



## Research article

# Leaching of valuable metals from cathode active materials in spent lithium-ion batteries by levulinic acid and biological approaches

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## ARTICLE INFO

## Keywords:

Spent lithium-ion batteries

Cathode active materials

Levulinic acid

Valuable metals

Bioleaching

*Acidithiobacillus ferrooxidans*

## ABSTRACT

Recycling of valuable metals from spent lithium-ion batteries (LIBs) is of paramount importance for the sustainable development of consumer electronics and electric vehicles. This study comparatively investigated two eco-friendly leaching methods for recovering Li, Ni, Co, and Mn from waste NCM523 ( $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ) cathode materials in spent LIBs, i.e., chemical leaching by a green organic solvent, levulinic acid (LA) and bioleaching by an enriched microbial consortium. In chemical leaching, mathematical models predicting leaching efficiency from liquid-to-solid ratio (L/S; L/kg), temperature ( $^{\circ}\text{C}$ ), and duration (h) were established and validated. Results revealed that LA of 6.86 M was able to achieve complete leaching of all target metals in the absence of reductants at the optimal conditions (10 L/kg, 90  $^{\circ}\text{C}$ , and 48 h) identified by the models. The evaluation of direct one- and two-step and indirect bioleaching indicated that the latter was more feasible for metal extraction from waste NCM523. L/S was found to impact the indirect bioleaching most significantly among the three operating variables. Pretreatment of waste NCM523 by washing with 1 vol% methanesulfonic acid significantly improved indirect bioleaching. The side-by-side comparison of these two leaching approaches on the same cathode active material (CAM) thus provided the technical details for further comparison with respect to cost and environmental impact.

## 1. Introduction

The worldwide emerging electric vehicles (EVs) industries and ongoing developments in consumer electronics are driving the growth of the blossoming lithium-ion battery (LIB) market. The global market size of LIBs was valued at \$41.97 billion in 2021 and its compound annual growth rate (CAGR) from 2022 to 2030 is estimated to be 18.1% [1]. However, a global supply shortage of critical metals (e.g., Li, Ni, Co) and geographical factors pose risks for LIB production [2]. Therefore, recycling of spent LIBs to recover key elements is considered as an ideal method for solving this issue. Due to technical, economic, and other factors, less than 5% of spent LIBs are collected and recycled nowadays. A few regions across the globe, such as East Asia and Europe, have accelerated implement of

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Received 16 March 2023; Received in revised form 20 April 2023; Accepted 21 April 2023

Available online 27 April 2023

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LIB recycling processes. The global LIB recycling market is expected to expand at a CAGR of 21.3% from 2022 to 2029 [3]. Hence, establishing efficient and cost-effective LIB recycling techniques is of utmost importance to feed the rapidly developing LIB recycling industry.

Generally, LIB recycling processes can be divided into pyrometallurgical and hydrometallurgical approaches [4,5]. The pyrometallurgical processes are popular in the industry [6], largely due to their simplicity and easiness for operation. However, they also possess obvious drawbacks, such as low recovery efficiency, intensive energy consumption, and toxic gas and dust release [7,8]. In contrast, the hydrometallurgical processes are more promising and their use has been increasing, especially for LIBs, which have been extensively examined in the academia [9,10] in light of their advantages, including higher recovery efficiency and lower energy consumption [11]. For instance, strong inorganic acids, e.g., HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, could achieve almost 99% recovery of Li and Co [12–14]. Toxic gases such as Cl<sub>2</sub>, NO<sub>x</sub>, and SO<sub>x</sub>, however, would be unavoidably generated during the recovery process using inorganic acids [4,15,16]. Other disadvantages include high safety risks and strict operational conditions [17].

To avoid these drawbacks associated with inorganic acids, hydrometallurgy using organic acids for metal recovery from LIBs has attracted significant interest. Numerous organic acids have been investigated for LIB recycling, such as aspartic acid [18], citric acid [19], formic acid [20], lactic acid [21], DL-malic acid [18], methanesulfonic acid (MSA) [11], oxalic acid [22], succinic acid [23], and L-tartaric acid [24]. For example, 1.25 M citric acid has been used to leach Li and Co from cathode active material (CAM), LiCoO<sub>2</sub> in the presence of 1 vol% H<sub>2</sub>O<sub>2</sub> [19]. Under the optimal conditions of 90 °C and 50 L/kg liquid-to-solid ratio (L/S), 99% of Li and 91% of Co were recovered within 30 min.

As a branch of hydrometallurgy, bio-hydrometallurgy (i.e., bioleaching) utilizes microorganisms and their metabolites to extract metals from various sources, such as ores and waste materials. The main microorganisms widely used in the bioleaching are two autotrophic and acidophilic bacteria, namely, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*, and a fungus, i.e., *Aspergillus niger*. Based on whether the microbes are in direct contact with the leachable solids, bioleaching is divided into direct and indirect leaching. Direct bioleaching involves the direct contact of the microbial culture with the solids, in which the solubilization of metals is achieved directly by the metabolism of leaching microbes. While in the indirect bioleaching process, contact among the microbes and solids is not required. In this case, metals are solubilized indirectly by the products of microbial metabolism. Direct leaching is further divided into one-step and two-step. In both cases, the leaching microorganisms are exposed to the solids. For direct one-step bioleaching, the leachable solids are added at the beginning of the microbial cultivation, while for two-step, the solids are added once the culture reaches certain density. Indirect bioleaching is also referred to as leaching by cell-free spent-medium where microbial growth and leaching are decoupled [25,26]. Both direct and indirect bioleaching have been investigated in recovery of valuable metals from spent LIBs [26–33].

Both organic acid-based hydrometallurgy and bioleaching for LIB recycling are eco-friendly, energy- and cost-efficient. For example, a life cycle assessment (LCA) study estimated that organic acid leaching using formic acid and bioleaching emitted 32.9 and 27.9 kg CO<sub>2</sub> equivalents to recycle 1 kg of CAM, respectively, which were much lower than alkali leaching by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (67.5 kg CO<sub>2</sub>-equiv/kg CAM) [34]. However, previous studies also reported both approaches had some limitations. For instance, the reductant (e.g., H<sub>2</sub>O<sub>2</sub>) was usually needed for the organic acid leaching with CAMs, the absence of which could largely decrease the extraction efficiency [35]. Moreover, high L/S (≥50 L/kg) were generally required for efficient organic acid leaching in previous studies [11,19,21]. Regarding bioleaching, slow kinetics has been recognized as one of the significant disadvantages. For example, the processing time for bioleaching with CAMs using *A. niger* ranged from 8 to 40 d [26,31–33].

To overcome these limitations, this work applied levulinic acid (LA) in the absence of reductants to leach Li, Ni, Co, and Mn from CAMs of spent LIBs, with much lower L/S. LA is a green and biodegradable organic acid and has been used to recover rare earth elements from waste materials, such as bauxite residue and spent fluorescent lamp phosphors [36,37]. Use of LA for LIB recycling has not been reported. In this study, mathematical models predicting leaching efficiency in response to L/S, temperature, and duration by the Box-Behnken design were developed. Employing these models, we identified the optimal conditions for reaching the maximal leaching efficiency. These optimal conditions were then verified by experimental studies. In addition to leaching by LA, we investigated the leaching behavior of a microbial consortium enriched from activated sludge. The bioleaching was conducted in three modes: direct one-step and two-step and indirect by using the spent medium.

