/L; C_{R0} is the initial reactant concentration, mol/L; k_f is the reaction rate constant of forward reaction, s^{-1}; X_R is the fractional conversion of reactant, and m is the forward reaction order.

(2) Rate of backward reaction. On the basis of the simplified reaction, the rate of the backward reaction in this experiment can be expressed as

$$-r_P = k_b (C_P)^n \tag{8}$$

where C_P is the concentration of product. The backward reaction rate in Eq. (8) can be expressed by the rate of reforming of reactant and can be defined as

$$r_{Rb} = -k_b C_{R0}^n X_R^n \tag{9}$$

For the one mole of reactant, $C_{R0} = 1$ mol/L. Thus,

$$r_{Rb} = -k_b X_R^n \tag{10}$$

where $-r_P$ is the rate of product consumption, mol/s; r_{Rb} is the rate of backward reaction, s^{-1}; k_b is the reaction rate constant of backward reaction, s^{-1}; X_R is the fractional conversion of reactant; and n is the backward reaction order.

The total reaction rate of this experiment can be derived by combining the rates of the forward and backward reactions. The resultant equation is defined as

$$(-r_{Rf}) + r_{Rb} = k_f \left(1 - X_R\right)^m - k_b X_R^n \tag{11}$$

The total reaction rate is the rate of conversion of reactant over time, which can be defined as

$$\frac{dX_R}{dt} = k_f \left(1 - X_R\right)^m - k_b X_R^n \tag{12}$$

where $\frac{dX_R}{dt}$ is the rate of fractional conversion of reactant over time, s^{-1}; and k_f is the reaction rate constant of forward reaction, s^{-1}.

2.5.2 Reaction kinetic parameters

The Arrhenius equation was used to evaluate the kinetics of the leaching reaction. The equations used to measure the parameters in this process are as follows [30]:

$$k_f = A_f \exp\left(-\frac{E_{Af}}{R_g T}\right) \tag{13}$$

$$k_b = A_b \exp\left(-\frac{E_{Ab}}{R_g T}\right) \tag{14}$$

Eqs. (13) and (14) can be linearized and defined as

$$\ln k_f = \ln A_f - \frac{E_{Af}}{R_g T} \tag{15}$$

$$\ln k_b = \ln A_b - \frac{E_{Ab}}{R_g T} \tag{16}$$

where A_f is the Arrhenius constant of forward reaction, s^{-1}; A_b is the Arrhenius constant of backward reaction, s^{-1}; E_{Af} is the activation energy of forward reaction, J/(mol·K); E_{Ab} is the activation energy of backward reaction, J/(mol·K); R_g is the universal gas constant, J/(mol·K); and T is the temperature of reaction, K.

2.5.3 Equilibrium constant

The equilibrium constant in the leaching reaction was determined using the following basic equilibrium equation:

$$K = \frac{\Pi[\text{Product}]^j}{\Pi[\text{Reactant}]^i} \tag{17}$$

The geometric sum of the reactant and product can be defined using the reaction rate equation; thus Eq. (17) becomes

$$K = \frac{\left(r_{Rb}/k_b\right)}{\left[(-r_{Rf})/k_f\right]} \tag{18}$$

In the equilibrium reaction state, the rates of the forward and backward reactions are equal to each other; thus, the equilibrium equation can be further simplified as

$$K = \frac{k_f}{k_b} \tag{19}$$

where K is the equilibrium constant of the leaching reaction.

2.5.4 Thermodynamic parameters

Achieving better understanding the reaction kinetics in the leaching process for purposes of process reproduction and scaling up requires evaluation of the thermodynamics parameters of the reaction. The basic parameters evaluated in this experiment are as follows [31]:

(1) Reaction enthalpy. Reaction enthalpy is the difference in energy level between the reactant and the product, which can be defined using the following equation:

$$\Delta H_{\rm r} = E_{\rm Af} - E_{\rm Ab} \tag{20}$$

where $\Delta H_{\rm r}$ is the enthalpy of reaction, J/mol.

(2) Gibbs free energy. The Gibbs free energy is the amount of energy produced by the reaction that can be converted into work. The relation between the equilibrium constant and the Gibbs free energy is defined as

$$-\Delta G^{\ominus} = R_{\rm g} T \ln K \tag{21}$$

where $\Delta G^{\ominus}$ is the standard Gibbs free energy change, J/mol.

