Science of the Total Environment 830 (2022) 154577

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Feasibility of reduced iron species for promoting Li and Co recovery from spent $LiCoO_2$ batteries using a mixed-culture bioleaching process

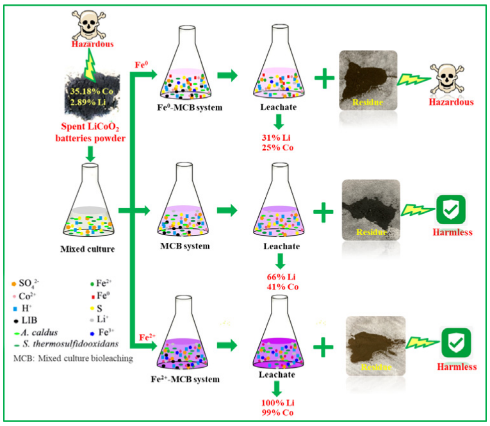
Xiaojian Liao [a], Maoyou Ye [b], Jialin Liang [b], Zhijie Guan [a], Shoupeng Li [a], Yanghong Deng [a], Qiaowei Gan [a], Zihang Liu [a], Xiaodi Fang [a], Shuiyu Sun [a,c,*]

[a] *Guangzhou Key Laboratory Environmental Catalysis and Pollution Control, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China*
[b] *College of Resources and Environment, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China*
[c] *Guangdong Polytechnic of Environmental Protection Engineering, Foshan 528216, China*

HIGHLIGHTS

- A mixed culture was used to improve metal recovery from spent $LiCoO_2$ battery (SLB).
- Effects of reductants Fe^{2+} and Fe^0 on leaching SLB by mixed culture were revealed.
- A mixed culture with the assistance of Fe^{2+} realized a yield of 99.31% Co and 100% Li.
- Fe^0 suppressed the metal extraction from SLB by mixed culture.
- Efficient SLB bioleaching needs a coordinated attack to $LiCoO_2$ by electron and H^+.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 January 2022
Received in revised form 3 March 2022
Accepted 11 March 2022
Available online 15 March 2022

Editor: Daniel CW Tsang

Keywords:
Spent $LiCoO_2$ batteries
Bioleaching
Reduced iron species
Metal recovery
Toxicity reduction

ABSTRACT

The recovery of metals from spent $LiCoO_2$ batteries (SLBs) is essential to avoid resource wastage and the production of hazardous waste. However, the major challenge in regard to recovering metals from SLBs using traditional bioleaching is the low Co yield. To overcome this issue, a mixed culture of *Acidithiobacillus caldus* and *Sulfobacillus thermosulfidooxidans* was designed for use in SLBs leaching in this study. With the assistance of Fe^{2+} as a reductant, 99% of Co and 100% of Li were leached using the above mixed-culture bioleaching (MCB) process, thus solving the problem of low metal leaching efficiency from SLBs. Analysis of the underlying mechanism revealed that the effective extraction of metals from SLBs by the Fe^{2+}-MCB process relied on Fe^{2+}-releasing electrons to reduce refractory Co(III) to Co(II) that can be easily bioleached. Finally, the hazardous SLBs was transformed into a non-toxic material after treatment utilizing the Fe^{2+}-MCB process. However, effective SLBs leaching was not achieved by the addition of Fe^0 to the MCB system. Only 25% Co and 31% Li yields were obtained, as the addition of Fe^0 caused acid consumption and bacterial apoptosis. Overall, this study revealed that reductants that cause acid consumption and harm bacteria should be ruled out for use in reductant-assisted bioleaching processes for extracting metals from SLBs.

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[*] Corresponding author at: Guangzhou Key Laboratory Environmental Catalysis and Pollution Control, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China.
E-mail address: sysun@gdut.edu.cn (S. Sun).

http://dx.doi.org/10.1016/j.scitotenv.2022.154577

1. Introduction

The extensive use of lithium-ion batteries (LIBs) has led to an increasing demand for Co and Li metals. However, it has been reported that the cumulative demand for Li in China will exceed its reserves by approximately 2028, and the depletion of Co on Earth will occur within the next 60 years if the annual production of LIBs reaches 20 million (Heydarian et al., 2018; Zeng et al., 2015). Fortunately, the concentrations of Co and Li in spent LIBs are often much higher than are those in the primary mineral reserves (Boxall et al., 2018). Therefore, waste LIBs can be used as valuable secondary materials. The $LiCoO_2$ battery is the first generation Li-ion battery that has been used for many years, leading to its waste accounting for the largest proportion of waste Li-ion batteries (Gratz et al., 2014; Niu et al., 2014). It has also been reported that the greatest economic value can be obtained from spent $LiCoO_2$ batteries (SLBs) compared to that from waste $LiMn_2O_4$, $LiNiO_2$, $LiFePO_4$, or $LiNi_XCo_YMn_ZO_2$ ($x + y + z = 1$, $0 < x,y,z < 1$) batteries (Gratz et al., 2014; Niu et al., 2014), as the SLBs contains a higher content of Co (up to 35.8%) (Niu et al., 2014). However, SLBs typically contain highly toxic organic electrolytes that can exert adverse effects on human health and the environment, and they also contain heavy metals such as Co, Cu, and Mn (He et al., 2022). Therefore, to avoid wastage of valuable metal resources and to reduce the risks associated with SLBs, it is necessary to develop an effective and economical method to recycle metals from SLBs.