## 2. Materials and methods

### 2.1. Chemicals and cathode active material preparation from spent LIBs

Levulinic acid (>98%), nitric acid (68–70%), hydrochloric acid (36.5–38%), sulfuric acid (95–98%), sodium hydroxide (98.8%), and potassium carbonate (99%) were purchased from Fisher Scientific (Waltham, MA, USA). MSA (>98%) was provided by Alfa Aesar (Haverhill, MA, USA). All water used was with ultrapure grade, which was obtained from a Millipore ultrapure water system. All reagents were used as supplied without any further purification.

The spent LIBs were collected from the university campus by the Office of Environmental Health & Safety of University at Albany, SUNY and offered to us. To acquire CAMs, the spent LIBs were first discharged by soaking in a 5 wt% K<sub>2</sub>CO<sub>3</sub> solution for 24 h, followed by manual dismantling to remove plastics and steel cases. The cathode aluminum (Al) foils were separated and cut into small pieces, which were then immersed in a 10 wt% NaOH solution for 5 h under mild stirring to separate CAMs and Al foils. The wet CAM residues were collected and rinsed by water, followed by calcination at 610 °C for 5 h in a muffle furnace to remove impurities (e.g., carbon black and PVDF binder) [21,38,39]. The obtained CAMs were ground using a mortar and pestle and screened with a 63 μm sieve. The powders smaller than 63 μm (Fig. S1) were collected for following experiments.

## 2.2. Chemical leaching using levulinic acid and Box-Behnken design for modeling

Leaching experiments using LA were performed in 20 mL closed glass vials. Three influential parameters, namely L/S, temperature (T), and duration (D), were investigated in the leaching experiments and included in the Box-Behnken design for modeling. In the leaching experiments, a certain mass of CAMs was added into the LA lixiviant with a certain concentration to reach the desired L/S. The reaction then proceeded under a magnetic stirring at 500 rpm and the designed temperature for a certain period of time. The pregnant leach solution (PLS) was filtrated through a 0.45  $\mu\text{m}$  polyester syringe filter at the end of experiments and the metal contents in the filtrate were quantified. The leaching efficiency under four LA concentrations, i.e., 0.98, 2.94, 4.90, and 6.86 M, were evaluated at 90 °C and an L/S of 10 L/kg for 48 h, and the concentration resulting in the highest efficiency was selected for experiments of Box-Behnken design. For each parameter, three coded levels, i.e., low (−1), middle (0), and high (+1), were examined within the ranges of 10–30 L/kg for L/S, 50–90 °C for temperature, and 24–72 h for duration [37] (Table 2). Leaching efficiency (% L), which was the response, was quantified by Equation (1):

$$\% L = \frac{m_l}{m_i} \times 100 \quad (1)$$

where  $m_l$  and  $m_i$  are the weight of the dissolved metal in the leachate and in the original CAMs, respectively. The Design-Expert software (Stat-Ease Inc., Minneapolis, MN, USA) was used to design the three-factor and three-level experiments, and to generate the second polynomial models (Equation (2)):

$$Y = \beta_0 + \sum \beta_i \chi_i + \sum \beta_i \chi_i^2 + \sum \beta_{ij} \chi_i \chi_j \quad (2)$$

where  $Y$  and  $\beta$  are the predicted response and coefficient, respectively, while  $\chi_i$  and  $\chi_j$  are coded levels of variables  $i$  and  $j$ , respectively. The statistical analysis of models and the quantification of variable significance were conducted by ANOVA (analysis of variance) and Fisher's  $F$ -test, respectively.

## 2.3. Enrichment of microbial consortium from WWTP activated sludge

The AS inoculum for microbial consortium enrichment was collected from a local municipal WWTP in the Capital Region of New York, USA. The ATCC 2039 A. *ferrooxidans* medium was used to enrich the consortium, which contained 0.8 g/L  $(\text{NH}_4)_2\text{SO}_4$ , 2 g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.4 g/L  $\text{K}_2\text{HPO}_4$ , 20 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 5 mL/L Wolfe's mineral solution [40]. The pH of the medium was adjusted by 0.5 M  $\text{H}_2\text{SO}_4$  or NaOH solutions. The enrichment was accomplished by three cycles. For the first cycle, 100 mL of ATCC 2039 medium and 20 mL of fresh AS were added to a 250 mL Erlenmeyer flask, which were incubated constantly at 28 °C and 140 rpm for 96 h. For the second and third cycles, 100 mL of fresh medium and 20 mL of culture from the prior cycle were mixed in the flasks and incubated at the same conditions for 108 or 120 h. After three cycles of enrichment, an autotrophic, aerobic, and acidophilic microbial consortium with a reddish-brown color was obtained (Fig. S2), which thrive at the pH of 2.5. Glycerol-frozen stock of the enriched consortium was prepared and stored at −80 °C for use in the bioleaching.

## 2.4. Direct and indirect bioleaching

Direct one- and two-step bioleaching by the enriched microbial consortium were performed to evaluate the feasibility of metal recovery from CAMs. In one-step bioleaching, CAMs were added together with the microbial inoculum into 250 mL Erlenmeyer flasks containing fresh ATCC 2039 medium in the beginning, followed by incubation at 28 °C and 140 rpm. The L/S was 200 L/kg (0.5% pulp density, w/v) and the leaching duration was 7 d. In two-step bioleaching, the microbial consortium was first inoculated into fresh medium and incubated at 28 °C and 140 rpm. CAMs were added at the exponential growth phase of the actively growing cultures with an L/S of 20 L/kg (5% pulp density, w/v), and the incubation continued at the same conditions for 24 h. The pH values were monitored routinely through the direct one- and two-step bioleaching processes.

Considering CAMs' high pH and potentially adverse effects on the microbial community, indirect spent-medium bioleaching was also examined in this study. To obtain the cell-free spent medium, the cultures at the stationary phase were centrifuged, followed by vacuum filtering the supernatant through a 0.45  $\mu\text{m}$  membrane. All spent medium used in this study was from the same batch, the pH of which was 2.36. The indirect bioleaching was performed under the conditions of three-level L/S (i.e., 10, 18, 100 L/kg), temperature (i.e., 30, 60, 90 °C), and duration (i.e., 1, 12.5, 24 h).

Furthermore, to reduce the impact of high pH on bioleaching, CAM powders were pretreated by washing with different combinations of water, spent medium, 0.1 or 1 vol% MSA, and 1 or 10 vol% LA, the original pH of which were shown in Table S1. One-, two-, or three-step washes with different reagents were performed, as shown in Table S2. The metal contents in the washing effluent after each wash step were measured to quantify the metal loss in the washing process. The washed CAMs were also conducted with indirect spent-medium bioleaching under 90 °C and different combinations of various L/S (i.e., 10, 20, 125, 200 L/kg) and durations (i.e., 0.5, 0.8, 1.2, 5, 10 h).