(3) Reaction entropy. Entropy describes the change in the degree of disorder in a reaction. The value of reaction entropy can be defined using the following equation of state:

$$\Delta S_{\rm r} = -\frac{\Delta G^{\ominus} - \Delta H_{\rm r}}{T} \tag{22}$$

where $\Delta S_{\rm r}$ is the entropy of reaction, J/(mol·K).

3. Results and discussion

3.1. Leaching efficiency of Li

The experimental results related to the leaching efficiency of Li at various pH levels, temperatures, H_2O_2 concentrations, and S/L ratios is shown in Fig. 1 in the form of the recovery of Li in the resultant leachate over time.

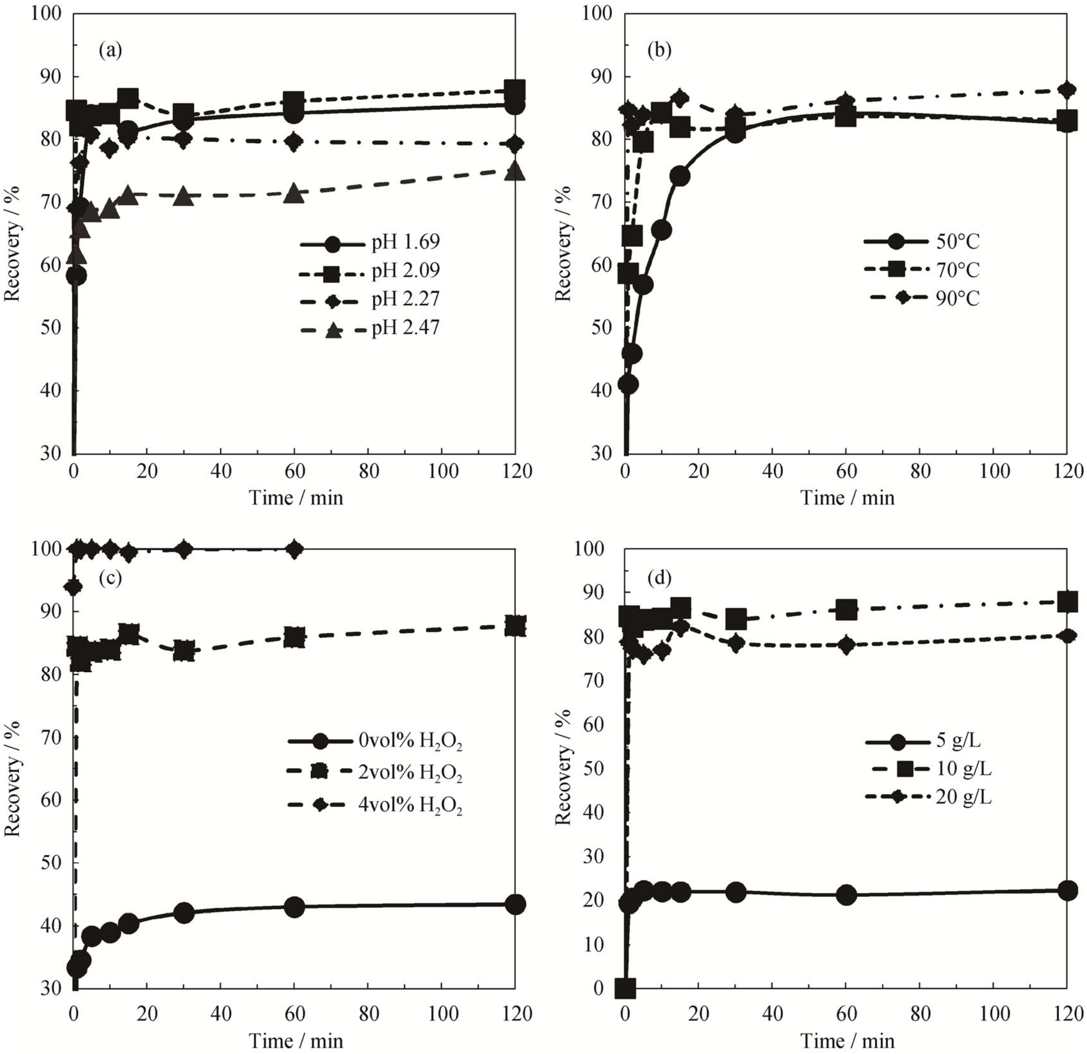

Fig. 1. Recovery of Li at various (a) pH levels, (b) temperatures, (c) H_2O_2 concentrations, and (d) S/L ratios.