Traditional pyrometallurgical and hydrometallurgical processes have been used to recover metals from discarded LIBs. However, both processes have some drawbacks. For instance, pyrometallurgy has high operational costs and energy requirements, and also generates secondary pollutants. (Roy et al., 2021a; Yan et al., 2021). Moreover, hydrometallurgy requires a large amount of chemicals and heating during leaching (Srivastava et al., 2020). In comparison, the bioleaching of metal ions from LIBs has received increasing attention due to its potential advantages such as cost-effectiveness, operational flexibility, and lower energy consumption (Srivastava et al., 2020; Tao et al., 2021). Currently, *Aspergillus niger*, *Acidithiobacillus thiooxidans*, and *Acidithiobacillus ferrooxidans* are commonly used for bioleaching of LIBs as indicated in Table S1. Among these, the processing time for bioleaching LIBs using fungi is longer than if that for bioleaching using acidophiles. Moreover, the application of fungi to leach LIBs is limited, as these microorganisms require high energy consumption for their growth and activity (Moazzam et al., 2021). Thus, acidophiles are preferred over fungi for leaching of LIBs. However, the highest leaching efficiency for Co was only 80% during the extraction of 1% LIBs using acidophiles (Table S1) (Xin et al., 2009). Thus, further research is required to improve the leaching efficiency to >80%.

Acidithiobacillus caldus and *Sulfobacillus thermosulfidooxidans* may serve as effective leaching species, as these two bacteria have been reported to possess a competitive advantage over *A. thiooxidans* and *A. ferrooxidans* in the process of chalcopyrite bioleaching in a mixed culture (Ma et al., 2017). Hence, *A. caldus* and *S. thermosulfidooxidans* possessing high leaching performance could potentially replace *A. thiooxidans* and *A. ferrooxidans* to accelerate SLBs bioleaching. Furthermore, an effective mixed culture could further improve bioleaching efficiency, thus providing higher functional stability and resistance compared to that of pure cultures (Moazzam et al., 2021). However, only a limited number of studies have examined the recycling of metals from SLBs via mixed culture. Therefore, the feasibility of using the mixed culture of *A. caldus* and *S. thermosulfidooxidans* to accelerate SLBs bioleaching must be explored comprehensively.

The Co yield from SLBs is typically low, as Co primarily exists in a trivalent form in SLBs resulting in a strong CoO bond energy within the structure (Meng et al., 2017). Therefore, one of the critical steps for effective Co recovery from SLBs via bioleaching is to facilitate the transition from Co(III) to Co(II) using a reductant. Currently, H_2O_2 is typically added as a reductant to reduce metals from high to low valence states to improve their leaching from LIBs by hydrometallurgy processes (Chen et al., 2020; Esmaeili et al., 2020). However, H_2O_2 is highly explosive, dangerous, and unstable (Wang et al., 2016). Moreover, it is also an oxidative stress agent that is toxic to microbial cells when used for SLBs bioleaching (Rezaei et al., 2020; Shekoohiyan et al., 2016). Thus, it is important to select a suitable reductant to establish a reducing bioleaching system for improving the leaching efficiency of SLBs. Compared to H_2O_2, reduced iron species are cost-effective and easily available reductants that exert low environmental impacts (Song et al., 2021). Currently, iron powder and ferrous ions (Fe^{2+}) can be used to improve the extraction efficiency of Co and Li from SLBs by hydrometallurgy, thus avoiding the use of high-cost H_2O_2 (Guan et al., 2016; Jiang et al., 2021; Peng et al., 2019). In particular, Fe^{2+} can not only be used as a reductant but can also provide electrons to promote bacterial growth (Ghassa et al., 2020). Therefore, it may be feasible to add Fe^{2+} to promote SLBs bioleaching. Zero-valent iron (Fe^0) is a strong reductant that can also produce Fe^{2+} under acidic conditions. Thus, it is necessary to compare and analyze the effects of Fe^{2+} and Fe^0 on the bioleaching of SLBs and reveal their underlying mechanisms.

In this study, a mixed culture of *A. caldus* and *S. thermosulfidooxidans* was designed to improve SLBs leaching. To further enhance the bioleaching efficiency, the influence of Fe^{2+} and Fe^0 on SLBs leaching facilitated by the mixed culture was compared. The changes in the SLBs surfaces were then analyzed to elucidate the bioleaching mechanism. Finally, detoxification analysis of bioleaching on SLBs was performed based on the change in metal leaching toxicity. Briefly, this study is helpful in regard to realizing the recovery of heavy metals from SLBs while simultaneously reducing the toxicity of SLBs.

2. Materials and methods

2.1. Spent $LiCoO_2$ batteries powder preparation

SLBs were first pre-treated by discharging, dismantling, and mechanically crushing at a new energy factory in Shenzhen, Guangdong Province (China). Crushed SLBs containing aluminum foil, copper foil, diaphragm, anode and cathode materials were obtained, as indicated in Fig. S1a. Then, a 200-mesh screen was used to screen the crushed SLBs material to collect the SLBs powder for use in the bioleaching test as presented in Fig. S1b. The SLBs powder was analyzed using X-ray diffraction (XRD, Ultima IV, Rigaku, Japan) and X-ray fluorescence spectrometry (XRF; 3600, Thermo Fisher, United States) to determine the phase and elemental compositions, respectively. The XRD results revealed that the SLBs primarily contained $LiCoO_2$ and graphite (Fig. S2). XRF data indicated that the SLBs powder contained Co, Cu, Al, Mn, and other elements, while the Li and C were beyond the detection range of the instrument (Table S2). Chemical acid digestion of the SLBs powder was also performed, and the concentrations of Co and Li were measured using coupled plasma-optical emission spectroscopy (ICP-OES; 7500, Agilent, US). Finally, it was determined that the SLBs contained 351,800 and 28,868 mg kg^{-1} of Co and Li, respectively.