## 2.5. Quantification of valuable metals in leachate and original CAMs

Four major valuable metals, i.e., Li, Ni, Co, and Mn, were analyzed in this study. The CAM solids were completely digested using the

EPA method 200.7 [41] for analyses of original metal contents [37]. Briefly, 4 mL of two-fold diluted HNO<sub>3</sub> and 10 mL of five-fold diluted HCl were added to a beaker containing 1 g of CAMs, followed by covering the beaker lip with a watch glass and heating the beaker constantly at ca. 95 °C for 30 min for reflux extraction. The extract was then quantitatively diluted to 100 mL and filtered through a 0.45 μm polyester syringe filter. The metal concentrations in the PLS and acid digestion extract were quantified by an inductively coupled plasma optical emission spectroscopy (ICP-OES; PerkinElmer Optima 3300 DV, Shelton, CT, USA).

## 2.6. Analysis of morphology and crystallinity of solids

The morphology and crystallinity of CAM powders before and after chemical and biological leaching were analyzed to better understand and compare the two leaching processes. The morphological analysis was performed by a scanning electron microscope (SEM, Zeiss LEO 1550, Oberkochen, Germany) and the crystal structures were inspected by a Rigaku MiniFlex 6G benchtop powder X-ray diffractometer (XRD, Rigaku Corporation, Tokyo, Japan) using Cu-Kα radiation. Four solids were examined, i.e., the original spent CAM powders, the solid residues after leaching by 6.86 M LA at the conditions of 10 L/kg, 50 °C, and 24 h, and the residual one-step and two-step 1 vol% MSA washed CAMs after indirect bioleaching under 200 L/kg, 90 °C, and 5 h.

## 3. Results and discussion

### 3.1. Chemical leaching of valuable metals from CAMs using levulinic acid

#### 3.1.1. Quantification of valuable metals in CAMs and the effect of LA concentration on leaching of metals

Layered LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> (NCM; x + y + z = 1) have become the most widely used CAMs in LIBs [24], making Li, Ni, Co, and Mn the most critical elements to manufacture LIBs. The four valuable metals were quantified by ICP-OES in the completely digested CAMs by the standard EPA method. As shown in Table 1, the total weight percentage of the four metals in CAMs was 58.56 ± 0.35%, with Ni and Li as the most and least metal by weight, respectively. The molar ratio of Ni:Co:Mn was 5:2:3, indicating that the CAM examined in this study was NCM523 (LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub>) which is one of the predominant CAMs in the state-of-the-art LIBs because of its lower cost and higher energy density compared to other CAMs such as LiCoO<sub>2</sub> and NCM111 (LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>) [42]. Based on the molar ratios of transition metals (Ni, Co, and Mn) to Li, there was a Li loss of 23% due to the degradation of CAMs over its lifetime, with the actual formula as Li<sub>0.77</sub>Ni<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub>. The Li loss, which could be as high as 40% [43], has been recognized as one of the major issues accountable for capacity degradation of commercial LIBs [44,45].

The spent NCM523 materials were then subjected to chemical leaching by diluted LA. Four LA concentrations, i.e., 0.98, 2.94, 4.90, and 6.86 M, were examined under conditions of 10 L/kg, 90 °C, and 48 h to identify the optimal LA concentration for maximal leaching efficiency. Results showed 0.98 M LA led to the lowest leaching efficiencies for all four metals under the tested conditions (Figure S3). The leaching efficiencies for all metals were drastically elevated as LA concentration increased from 0.98 to 2.94 M, while they only rose slightly as the concentration increased from 2.94 to 4.90 M. With 6.86 M LA at the same conditions, 100% of all metals were leached out (Figure S3). Thus, 6.86 M LA was selected as the optimal concentration for the following experiments. Among the four metals for all LA concentrations, Li had the highest leaching efficiencies, suggesting that it was the easiest to be leached out, despite its lowest amount in the CAMs. By pure water, 4.63 ± 0.66% of Li, but none of the transition metals were dissolved from the original CAMs under conditions of 200 L/kg, 90 °C, and 1.2 h. These findings help explain the common Li loss during its lifetime.

#### 3.1.2. Development of models for metal leaching from CAMs by LA

To establish mathematical models for predicting leaching of metals from CAMs by 6.86 M LA, we chose to use a three-factor and three-level Box-Behnken design with leaching efficiencies as the response (Table 2). It can be observed that the efficiencies were generally high, with most of them being higher than 85%, indicating 6.86 M LA was effective to extract Li, Ni, Co, and Mn from CAMs under the examined conditions. With the experimental data from the 17 runs, polynomial regression models relating the leaching efficiency to the examined variables, namely L/S ( $X_1$ ), temperature ( $X_2$ ), and duration ( $X_3$ ) in coded units were generated by the response surface methodology. Response surface of (reduced) quadratic models (second order) for Li, Ni, Co, Mn, and total efficiencies were developed as Equations (3)–(7), respectively:

$$\text{Li efficiency} = -1.16 - 8.76 \times 10^{-3}X_1 + 5.22 \times 10^{-2}X_2 + 1.68 \times 10^{-2}X_3 - 3.40 \times 10^{-4}X_2^2 - 1.81 \times 10^{-4}X_3^2 \quad (3)$$

$$\begin{aligned} \text{Ni efficiency} = & -5.52 \times 10^{-1} + 3.68 \times 10^{-3}X_1 + 2.30 \times 10^{-2}X_2 + 2.41 \times 10^{-2}X_3 + 1.05 \times 10^{-4}X_1X_2 + 1.04 \times 10^{-4}X_1X_3 - 1.06 \\ & \times 10^{-4}X_2X_3 - 3.59 \times 10^{-4}X_1^2 - 1.15 \times 10^{-4}X_2^2 - 1.86 \times 10^{-4}X_3^2 \end{aligned} \quad (4)$$

**Table 1**

The main composition of CAMs in LIBs. Metal detection limit is 1 mg/kg. Data are expressed as mean ± standard deviation for triplicate experiments. Only Li, Ni, Co, and Mn were analyzed in this study.

Component	Li	Ni	Co	Mn	Total
wt (g/kg)	49.7 ± 1.3	276.9 ± 1.6	110.6 ± 0.5	148.5 ± 1.3	585.6 ± 3.5

**Table 2**

The Box-Behnken design of the variables with Li, Ni, Co, Mn, and total leaching efficiency as the response. LA of 6.86 M was the leaching reagent.

Run	L/S (L/kg)	Temperature (°C)	Duration (h)	Leaching efficiency (%)				
				Li	Ni	Co	Mn	Total
1	20	90	72	83.1	89.9	90.9	89.8	89.5
2	20	90	24	91.5	98.6	98.6	98.9	98.1
3	20	70	48	100.2	106.7	107.2	107.6	106.5
4	10	70	72	101.2	90.7	91.3	91.6	91.9
5	10	50	48	97.2	84.9	86.8	88.3	87.2
6	20	50	24	64.7	77.9	79.1	82.4	78.1
7	20	50	72	78.9	89.7	89.4	90.6	88.9
8	20	70	48	90.9	98.5	99.5	99.1	98.2
9	20	70	48	96.9	100.6	101.2	101.3	100.6
10	10	90	48	105.1	101.4	101.6	99.9	101.4
11	30	70	72	80.6	96.4	96.3	95.9	94.9
12	20	70	48	103.8	102.4	99.9	100.3	101.5
13	20	70	48	126.8	113.3	111.2	111.7	113.7
14	30	50	48	65.2	86.6	87.4	88.3	85.4
15	10	70	24	104	88.6	90.1	91.1	90.8
16	30	70	24	93.1	84.3	84.7	85.3	85.4
17	30	90	48	98.5	111.6	111.1	111.9	110.5