Fig. 1 shows that changes in the pH value, H_2O_2 concentration, and S/L ratio resulted in increased resulting recovery of Li, which is the recovery of Li at the end of the experiment (120 min), but did not substantially affect the rate of recovery of Li over time (as indicated by the time required to achieve the maximum recovery of Li). In Fig. 1(a), the resulting recovery of Li increased with decreasing pH value and reached a maximum at pH 2.09, with a resulting recovery of 87.85%. The lower resulting recovery of Li at pH 1.69 was caused by the saturation of acetic acid that covered the surface of the cathode powder ($LiCoO_2$) and hindered desorption of the leaching product.

Fig. 1(b) shows that an increase in temperature increased the rate of recovery of Li but only slightly increased the resulting recovery. The time required to achieve the maximum recovery of Li decreased from 60 min at 50°C to 10 min at 90°C. The same behavior was also observed in the leaching of spent LIBs using inorganic acids such as H_2SO_4 and HCl and also using organic acids such as malic acid, aspartic acid, and citric acid. These results show that the leaching reaction was controlled by a surface reaction [2,9,32].

The resulting recovery of Li increased only approximately 5%, from 82.61% to 87.85%, when the temperature was increased by 40°C. Although insignificant, the increase in the resulting recovery with increasing temperature is a distinctive feature of endothermic reactions [31].

As shown in Fig. 1(c), with increasing H_2O_2 concentration in the leaching solution, the resulting recovery of Li increased. This phenomenon indicates that, although H_2O_2 mainly functions as a reducing agent for Co ions, the increase in the rate of reduction of Co also enables Li^+ ions to more easily desorb into the liquid body.

Fig. 1(d) shows that increasing the S/L ratio increased the resulting recovery of Li until it reached a maximum of 83.58% at an S/L ratio of 10 g/L. At an S/L ratio of 20 g/L, the resulting recovery of Li decreased because insufficient acetic acid was available to react with the cathode powder.

3.2. Leaching efficiency of Co

The experimental results of the leaching of Co at various pH levels, temperatures, H_2O_2 concentrations, and S/L ratios are shown in Fig. 2 in the form of the recovery of Co in the resulting leachate over time.