2.2. Bioleaching experiment

2.2.1. Microorganism cultivation

A. caldus and *S. thermosulfidooxidans* obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (Germany) were used for the SLBs bioleaching. Prior to the bioleaching experiment, *A. caldus* and *S. thermosulfidooxidans* were sub-cultured in 100 mL of “Modified 9K” medium with a basal salt composition consisting of 3.00 g L^{-1} of $(NH_4)_2SO_4$, 0.10 g L^{-1} of KCl, 0.50 g L^{-1} of K_2HPO_4, 0.50 g L^{-1} of $MgSO_4{\cdot}7H_2O$, and 0.01 g L^{-1} of $Ca(NO_3)_2$. Additionally, the initial pH for the growth of *A. caldus* and *S. thermosulfidooxidans* was adjusted to 2.5 and 2.0, respectively, by the addition of 50% H_2SO_4; furthermore, 10 g L^{-1} of elemental sulfur was added as an energy source to promote their growth. Under the above culture conditions, a bacterial growth curve was obtained (Fig. S3). All experiments were performed at 30 °C and 170 rpm unless otherwise specified.

2.2.2. Effect of operational factors on spent $LiCoO_2$ batteries bioleaching

For SLBs bioleaching, a two-step approach was used in which SLBs powder was added to the leaching system during the logarithmic phase of microorganism growth (Heydarian et al., 2018; Naseri et al., 2019b). Three single-factor experiments examining the effects of pH, sulfur dosage, and pulp density on SLBs leaching by *A. caldus* and *S. thermosulfidooxidans* were conducted at an initial concentration of 5×10^7 cells mL^{-1} as presented in Table 1. Specifically, these bacteria were cultured in 100 mL of "Modified 9 K" medium based on pH and sulfur dosage (Table 1). Based on the bacterial growth curves (Fig. S3), the pH and bacterial concentration in the *A. caldus* and *S. thermosulfidooxidans* systems were determined during the logarithmic growth phase (12 days). Subsequently, SLBs powder at different pulp densities was added to the leaching systems for 48 h of leaching. Finally, the leaching efficiencies of Li and Co were determined. All tests were performed twice to ensure repeatability.

2.2.3. Spent $LiCoO_2$ batteries bioleaching

Under the conditions of an initial pH of 2.5, sulfur dosage of 10 g L^{-1}, and pulp density of 20 g L^{-1}, SLBs bioleaching was conducted using *A. caldus*, *S. thermosulfidooxidans*, and their mixed cultures (*A. caldus*: *S. thermosulfidooxidans* = 1: 1) at the same initial cell concentration (5×10^7 cells mL^{-1}). Simultaneously, SLBs leaching was performed using 100 mL of "Modified 9K" medium at pH 2.5 under the same conditions, and this was considered as the abiotic control group. At specified time intervals, pH, bacterial concentration, and metal ion concentrations were all measured. The aforementioned experiments were performed twice.

2.2.4. Effect of reduced iron species on spent $LiCoO_2$ batteries bioleaching by mixed culture

The effect of reduced iron species (2, 4, 5 and 6 g L^{-1}) on SLBs leaching by mixed culture bioleaching (MCB) was evaluated at an initial pH of 2.5, sulfur dosage of 10 g L^{-1}, and pulp density of 20 g L^{-1}. Simultaneously, the effect of reduced iron species-chemical leaching as a control group was examined under the same conditions. The reduced iron species contained analytical grade $FeSO_4{\cdot}7H_2O$ and Fe^0 powder of a 100-mesh size acquired from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). During bioleaching, a liquid sample was removed from the leaching system to monitor the changes in pH, cell density, Fe^{2+} concentration [Fe^{2+}], total iron concentration [TFe], and metal ion concentrations. This experiment was repeated twice. A specific description of the experimental steps is provided in Supplementary Material Text 1.

2.3. Analysis methods

2.3.1. Analysis of leaching parameters during bioleaching

pH and metal concentration in the leachate solution were determined using a digital pH meter (STARTER 2100, OHAUS, US) and ICP-OES, respectively. The direct counting method was used to quantify cell density using a binocular biological microscope (B203LED, OPTEC, China). The ferric ion concentration [Fe^{3+}] and [TFe] were determined by spectrophotometry using 5-sulfosalicylic acid at wavelengths of 500 and 425 nm, respectively (Liao et al., 2021). Thus, [Fe^{2+}] was equal to the difference between [TFe] and [Fe^{3+}] (Liao et al., 2019; Zhang et al., 2020).

Table 1
The experimental conditions of three single factor experiments.

Serial number	pH	Sulfur dosage (g L^{-1})	Pulp density (g L^{-1})
1	2.5	10	30
2	2	10	30
3	1.5	10	30
4	2.5	2.5	30
5	2.5	6.25	30
6	2.5	10	30
7	2.5	10	10
8	2.5	10	20
9	2.5	10	30
10	2.5	10	50

2.3.2. Analysis of the surface characteristics of spent $LiCoO_2$ batteries before and after leaching

The remaining SLBs residues were collected by centrifugation at 5000 *g* for 8 min, washed three to four times, and then dried in a vacuum drying chamber at 45 °C. The phase variations of the residues were characterized using XRD. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher, UK) was used to identify the transformation of elements on the SLBs surface.