$$\begin{aligned} \text{Co efficiency} = & -3.68 \times 10^{-1} + 5.42 \times 10^{-5}X_1 + 2.03 \times 10^{-2}X_2 + 2.23 \times 10^{-2}X_3 + 1.12 \times 10^{-4}X_1X_2 + 1.09 \times 10^{-4}X_1X_3 - 9.41 \\ & \times 10^{-5}X_2X_3 - 2.97 \times 10^{-4}X_1^2 - 1.02 \times 10^{-4}X_2^2 - 1.78 \times 10^{-4}X_3^2 \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Mn efficiency} = & -2.01 \times 10^{-1} - 1.67 \times 10^{-3}X_1 + 1.75 \times 10^{-2}X_2 + 2.11 \times 10^{-2}X_3 + 1.51 \times 10^{-4}X_1X_2 + 1.06 \times 10^{-4}X_1X_3 - 9.03 \\ & \times 10^{-5}X_2X_3 - 3.16 \times 10^{-4}X_1^2 - 9.30 \times 10^{-5}X_2^2 - 1.71 \times 10^{-4}X_3^2 \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Total efficiency} = & -4.81 \times 10^{-1} - 1.36 \times 10^{-3}X_1 + 2.35 \times 10^{-2}X_2 + 2.33 \times 10^{-2}X_3 + 1.36 \times 10^{-4}X_1X_2 + 8.77 \times 10^{-5}X_1X_3 - 1.01 \\ & \times 10^{-4}X_2X_3 - 2.94 \times 10^{-4}X_1^2 - 1.26 \times 10^{-4}X_2^2 - 1.80 \times 10^{-4}X_3^2 \end{aligned} \quad (7)$$

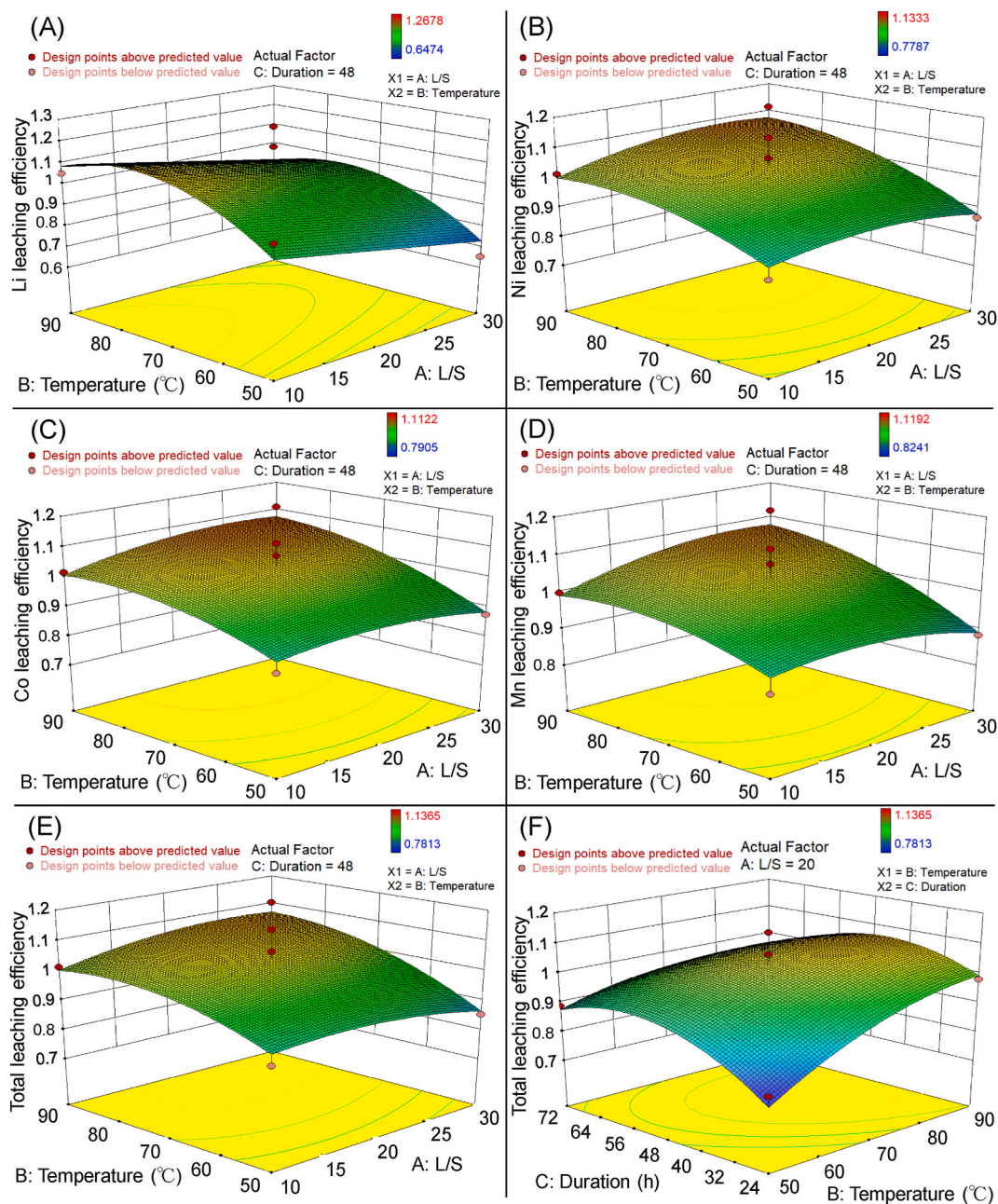
The resulting models can be applied to predict the response (i.e., leaching efficiency) with a given level of each variable in the original unit. The dominant variables and the relative significance of each variable, as well as the adequacy of the developed models were elucidated by ANOVA [37]. The relatively high  $F$  and low  $p$  ( $<0.05$ ) values for all five models from the ANOVA results, as shown in Table 3, revealed that all models were significant and able to depict the experimental data correctly. The five models were also well-fitted, demonstrated by the insignificant lack-of-fit compared to the pure error with the low  $F$  and high  $p$  ( $>0.05$ ) values. These were also supported by the excellent fitting between predicted and experimental data for all five models (Figure S4). Moreover, the error terms for all models were normally distributed, proven by the linear normal probability plot of the residuals (Figure S5). The established models thus allowed us to determine a desired or the maximal leaching efficiency via various combinations of leaching parameters, as well as to fine-tune the operation conditions to fulfill certain needs regarding leaching efficiency and the related costs.

Additionally, the variables with significant impacts on leaching efficiency can be identified from the ANOVA results by examining the corresponding  $F$  and  $p$  values. The results revealed that L/S and temperature exerted the most significant impacts on the leaching of Li, while only temperature significantly affected the leaching of transition metals, i.e., Ni, Co, and Mn. In contrast, the total leaching efficiency was significantly impacted by temperature and duration. These findings indicated that the three transition metals may share a similar leaching mechanism, which was distinct from that of Li. The discrepancy between the leaching of individual and total metals may also be attributed to the different leaching mechanisms between Li and the transition metals.