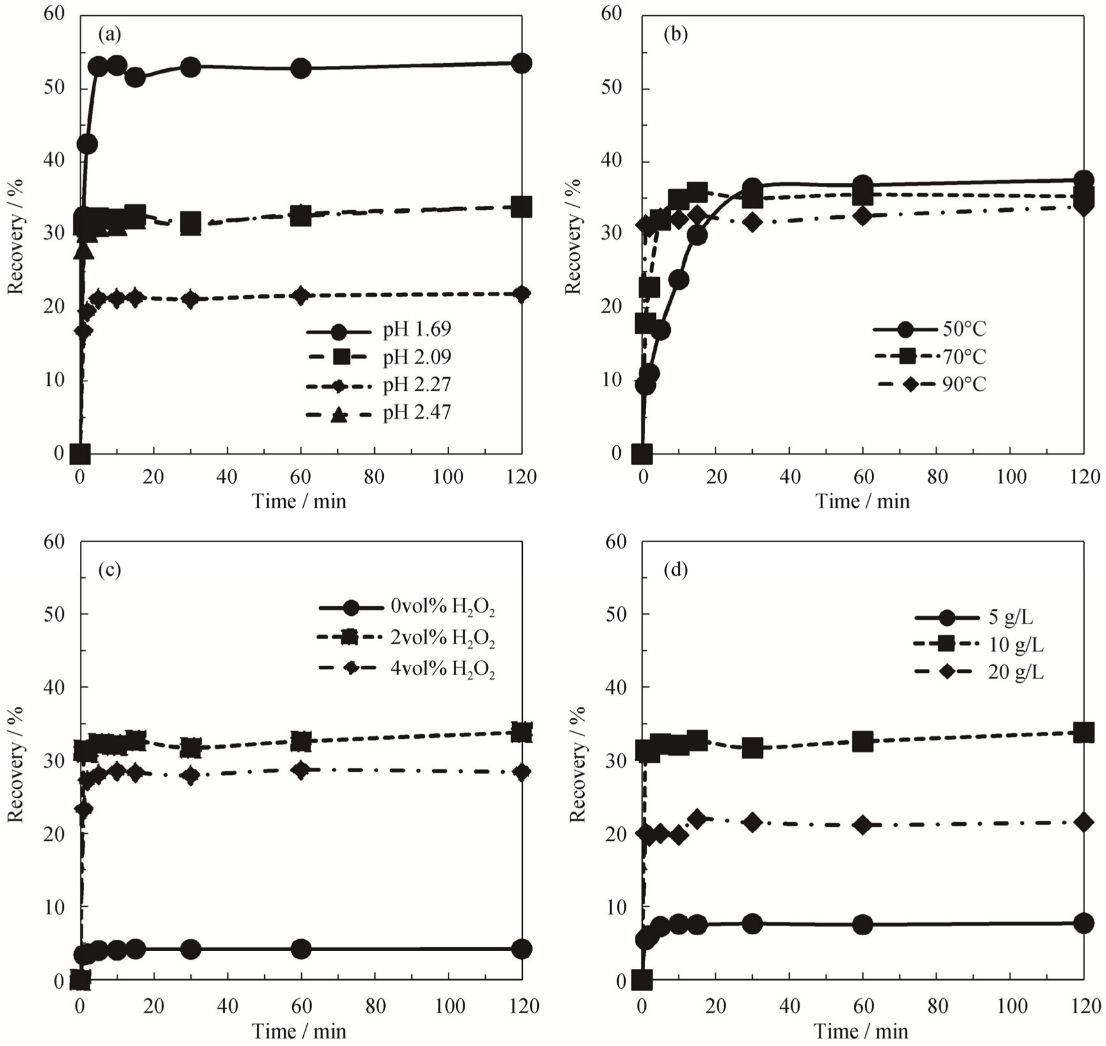

Fig. 2. Recovery of Co at various (a) pH levels, (b) temperatures, (c) H_2O_2 concentrations, and (d) S/L ratios.

Fig. 2 shows that pH value, H_2O_2 concentration, and S/L ratio, although contributed to the increase in the resulting recovery of Co (i.e., the recovery of Co at the end of the experiment, which was conducted for approximately 120 min), did not substantially affect the rate of recovery (i.e., the time needed to reach the maximum recovery of Co). Fig. 2(a) shows that, with decreasing leaching pH value, the resulting recovery of Co increased. Unlike the resulting recover of Li, the resulting recovery of Co still increased at pH 1.67 because of the lower affinity of the complex reaction of Co and acetic acid compared with that of the ionization reaction of Li.

Fig. 2(b) shows that increasing temperature increased the rate of recovery of Co but only slightly increased the resulting recovery. The time needed to achieve the maximum recovery decreased from 30 min at 50°C to 5 min at 90°C. The same behavior was also observed in the leaching process of spent LIBs using inorganic acids such as H_2SO_4 and HCl and also organic acids such as malic acid, aspartic acid, and citric acid. These results show that the leaching reaction of Co was controlled by a surface reaction [2,9,32]. The resulting recovery decreased from 37.84% to 33.80%. Although insignificant, this decrease in recovery with increasing temperature shows that the reaction is exothermic [31].

In Fig. 2(c), the resulting recovery of Co increased with increasing H_2O_2 concentration, which peaked at 2vol% H_2O_2 with a resulting recovery of 35.42%. However, at 4vol% H_2O_2, the recovery of Co decreased. We attributed this decrease to the presence of peracetic acid, which is a strong oxidizing agent produced by the following reaction:

$$\mathrm{CH_3COOH_{(aq)}} + \mathrm{H_2O_{2(aq)}} \rightleftharpoons \mathrm{CH_3COOOH_{(aq)}} + \mathrm{H_2O_{(l)}} \tag{23}$$

Peracetic acid reoxidized the Co ions reduced by H_2O_2, resulting in the formation of a solid.

Fig. 2(d) shows that the recovery of Co increased with increasing S/L ratio and peaked at 10 g/L, with a recovery of 35.42%; however, the recovery decreased at 20 g/L because of the saturation of solid reactant, which could not react because of insufficient acetic acid.

3.3. Reaction kinetic parameters

The reaction kinetic parameters were calculated and fitted using MATLAB with iteration. The results of the data processing for Li and Co are shown in Figs. 3 and 4.