2.3.3. Analysis of the leaching toxicity of spent $LiCoO_2$ batteries before and after leaching

A toxicity characteristic leaching procedure (TCLP) was used to assess the toxicity of the metals in the SLBs before and after leaching. Specifically, acetic acid was used as a leaching agent to leach raw SLBs and its leached residues using a solid–liquid ratio of 1:20 (kg L^{-1}) with continuous agitation at 30 rpm for 18 h (Liao et al., 2021). Subsequently, the leachates were collected to determine the metal concentrations using ICP-OES, and the obtained metal concentrations were compared to the threshold limit.

3. Results and discussion

3.1. Effects of three factors on spent $LiCoO_2$ batteries bioleaching

For any microbial activity, microorganism growth is a key factor affecting the entire process (Ilyas et al., 2021). Hence, it is important to understand the effects of the initial pH and sulfur dosage on bacterial growth. The suitable pH range for growth of *A. caldus* and *S. thermosulfidooxidans* has been reported to range between 1.5 and 2.5 (Roy et al., 2021a). However, the cell density of the above bacteria declined with a reduction in the initial pH from 2.5 to 1.5 (Fig. 1a), resulting in a decrease in the production of biogenic acid (Fig. 1b). This can be attributed to the observation that low initial pH affects the synthesis of enzymes related to bacterial growth and metabolism (Heydarian et al., 2018; Jegan Roy et al., 2021). Therefore, a pH of 2.5 was selected as the optimal value for the growth of both bacteria. Subsequently, to increase the oxidation rate of sulfur to produce more biogenic acid, the influence of sulfur dosages on bacterial growth was determined over the range of 2.5 to 10 g L^{-1} at pH 2.5 (Ilyas et al., 2021). The results indicated a significant improvement in cell density when the sulfur dosage was increased from 2.5 to 10 g L^{-1} (Fig. 1c), as this caused the production of more biogenic acids (Fig. 1d). This behavior is related to a sufficient sulfur supply that provides a greater amount of energy for microbial growth (Ghassa et al., 2020; Naseri et al., 2019b). The produced biogenic acid can also act as an oxidizing agent to improve the dissolution of metal ions from the SLBs (Ilyas et al., 2022). Thus, an initial pH of 2.5 and a sulfur dosage of 10 g L^{-1} were selected as optimal values for SLBs leaching by *A. caldus* and *S. thermosulfidooxidans*, and this is reflected in the metal leaching efficiencies listed in Tables S3 and S4.

Under optimal initial pH and sulfur dosage conditions, the influence of pulp density on SLBs bioleaching by *A. caldus* and *S. thermosulfidooxidans* was investigated (Fig. S4). After 2 days of leaching, the final extraction yields for Li and Co exhibited a steady decrease with an increase in pulp density from 10 to 50 g L^{-1} in both leaching systems. This can be attributed to the observation that the usable surface per unit volume of the solution was reduced with an increase in the pulp density (Liu et al., 2021; Zhang et al., 2018). Thus, SLBs bioleaching can be conducted at a pulp density of 10 g L^{-1}, and this is similar to conditions that have been applied in previous studies (Horeh et al., 2016; Zeng et al., 2012). However, the use of a relatively low pulp density (10 g L^{-1}) would result in a low economic benefit; thus, the pulp density of SLBs should be improved as much as possible (Moazzam et al., 2021). Moreover, it is challenging to achieve extraction yields of >90% for both Co and Li when the pulp concentration is 20 g L^{-1} (Niu et al., 2014). In summary, this study aimed to improve the