Interactions between leaching efficiency and parameters for individual and total metals were intuitively depicted by the three-dimensional response surface plots, as displayed in Fig. 1A–F. It can be observed that with a fixed duration at 48 h, the response surface plots exhibited distinguishable contours between Li and the three transition metals, supporting their different leaching mechanisms from the ANOVA results. Specifically, for the leaching of Li under the fixed duration of 48 h, an increase in temperature resulted in an increase and then a slight decrease in leaching efficiency under a certain L/S, while the increasing L/S reduced the efficiency at a determined temperature (Fig. 2A), confirming the significant impacts of temperature and L/S. Regarding the three transition metals, the increasing temperature raised the leaching efficiency, while the change in L/S generally did not alter the efficiency (Fig. 2B–D), which was consistent with the ANOVA results. The response surface plot of total metals under the fixed duration of 48 h displayed a similar contour with those of transition metals (Fig. 2E). The unchanged leaching efficiency under different L/S implied a high potential of 6.86 M LA to leach metals with a low L/S, which was verified in the following section. On the other hand, under the fixed L/S of 20 L/kg, the increasing duration affected the total metal leaching efficiency positively at first and then negatively, whereas the increasing temperature elevated the efficiency at a certain duration. Based on these analyses, the optimal

**Table 3**  
Analysis of variance (ANOVA) for the developed models of leaching by 6.86 M LA.

Source	Li			Ni			Co			Mn			Total		
	DOF	F	p	DOF	F	p	DOF	F	p	DOF	F	p	DOF	F	p
<b>Model</b>	5	4.95	0.01	9	4.84	0.02	9	5.42	0.02	9	3.94	0.04	9	4.53	0.03
$X_1$ (L/S)	1	5.87	0.03	1	0.69	0.43	1	0.46	0.52	1	0.47	0.51	1	0.01	0.93
$X_2$ (temperature)	1	8.88	0.01	1	15.47	0.01	1	17.96	<0.01	1	11.04	0.01	1	5.21	0.05
$X_3$ (duration)	1	3.99	0.07	1	1.19	0.31	1	1.21	0.31	1	0.44	0.53	1	12.67	0.01
$X_1X_2$	–	–	–	1	0.56	0.48	1	0.81	0.40	1	1.24	0.30	1	0.96	0.36
$X_1X_3$	–	–	–	1	0.78	0.41	1	1.10	0.33	1	0.89	0.38	1	0.57	0.47
$X_2X_3$	–	–	–	1	3.31	0.11	1	3.31	0.11	1	2.57	0.15	1	3.04	0.12
$X_1^2$	–	–	–	1	1.72	0.23	1	1.51	0.26	1	1.44	0.27	1	1.18	0.31
$X_2^2$	1	7.49	0.02	1	2.81	0.14	1	2.84	0.14	1	1.99	0.20	1	3.47	0.10
$X_3^2$	1	4.37	0.06	1	15.33	0.01	1	17.87	<0.01	1	13.97	0.01	1	14.70	0.01
<b>Residual</b>	11	–	–	7	–	–	7	–	–	7	–	–	7	–	–
<b>Lack-of-fit</b>	7	0.30	0.92	3	0.80	0.56	3	0.81	0.55	3	1.02	0.47	3	0.58	0.66
<b>Pure Error</b>	4	–	–	4	–	–	4	–	–	4	–	–	4	–	–
<b>Cor Total</b>	16	–	–	16	–	–	16	–	–	16	–	–	16	–	–

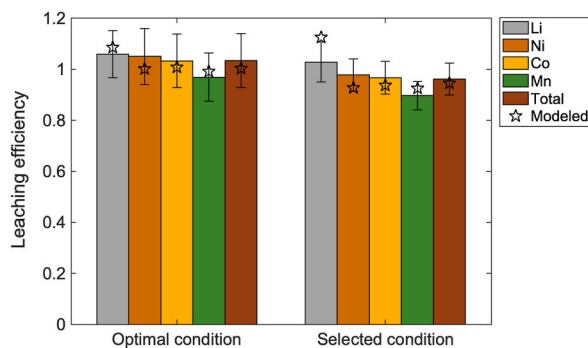


**Fig. 1.** Three-dimensional response surface plots of Li (A), Ni (B), Co (C), Mn (D), and total metals (E, F) efficiency as a function of different variables for CAMs with a fixed duration at 48 h (A–E) and a fixed L/S at 20 L/kg (F).

conditions for total metal leaching were determined as 10 L/kg (L/S), 90 °C (temperature), and 48 h (duration) with a maximal efficiency of 100%.

### 3.1.3. Validation of models under optimal and randomly selected conditions

The developed models for leaching of each and total metals from CAMs by 6.86 M LA were validated by comparing the experimental and predicted leaching efficiencies under the optimal (10 L/kg, 90 °C, and 48 h) and the randomly selected (7.5 L/kg, 77 °C, and 62 h) conditions. Results showed that the calculated leaching efficiencies of individual and total metals matched well with the experimental values under both optimal and randomly chosen conditions (Fig. 2). The modeled efficiencies were distributed generally within one standard deviation of the mean measured values, indicating an excellent predictive power. The findings confirmed that the established models with the experimental design were effectual to determine optimal operation parameters and predict the leaching efficiency. Moreover, with a lower L/S (7.5 L/kg), a high total leaching efficiency of 96% can still be achieved, confirming the high



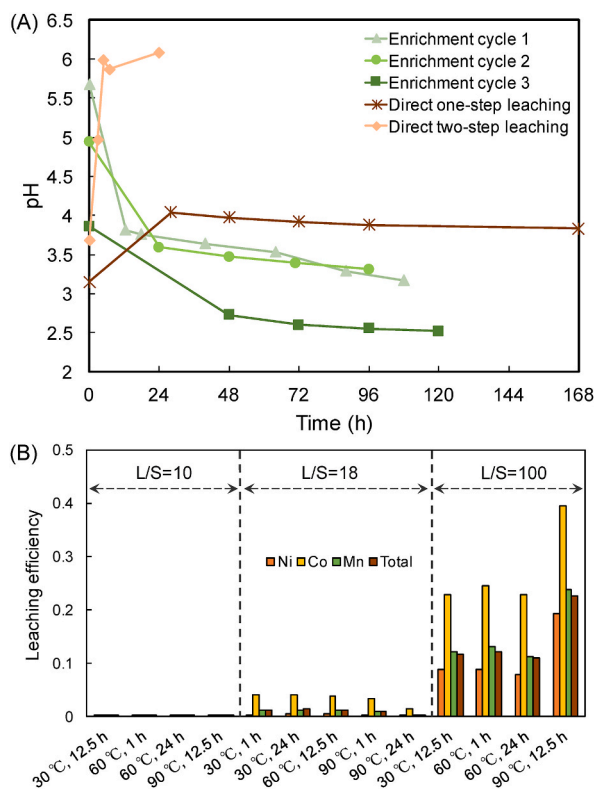
**Fig. 2.** Validation of models under the optimal (L/S = 10 L/kg, T = 90 °C, D = 48 h) and the randomly selected (L/S = 7.5 L/kg, T = 77 °C, D = 62 h) conditions for 6.86 M LA leaching with CAMs. Error bar indicates standard deviation of the mean for triplicate experiments. Pentagram indicates predicated leaching efficiency by models.

leaching capacity of 6.86 M LA at the low L/S.