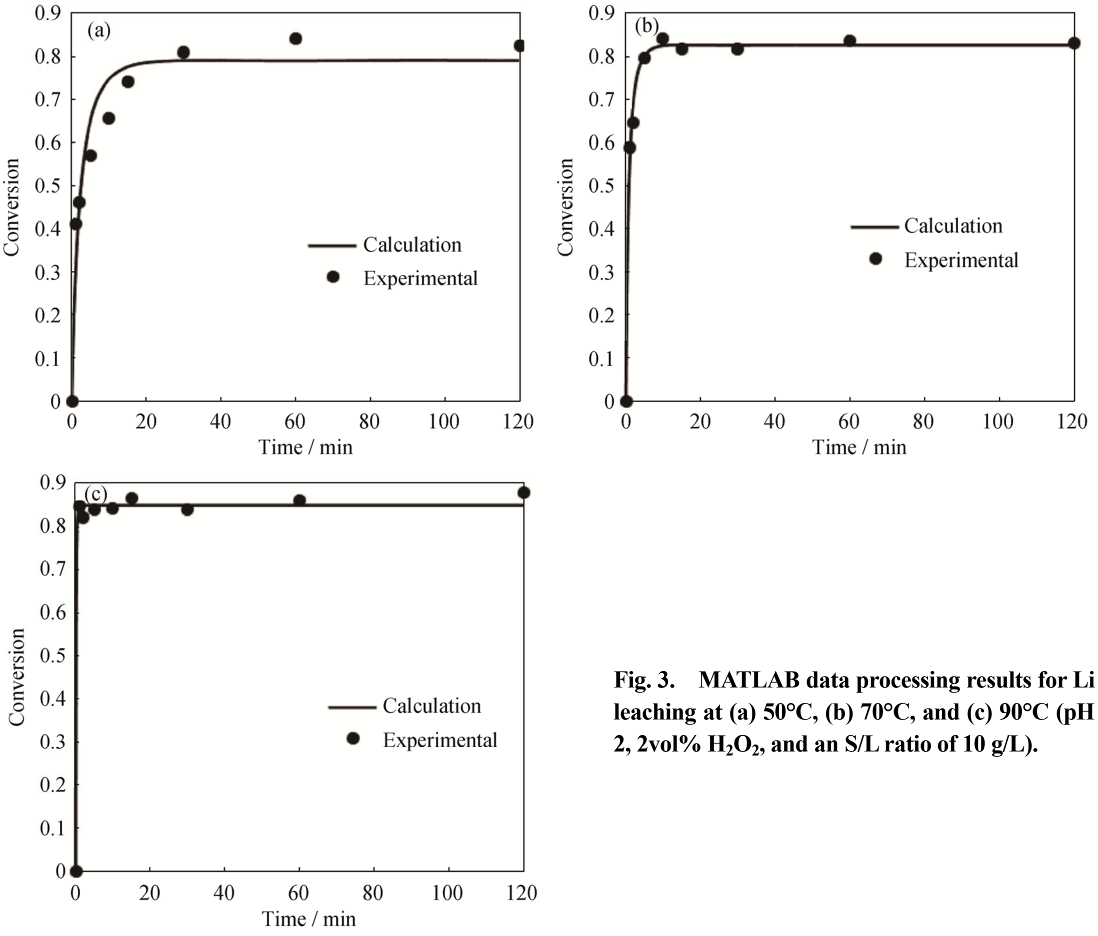

Fig. 3. MATLAB data processing results for Li leaching at (a) 50°C, (b) 70°C, and (c) 90°C (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L).