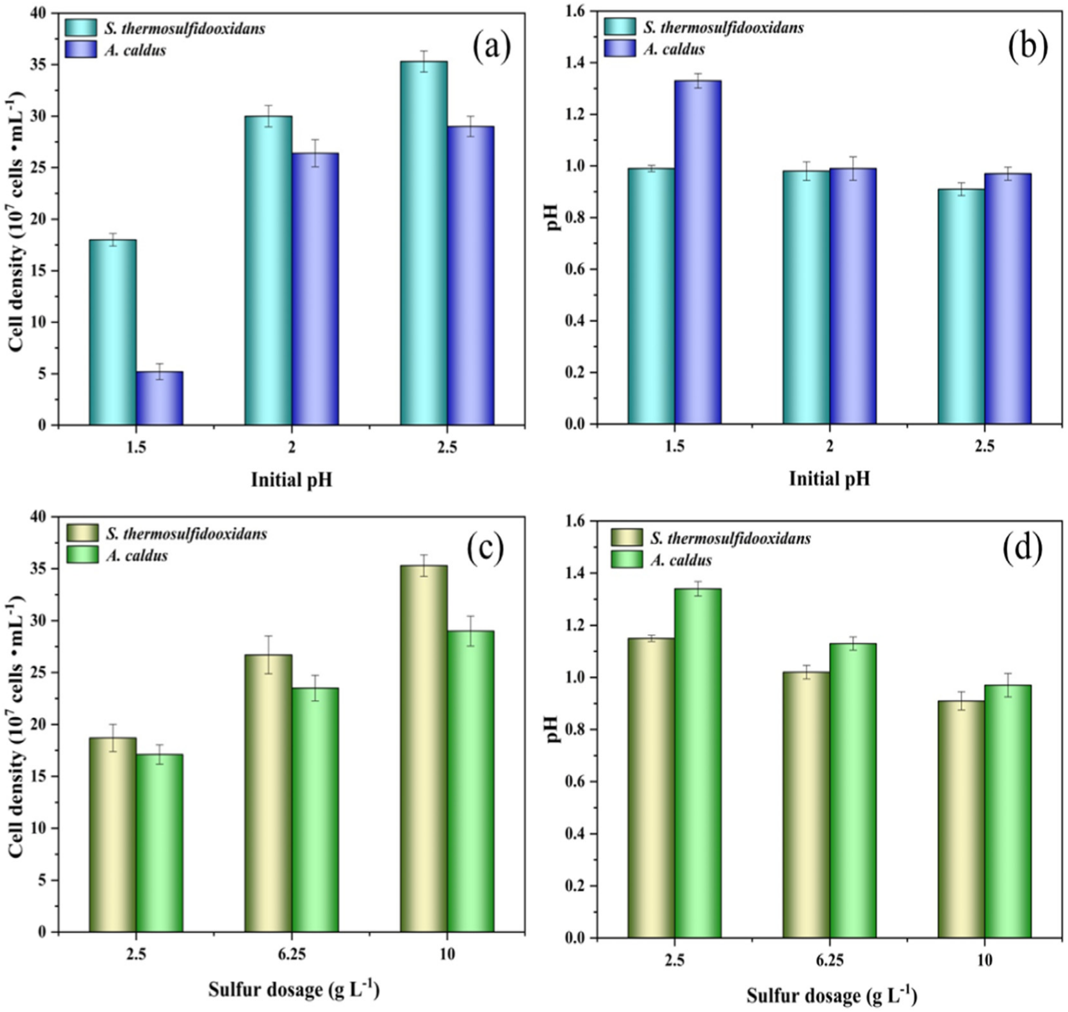

Fig. 1. The effect of initial pH on cell density (a) and pH (b) in *A. caldus* and *S. thermosulfidooxidans* culture systems (Initial conditions: pH of 2.5, 2, and 1.5, sulfur dosage of 10 g L^{-1}, cell concentration of 5×10^7 cells mL^{-1}); The effect of sulfur dosage on cell density (c) and pH (d) in *A. caldus* and *S. thermosulfidooxidans* culture systems (Initial conditions: initial pH of 2.5, sulfur dosages of 10, 6.25 and 2.5 g L^{-1}, cell concentration of 5×10^7 cells mL^{-1}).

leaching efficiency at a pulp density of 20 g L^{-1} through process optimization to overcome the challenges listed above.

3.2. Enhanced bioleaching efficiency of spent $LiCoO_2$ batteries by mixed cultures

A combination of *S. thermosulfidooxidans* and *A. caldus* was used to accelerate SLBs bioleaching at an initial pH of 2.5, a sulfur dosage of 10 g L^{-1}, and a pulp density of 20 g L^{-1}. Fig. 2a indicates that the pH increased from 1.08–2.5 to 2.12–6.60 as the leaching process proceeded, and this was attributed to acid consumption by the alkaline battery powder (Roy et al., 2021b). In the abiotic control system, the increase in pH was more severe than it was in the bioleaching systems, thereby verifying that microorganisms within the leaching system effectively maintained a low pH environment. In particular, lower pH conditions were observed in the mixed culture system compared to those in the pure culture systems, thus indicating that the two bacteria acted synergistically and generated more acid in combination than they did individually. However, cell density decreased sharply during the initial period (0–6 h) in each bioleaching group (Fig. 2b). This was due to the bacteria growing in extreme environments after SLBs was added to the leaching systems that included a sudden increase in pH and the release of metal ions and electrolytes (Naseri et al., 2019b). When bacteria progressively adapted to these extreme environments, they gradually recovered their activity and grew over 6–24 h (Fang et al., 2022). However, bacteria exhibit a limited resistance to extreme environments. If the environmental extremes exceed the tolerance of the bacteria, they grow slowly or die; this ultimately results in a relatively stable bacterial concentration or a slight decrease at 24–48 h (Naseri et al., 2019b). A higher cell density was observed in the MCB system compared to that in the pure culture bioleaching systems. Overall, these observations confirmed that both, the acid production capacity and activity of bacteria in mixed culture, were significantly improved compared to those under pure culture conditions.

After 48 h of leaching, the Li yields were 59% and 45% using *S. thermosulfidooxidans* and *A. caldus*, respectively (Fig. 2c–d). Compared to the abiotic control, the Li leaching efficiency was improved by 43–58% in the bioleaching group, and this was due to the microbial production of sulfuric acid as a leaching agent to extract metals from solid waste via an acidolysis mechanism (Heydarian et al., 2018; Xin et al., 2009). However, these two pure cultures only achieved 28–35% Co leaching from the SLBs. The leaching efficiencies of Co and Li increased to 41% and 66% in the MCB system, respectively, ultimately achieving an enhanced leaching performance compared to that of the pure culture systems. A possible explanation is that the synergistic growth of these strains produces a collective effect that leads to effective metal dissolution (Priya and Hait, 2020). However, the Co leaching efficiency remains low. This phenomenon may be due to the fact that Co primarily exists in a trivalent form in $LiCoO_2$ that leads to a strong CoO chemical bond (Meng et al., 2017). Therefore, reductants are required to weaken the CoO chemical bond and facilitate Co recovery.