### 3.2. Bioleaching of metals from CAMs using the enriched microbial consortium

#### 3.2.1. Enrichment of microbial consortium and direct bioleaching of metals from CAMs

A microbial consortium for bioleaching was enriched from wastewater treatment activated sludge by a three-cycle process as described above. The growth medium specific for *A. ferrooxidans* was employed to enrich autotrophic and acidophilic strains in the community. The pH change during the enrichment process was displayed in Fig. 3A. Throughout the enrichment process, the microbial consortium became progressively adaptive to the low pH by exposure to the gradually reduced initial pH, which was 5.68, 4.94, and



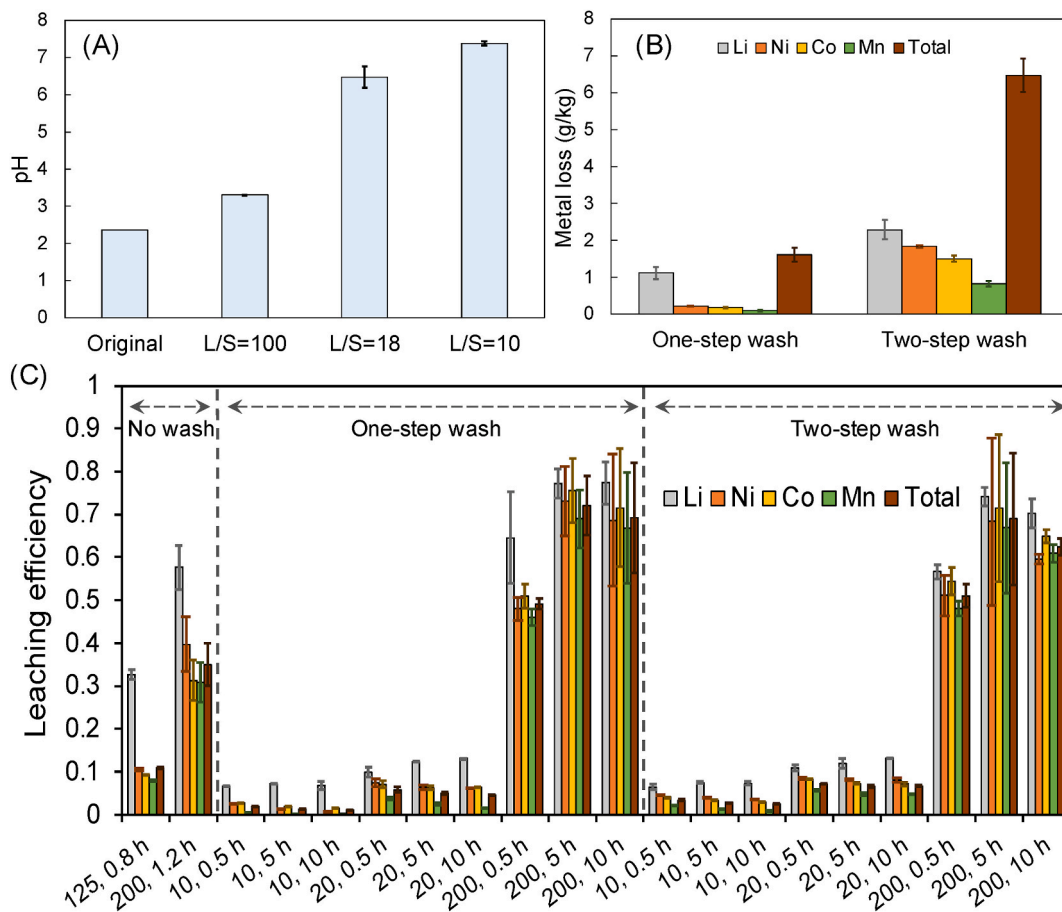
**Fig. 3.** (A) The pH changes in the three cycles of enrichment of the microbial consortium and direct one- and two-step bioleaching using the enriched consortium. The L/S in direct one- and two-step bioleaching were 200 and 20 L/kg, respectively. (B) The indirect spent-medium bioleaching efficiency of Ni, Co, Mn, and total transition metals from original CAMs under the conditions with different combinations of three-level L/S (i.e., 10, 18, 100 L/kg), temperature (i.e., 30, 60, 90 °C), and duration (i.e., 1, 12.5, 24 h). The two values in the bottom are temperature and duration, respectively.



3.86, for the three cycles, respectively. In each enrichment cycle, the pH dropped fast initially and slowly afterwards, to 3.17, 3.31, and 2.52 at the end, respectively, indicating an effective enrichment of the microbial consortium capable of bioleaching. After the three-cycle enrichment, the microbial consortium was applied in direct one- and two-step bioleaching and the pH was monitored to evaluate their feasibility. As shown in Fig. 3A, with an L/S of 200 L/kg in the direct one-step bioleaching of metals from CAMs, the pH increased from an initial 3.15 to 4.04 within 28 h and stayed stable afterwards during the 168 h of leaching process. In the direct two-step bioleaching, the pH rose rapidly from an initial 3.68 to final 6.08 during the 24 h duration. The high pH indicated the ineffectiveness of the direct bioleaching by the enriched consortium, probably due to the intrinsic high pH of CAMs and the irreducible toxicity of the heavy metals on the microbes.

### 3.2.2. Indirect bioleaching of metals from CAMs using cell-free spent medium

Previous comparisons among direct one/two-step and indirect spent-medium bioleaching indicated that the indirect bioleaching showed the highest efficiency in metal recovery from spent LIBs [31]. Additionally, from our and previously documented results [26, 31–33], direct bioleaching usually necessitated a long time (e.g., >10 d) with slow kinetics, which is one of its notable drawbacks. With the indirect bioleaching, in contrast, a much shorter leaching time could be expected. In the practical application, use of the spent medium generated from large volume culturing is simply and easy and without long process time and complexity associated with microbial cultivation. Therefore, the indirect bioleaching of metals from CAMs was investigated in this study. Only transition metals, which seemed more difficult to be leached out than Li, were examined to evaluate the effectiveness of indirect bioleaching. The results revealed that L/S exerted a remarkable impact on the leaching efficiency, with a higher L/S (i.e., a lower pulp density) leading to a higher efficiency under the same temperature and duration (Fig. 3B). The leaching efficiencies were negligible for all three metals at the L/S of 10 L/kg, while they reached up to 39.4% for Mn and 22.6% for total transition metals at the L/S of 100 L/kg. Temperature exhibited a notable impact under the high L/S (i.e., 100 L/kg), with a higher temperature favorable for the leaching, while it



**Fig. 4.** (A) The pH of original spent medium and that with CAMs at the L/S of 100, 18, or 10 L/kg. (B) The loss of Li, Ni, Co, Mn, and total metals in the pretreatment of CAMs by one-step or two-step washes using 1 vol% MSA. Error bar indicates standard deviation of the mean for triplicate experiments. (C) The indirect spent-medium bioleaching efficiency of Li, Ni, Co, Mn, and total metals from original, one-step-, and two-step-washed CAMs under 90 °C and different combinations of various L/S (i.e., 10, 20, 125, 200 L/kg) and durations (i.e., 0.5, 0.8, 1.2, 5, 10 h). The two values in the bottom are L/S (L/kg) and duration, respectively. Error bar indicates standard deviation of the mean for triplicate experiments.

manifested a minimal effect at the lower L/S. Moreover, duration increasing from 1 to 24 h seemed having no effects on the leaching efficiency. Generally, the efficiency of indirect bioleaching of metals from the original CAMs was relatively low, which may still be attributed to the high pH of the CAMs. To understand better the effect led by CAM's high pH, different pretreatments of the CAMs were performed and discussed in the following section.