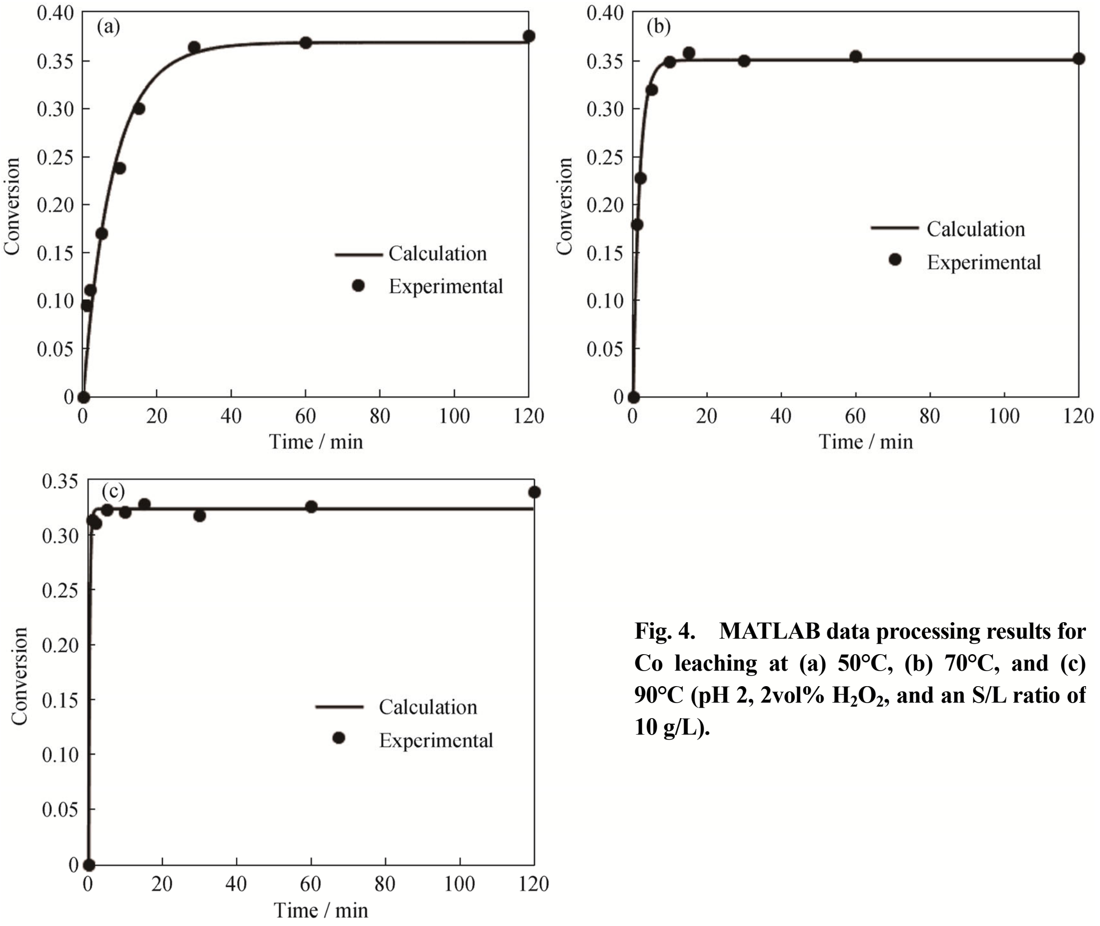

Fig. 4. MATLAB data processing results for Co leaching at (a) 50°C, (b) 70°C, and (c) 90°C (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L).

The data processing results in Figs. 3 and 4 indicate that the calculation results do not substantially deviate from the data obtained from the experiments, which means that the kinetics model sufficiently represents the reaction kinetics in the leaching experiments. The results of the calculations of the kinetics parameters for leaching of Li and Co are summarized in Tables 1 and 2.

The calculation results show that, with increasing temperature, the rate of recovery also increased, as indicated by an increase in the leaching reaction rate constant. With an increase in both the forward and backward reaction rates, the process will reach equilibrium within a shorter time. This phenomenon is consistent with the Arrhenius rate law, which states that an increase in temperature will increase the rate of a reaction [33]. The rate constant for Li leaching is substantially greater than that for Co leaching, indicating that the overall surface reaction favors the leaching of Li.

Table 1. Kinetic parameters for the leaching reaction of Li (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L)

Temperature / °C	A_f	E_{Af} / (J·mol^{-1})	A_b	E_{Ab} / (J·mol^{-1})	k_f / (L^2·mol^{-1}·s^{-1})	k_b / (L^2·mol^{-1}·s^{-1})
50	1.6869×10^{13}	8.4801×10^4	1.4113×10^9	6.7394×10^4	0.4282	0.0236
70					1.2782	0.0468
90					13.4624	0.3626

Note: Forward reaction order = 2, backward reaction order = 1.

Table 2. Kinetic parameters for the leaching reaction of Co (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L)

Temperature / °C	A_f	E_{Af} / (J·mol^{-1})	A_b	E_{Ab} / (J·mol^{-1})	k_f / (L^2·mol^{-1}·s^{-1})	k_b / (L^2·mol^{-1}·s^{-1})
50	1.9256×10^{11}	7.8125×10^4	2.4289×10^{12}	8.4758×10^4	0.0484	0.0524
70					0.2174	0.2617
90					1.1819	1.6764

Note: Forward reaction order = 2, backward reaction order = 1.