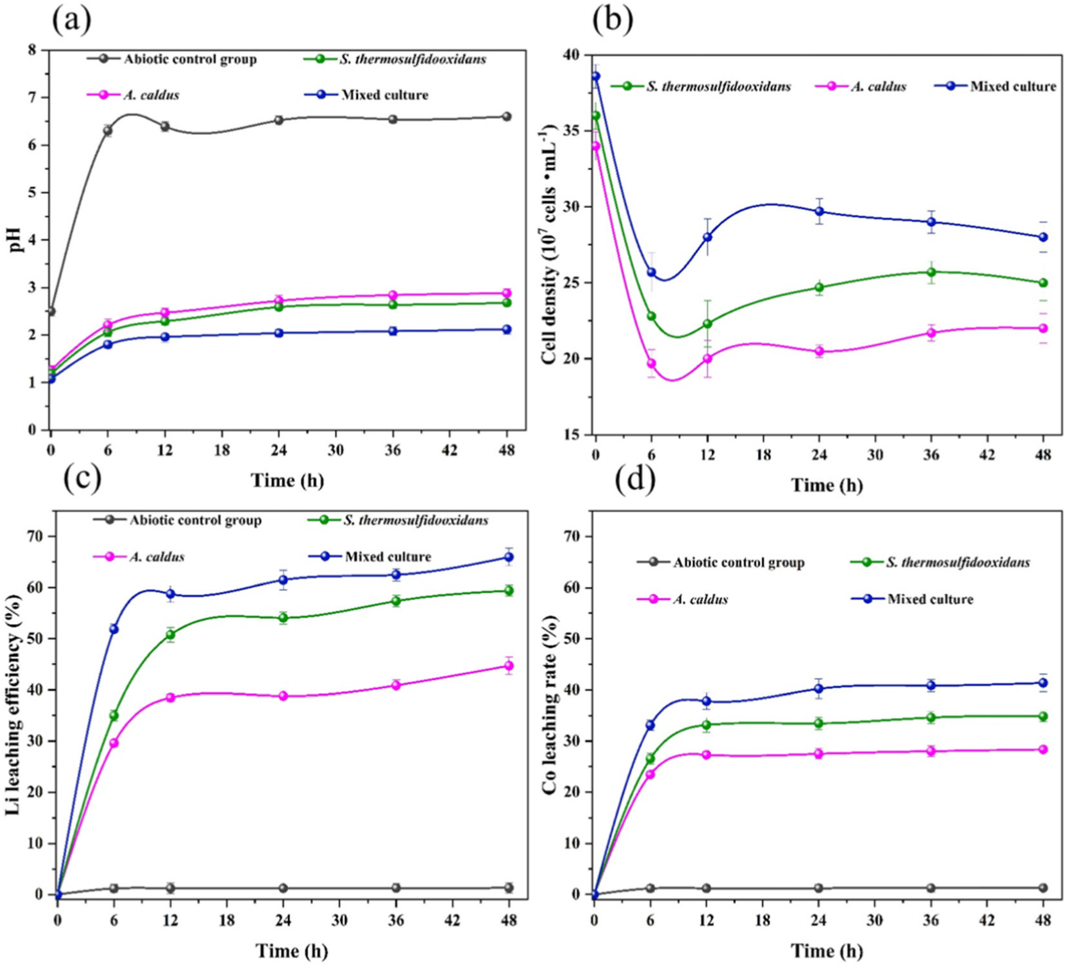

Fig. 2. Variation in physicochemical parameters during SLBs leaching by pure and mixed culture processes: (a) pH; (b) cell density; (c) Li leaching efficiency; and (d) Co leaching efficiency. (Initial conditions: pH of 2.5; sulfur dosage of 10 g L^{-1}; pulp concentration of 20 g L^{-1}; cell concentration of 5×10^7 cells mL^{-1}; microorganisms: pure *A. caldus*, pure *S. thermosulfidooxidans* and a mixed culture (*A. caldus*: *S. thermosulfidooxidans* = 1:1)).

3.3. Comparative effects of Fe^{2+} and Fe^0 on spent $LiCoO_2$ batteries bioleaching using mixed culture

A combination of reduced iron species (Fe^{2+}, Fe^0) and a mixed culture was used to leach metals from the SLBs as presented in Figs. 3–4. When [Fe^{2+}] was increased from 0 to 6 g L^{-1} in the MCB system, the pH increased from 1.08 to 1.80–3.01 after 6 h of leaching and then remained relatively stable (Fig. 3a). A possible reason for this is that under the action of Fe^{2+}, H^+ is more likely to promote the dissolution of SLBs and to subsequently be consumed. Notably, compared to the 5 g L^{-1} Fe^{2+}-MCB system, the pH in the 6 g L^{-1} Fe^{2+}-MCB system was lower, at a level of 2.5, that was the optimal pH condition for the growth of *S. thermosulfidooxidans* and *A. caldus*. A possible reason is that more Fe^{3+} was produced after more Fe^{2+} was added to the MCB system to improve SLBs leaching, and it is possible that it was hydrolyzed or transformed into jarosite to release H^+. However, a marked increase in pH from 1.08 to 3.92–4.92 occurred in the Fe^0-MCB system as the acid was consumed by Fe^0 (Fig. 3b), and this resulted in reduced microbial activity and metal leaching efficiency (Sethurajan and Gaydardzhiev, 2021).

Fig. 3c indicates a considerable level of cell death after SLBs was leached for 6 h. This phenomenon was possibly due to the inhibition of bacterial growth by severe environments caused by factors such as the release of more metals and electrolytes from the SLBs and the dramatic increase in pH (Naseri et al., 2019b). Fortunately, bacteria can grow after adapting to severe environments after 6 h (Fang et al., 2022). In particular, the cell density increased rapidly in the 6 g L^{-1} Fe^{2+}-MCB system, as increased Fe^{2+} serving as an electron donor can increase the metabolism and activity of acidophilic bacteria (Ghassa et al., 2020). Additionally, the pH in the 6 g L^{-1} Fe^{2+}-MCB system remained at a value of approximately 2.5, which was conducive to bacterial growth (Fig. 3a). However, apoptosis continued to occur in the Fe^0-MCB system after 6 h until no live cells remained (Fig. 3d). The likely reason was that Fe^0 was first oxidized to generate Fe^{2+} and H_2O_2 under aerobic and acidic conditions, and this caused the Fenton reaction to generate reactive oxygen species (ROS) that are toxic to bacteria (Ken and Sinha, 2020). Additionally, a significant increase in pH due to acid consumption by Fe^0 was not conducive to bacterial growth. Thus, the addition of Fe^0 exerted a toxic effect on the growth of bacteria during SLBs bioleaching, and this is also confirmed in Fig. S5.