### 3.2.3. Indirect bioleaching of valuable metals from CAMs pretreated by washing

The high pH of the CAM powders was verified by our data showing that a lower L/S (i.e., a higher pulp density) resulted in a higher pH value in the spent medium suspended with CAMs, with the pH rising from 3.30 at 100 L/kg to 7.38 at 10 L/kg (Fig. 4A). To lessen the high pH, the washing pretreatments of CAMs were performed using various reagents (Table S2). After screening by considering the final pH and process complexity, one- and two-step washes using 1 vol% MSA with an L/S of 10 L/kg were selected. The pH was decreased to 7.66 and 1.34 after one- and two-step washes using 1 vol% MSA, respectively. The metal loss during the washes was quantified, showing that the total metal loss was  $1.61 \pm 0.19$  and  $6.46 \pm 0.45$  g/kg, accounting for 0.27% and 1.1% of total metal weight after one- and two-step washes, respectively (Fig. 4B). Additionally, consistent with the results from leaching by LA, Li was found the easiest to be washed out among the four metals, losing  $1.12 \pm 0.16$  g/kg during the one-step and  $2.29 \pm 0.26$  g/kg during the two-step washes (Fig. 4B).

The pretreated CAMs were then processed by indirect spent-medium bioleaching under various L/S (10–200 L/kg) and durations (0.5–10 h) and a fixed temperature of 90 °C. The leaching efficiency (Fig. 4C) was quantified based on the metal contents in the original CAMs subtracted by the metal loss during the pretreatment. A significant impact of L/S on the leaching efficiency, similar with the indirect bioleaching with the original CAMs, was observed, with much higher efficiencies at L/S of 200 L/kg than those at the lower L/S. Notably, the washing pretreatment of CAMs manifested a remarkable positive effect on leaching, improving the total leaching efficiency from  $35.0 \pm 5.0\%$  (200 L/kg and 1.2 h) to  $49.2 \pm 1.3\%$  (200 L/kg and 0.5 h) for one-step wash. Whereas there seemed no improvement of leaching between one-step and two-step washing pretreatment, suggesting one-step wash was enough for pretreating CAMs. Additionally, as the leaching duration increased from 0.5 to 5 h, the total leaching efficiencies were significantly elevated for both one- and two-step washed CAMs at 200 L/kg, while they were slightly reduced as the duration further increased from 5 to 10 h, indicating a medium duration of 5 h was more beneficial for leaching. Overall, based on the tested conditions, the highest total leaching efficiency of  $72.1 \pm 6.9\%$  was achieved with one-step washed CAMs at the optimal conditions of 200 L/kg, 90 °C, and 5 h, with the highest leaching efficiencies as  $77.3 \pm 3.4\%$ ,  $73.1 \pm 8.1\%$ ,  $75.6 \pm 7.5\%$ , and  $69.0 \pm 6.7\%$  for Li, Ni, Co, and Mn, respectively.

### 3.3. Comparison between chemical and biological leaching

Compared to the previous efforts using various organic acids to leach metals from CAMs, during which a reductant was always added, our study showed that 6.86 M levulinic acid completely dissolved Li, Ni, Co, and Mn from NCM523 in the absence of reductants and with a much lower L/S than those reported. For example, Li et al. [21] employed 1.5 M lactic acid as the organic lixiviant and H<sub>2</sub>O<sub>2</sub> as a reductant (0.5 vol%) and achieved around 98% recoveries of Li, Ni, Co, and Mn from NCM111 at 70 °C with an L/S of 50 L/kg within 20 min. *m*-Malic acid with 2 vol% H<sub>2</sub>O<sub>2</sub> was reported to recover 99% of Li and 93% of Co from LiCoO<sub>2</sub> at 90 °C and a L/S of 50 L/kg within 30 min [18]. Wang et al. [11] leached Li and Co from LiCoO<sub>2</sub> using 1 M MSA with 0.9 vol% H<sub>2</sub>O<sub>2</sub>, achieving ca. 100% leaching efficiency for both metals at 70 °C and a L/S of 50 L/kg within 60 min. Although the concentration of LA (6.86 M) was higher than those reported, the much lower L/S ( $\leq 10$  L/kg) significantly reduced the amount of leaching agent required, resulting in less liquid wastes generated and lower overall cost of the process. The mechanism behind the low L/S in the leaching process of LA is worth exploring further in future studies. Additionally, leaching of target metals from CAM by LA required no addition of any reductants. The duration we tested was longer than the reported times. However, the insignificant impacts ( $p < 0.05$ ) of duration shown in the models for leaching of single metals suggested that a shorter time may still be effective to achieve a high leaching efficiency. The LA leaching with a shorter duration and recovery of LA in the pregnant solution merit further investigations in future research.

A few investigations have been performed on extracting metals from CAMs using *A. ferrooxidans* and *A. thiooxidans* [27–30]. These studies showed while some leaching process could be completed as fast as in 3 d [30], a duration of 10–15 d was typically needed to achieve an efficiency of 80–95% for metal leaching [26]. The fungus *A. niger* was also employed for metal recycling from spent LIBs [26,31–33]. The findings indicated that the organic acids (e.g., citric and malic acids) produced by *A. niger* led to ca. 54–100% of recovery for Li, Ni, Co, and Mn with the L/S of 50–100 L/kg within 8 d [33]. In contrast, the indirect bioleaching with pretreated CAMs as discussed above merely needed a much shorter leaching time (5 h) to reach the highest efficiencies of 69.0–77.3% for Li, Ni, Co, and Mn.

As elaborated above, both LA leaching and bioleaching were feasible to recover Li, Ni, Co, and Mn from CAMs. Use of LA at 6.86 M led to 100% leaching efficiencies for all target metals, much higher than those in the indirect bioleaching. Additionally, LA leaching required much lower L/S compared to indirect bioleaching. However, LA with high purity is not inexpensive. The spent medium on the other hand is much cheaper. Use of the spent medium also necessitated much shorter time than that for LA leaching. However, separate time for culturing the microbes to obtain the spent medium is needed. Thus, given each leaching approach's benefits and drawbacks, to extract metals from the CAMs at large scales, both economic and life cycle analyses need to be performed to prove the processes' environmental friendliness and cost effectiveness. This study thus provides the technical details and data to enable such comparative analysis.