The order of reaction was obtained purely as an experimental value [18]. The order of the forward reaction is 2, which means that the forward reaction will increase proportionally with the square of the reactant concentration. By contrast, the order of the backward reaction is 1, indicating that the backward reaction rate will increase proportionally with the concentration of reactant.

3.4. Thermodynamic parameters

The calculation results related to the values of thermodynamic parameters in the leaching of Li and Co are shown in Tables 3 and 4.

Table 3. Thermodynamic parameters for the leaching reaction of Li (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L)

Temperature / °C	K	ΔH / (J·mol^{-1})	ΔG / (J·mol^{-1})	ΔS / (J·mol^{-1}·K^{-1})
50	18.1645	1.7407×10^4	-7.7900×10^3	77.9722
70	27.2966		-9.4340×10^3	78.2188
90	37.1235		-1.0912×10^4	77.9816

Table 4. Thermodynamic parameters for the leaching reaction of Co (pH 2, 2vol% H_2O_2, and an S/L ratio of 10 g/L)

Temperature / °C	K	ΔH / (J·mol^{-1})	ΔG / (J·mol^{-1})	ΔS / (J·mol^{-1}·K^{-1})
50	0.9241	-6.6328×10^3	2.1210×10^2	−21.1818
70	0.8307		5.2930×10^2	−20.8715
90	0.7051		1.0551×10^3	−21.1700

In the leaching of Li, the value of K increases with increasing temperature, demonstrating that an increase in temperature will favor the forward reaction of Li and that the resulting product of recovery will be rich in the product of the Li reaction. For Co, the equilibrium constant is less than 1, which indicates that the reaction in the leaching of Co favors regeneration of the reactant. An increase in temperature further lowers the value of K, which means that the backward reaction rate increases more than the forward reaction rate with increasing temperature. Thus, in the leaching of Co, the resulting recovery of Co will be low [18,30–31].

The enthalpy of the Li reaction shows that the reaction is endothermic, which explains the increase in the resulting recovery of Li with increasing temperature. The resulting recovery of Co, which decreased with increasing temperature, is explained by this reaction being exothermic, as indicated by the value of the reaction enthalpy for the leaching of Co [31,34–36].

The value of the standard Gibbs energy for the leaching reaction of Li is a negative value, which shows that the reaction was spontaneous, with no need for an influx of energy for the reaction proceeding. The standard Gibbs energy of the leaching of Co, however, is a positive value, which means that the reaction is nonspontaneous and energy is needed for the reaction to proceed. This energy was likely provided by another reaction during the leaching process [30–31].

The positive value of entropy for the leaching reaction of Li indicates that the reaction of Li produces a species more disorderly than the reactant. This result confirms the hypothesized reaction in which Li produces Li^+ ions, which is a species that can move freely. However, the entropy of the Co reaction is negative, indicating that the product of the leaching reaction of Co is a species that moves less freely than the reactant. As previously postulated, the leaching product of Co is an octahedral complex molecule $Co(CH_3COO)_2·4H_2O$. The Co in these molecules is more orderly than the Co in the reactant because it is bound by two acetate ligands and water molecules that restrict its movement [27–28,31].

The calculation results obtained with the parameters in Tables 3 and 4 show that the leaching reactions of Li and Co exhibit opposite behaviors when subjected to an increase in temperature. Thus, temperature is a critical factor in the leaching process of spent LIBs using acetic acid. The difference in temperature will decide the resulting recovery Li or Co in which a high temperature will favor Li and a low temperature will favor Co.

4. Conclusions

The results of the experiments conducted in this work lead to the conclusion that, in the leaching of Li and Co, numerous factors, including the pH value, temperature, H_2O_2 concentration, and S/L ratio, affect the resulting recovery to various degrees. However, only temperature strongly affects the rate of recovery. With increasing temperature, the leaching behaviors of Li and Co contradict each other: the resulting recovery of Li increases, whereas that of Co decreases. This difference in behavior is attributed to the reaction of Li being endothermic, favoring the formation of product, and that of Co being exothermic, favoring the formation of reactant. The product of Li leaching has a lower entropy value than the reactant because it moves more freely as an ion; by contrast, the product of Co leaching has a higher entropy value because of its stiff crystal complex structure. These factors make the temperature conditioning a pivotal factor in the leaching of spent LIBs.

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