As presented in Fig. 3e, a sharp reduction in [Fe^{2+}] was observed from 0 to 6 h in the Fe^{2+}-MCB process, and this was primarily due to the ability of Fe^{2+} to act as a reductant with $LiCoO_2$ under acidic conditions and transform into Fe^{3+} (Ghassa et al., 2020). However, the accumulated Fe^{3+} is hydrolyzed into $Fe(OH)_3$ or jarosite on the SLBs surface, thereby enhancing the consumption of Fe^{3+} and producing H^+ (Pourhossein and Mousavi, 2019). Consequently, although 6 g L^{-1} Fe^{2+} was added into the MCB system, the final [TFe] was the lowest at 0.60 g L^{-1} (Fig. 3g). In contrast, the [Fe^{2+}] was enhanced from 0 to 1.7–2.6 g L^{-1} over 0–6 h in the Fe^0-MCB system (Fig. 3f), which was likely due to the dissolution of Fe^0 by biogenic acid. After 6 h, there was no significant reduction in [Fe^{2+}] in the Fe^0-MCB process, indicating that only a small amount of Fe^{2+} participated in the

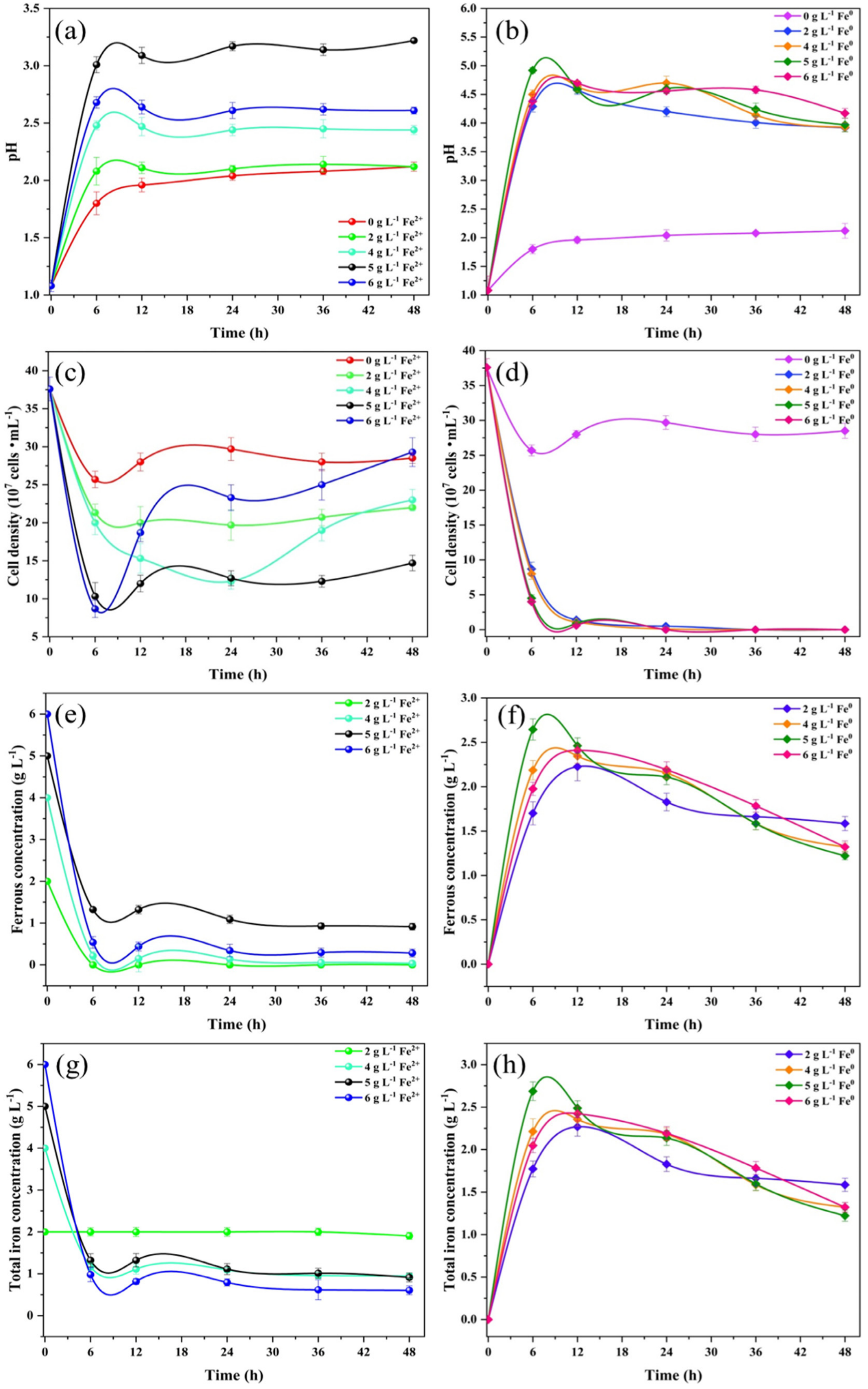

Fig. 3. Variation in physicochemical parameters during SLBs leaching by Fe^{2+}-MCB and Fe^0-MCB processes: (a–b) pH; (c–d) cell density; (e–f) ferrous ion concentration and (g–h) total iron concentration. (Initial conditions: pH of 2.5; sulfur dosage of 10 g L^{-1}; pulp concentration of 20 g L^{-1}; cell concentration of 5×10^7 cells mL^{-1}; microorganisms: a mixed culture (*A. caldus* : *S. thermosulfidooxidans* = 1:1); Fe^{2+} concentrations: 2, 4, 5 and 6 g L^{-1} or Fe^0 concentrations: 2, 4, 5 and 6 g L^{-1})).