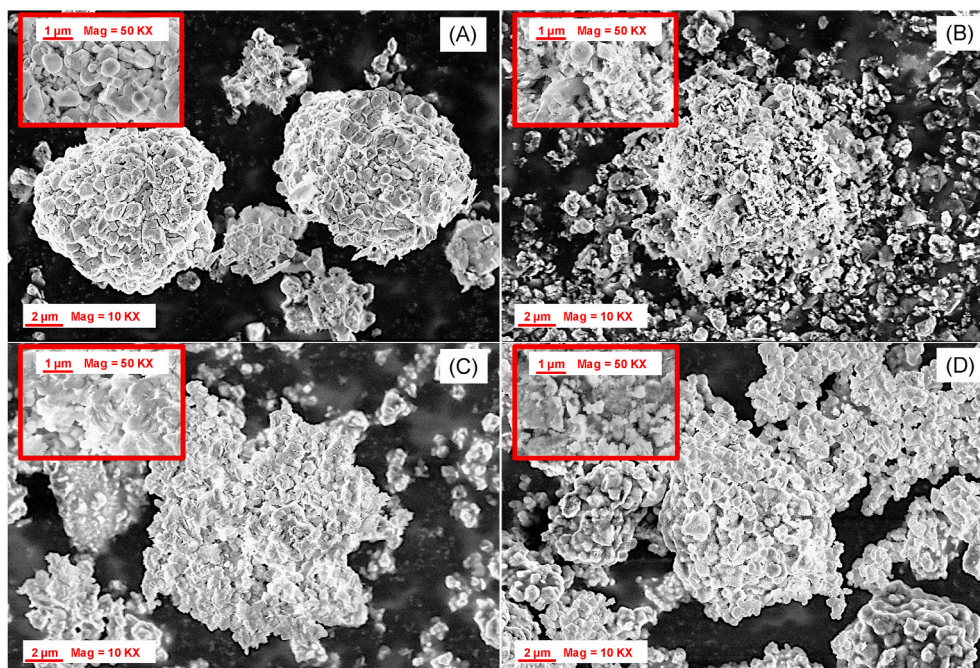
### 3.4. Comparative analysis of morphology and crystallinity of CAMs before and after leaching

The morphology and microstructures of the original spent CAMs and residues after leaching were characterized by SEM. As displayed in Fig. 5A, the original spent CAM powders, which were agglomerated from many small nanoparticles, possessed a relatively clear and smooth surface and regular spherical morphology. After chemical leaching, the large agglomerates of CAMs powders were severely damaged and collapsed into numerous small fragments (Fig. 5B), indicating the strong leaching forces by LA under the examined conditions. In contrast, biological leaching processes resulted in irregular spheres and slight structural collapse (Fig. 5C and D). Indistinct morphology and microstructures between the two residual solids after bioleaching suggested the limited impacts of pretreatment between one-step and two-step washing by MSA, which was consistent with the similar leaching efficiencies between those two solids (Fig. 4C). The lower degrees of particle agglomeration of residual CAMs after chemical leaching than those after bioleaching was also congruent with the higher leaching efficiencies of the former (calculated by the models).

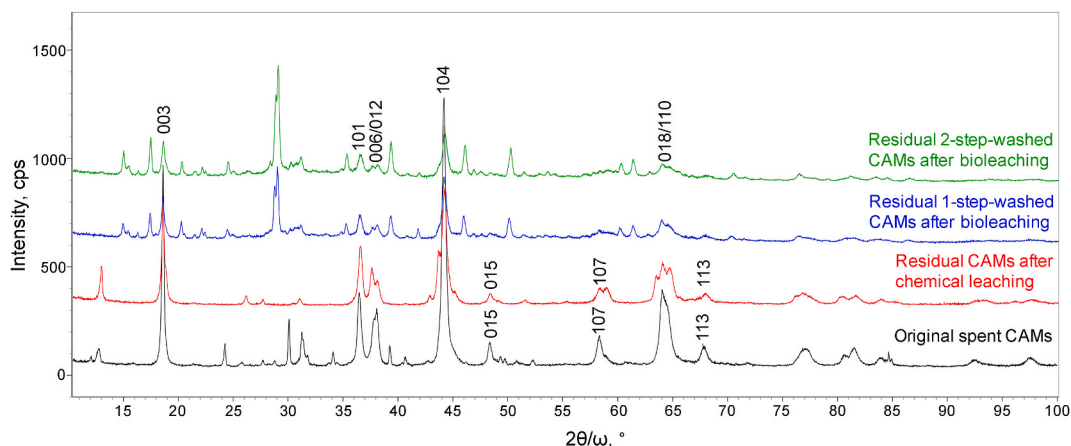
The crystal structures and phase purity of the four solids analyzed by XRD were displayed in Fig. 6. The diffraction peaks of the original spent CAMs appeared noticeably sharper than all three residual CAMs after leaching, suggesting that the former possessed the higher crystallinity [46]. This was further supported by the calculation of the crystallinity degrees, which were 98.48%, 97.2%, 90.3%, and 83.8% for the original spent CAMs, residual solids after LA leaching, residual one-step- and two-step-washed CAMs after indirect bioleaching, respectively. Moreover, the interplanar spacing analysis revealed a slightly decreased distance between two consecutive planes for CAMs after both leaching processes. The low intensity ratio of (003) and (104) peaks ( $<1$ ) and the indistinct split of (006/012) and (018/110) pair diffraction peaks indicated that the well-defined layered structures of pristine CAMs were damaged for all four solids. It was consistent with a previous finding showing the absence of highly ordered layered structures in spent NCM523 [47]. It can also be observed that the two residual CAMs after bioleaching exhibited similar peaks, demonstrating that one and two steps of MSA washes had indistinguishable impacts on crystal structures and phase purities of CAMs.

## 4. Conclusions

Both chemical leaching by levulinic acid and bioleaching using the enriched microbial consortium were applied to recycle Li, Ni, Co, and Mn from waste NCM523 ( $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ) in spent LIBs. Results showed that among the four tested concentrations of LA, the highest one (6.86 M) resulted in the most complete leaching. The developed mathematical models identified 10 L/kg, 90 °C, and 48 h as the optimal conditions, at which all four target metals were completely leached out by 6.86 M LA. The results also revealed that the leaching of Li and transition metals were significantly impacted by L/S and temperature, and temperature only, respectively. In contrast, L/S exerted the most remarkable impact among the three parameters on indirect bioleaching. The leaching efficiency of total transition metals reached up to 22.6% at 100 L/kg, 90 °C, and 12.5 h. Notably, the leaching of metals was enhanced after one-step



**Fig. 5.** Morphological analysis by SEM of original spent CAMs (A), residual CAMs after chemical leaching by 6.86 M LA (B), residual one-step-washed CAMs after indirect bioleaching (C), and residual two-step-washed CAMs after indirect bioleaching (D). The conditions were 10 L/kg, 50 °C, and 24 h for chemical leaching, and were 200 L/kg, 90 °C, and 5 h for indirect bioleaching. The magnifications are 10,000 $\times$  for the large images and are 50,000  $\times$  for the small images (in red frames).



**Fig. 6.** XRD patterns of original spent CAMs (black), residual CAMs after chemical leaching by 6.86 M LA (red), residual one-step-washed CAMs after indirect bioleaching (blue), and residual two-step-washed CAMs after indirect bioleaching (green). The conditions were 10 L/kg, 50 °C, and 24 h for chemical leaching, and were 200 L/kg, 90 °C, and 5 h for indirect bioleaching.

washing of NCM523 by 1 vol% MSA, achieving up to 72.1% for the total efficiency. The findings obtained from this study provide guidelines for selection of leaching methods in LIB recycling and add insights for process optimization in both approaches.

#### Funding statement

This work was supported by University at Albany, State University of New York.

#### Author contribution statement

Tao Jiang: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Qiantao Shi, Kevin Shah, Haralabos Efstathiadis, Xiaoguang Meng: Contributed reagents, materials, analysis tools or data.

Zheng Wei: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Yanna Liang: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

#### Data availability statement

Data will be made available on request.

#### Additional information

Supplementary content related to this article has been published online at [URL].

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e15788>.

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