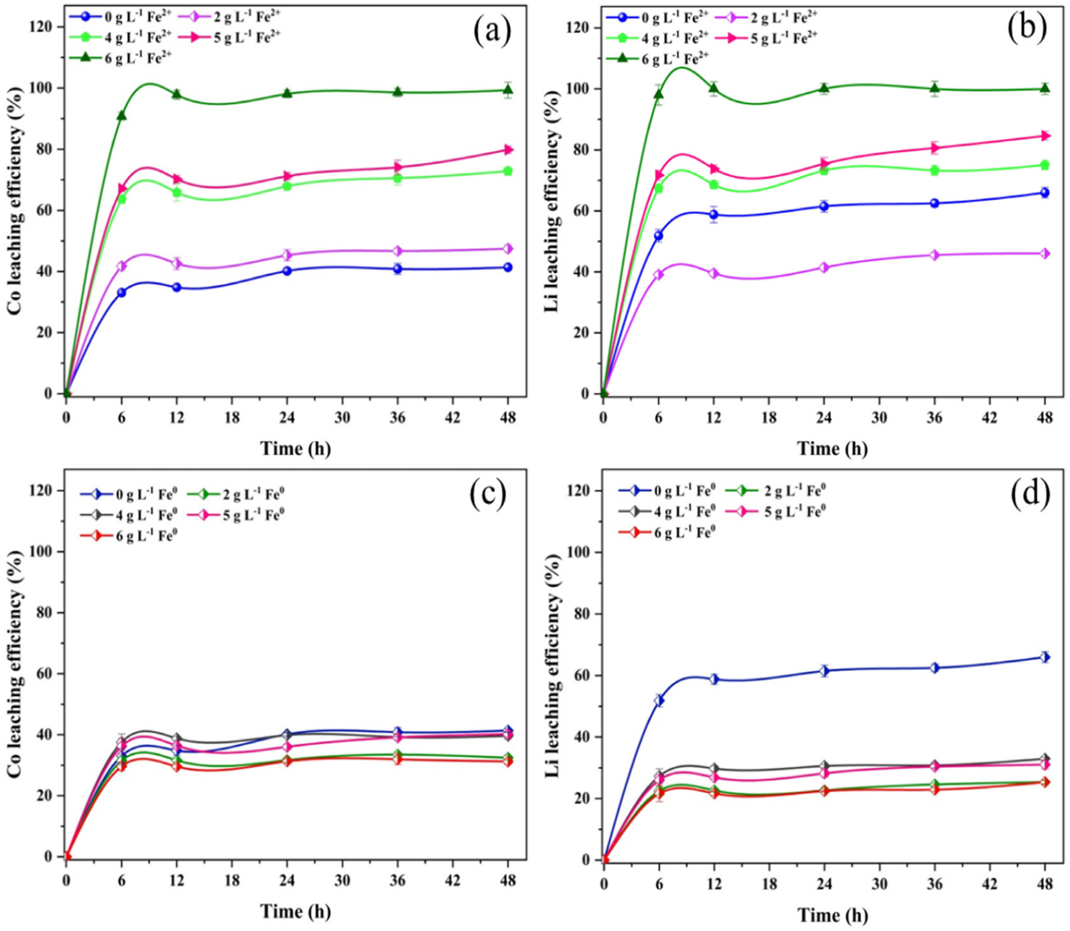

Fig. 4. The leaching efficiencies of Co and Li from SLBs by Fe^{2+}-MCB process (a-b) and Fe^0-MCB process (c-d). (Initial conditions: pH of 2.5; sulfur dosage of 10 g L^{-1}; pulp concentration of 20 g L^{-1}; cell concentration of 5 × 10^7 cells mL^{-1}; microorganisms: a mixed culture (*A. caldus* : *S. thermosulfidooxidans* = 1:1); Fe^{2+} concentrations: 2, 4, 5 and 6 g L^{-1} or Fe^0 concentrations: 2, 4, 5 and 6 g L^{-1})).

leaching of SLBs under weakly acidic conditions. However, a higher [TFe] (1.2–1.6 g L^{-1}) was still observed in the Fe^0-MCB system (Fig. 3h), which would increase the difficulty of iron ion separation from Co^{2+} and Li^+ in this system after bioleaching.

As presented in Fig. 4a, a marked increase in the Co yield from 41% to 99% was achieved in the MCB system when [Fe^{2+}] was increased from 0 to 6 g L^{-1}. This is because more electrons are released from Fe^{2+} to attack $LiCoO_2$, thereby causing Co to transform to a lower oxidation state to facilitate Co leaching under the action of biogenic acids (Jiang et al., 2021). However, the sufficient destruction of the chemical bonds of LiCoO2 by Fe^{2+} can also improve the dissolution of Li (Fig. 4b). It was determined that the Li yield also increased by 34% when 6 g L^{-1} Fe^{2+} was added to the MCB system. Finally, the Co and Li concentrations reached their highest values of 6988.75 mg L^{-1} and 577.36 mg L^{-1} in the 6 g L^{-1} Fe^{2+}-MCB system, respectively. Notably, the bacteria continued to grow faster after 6 h in the 6 g L^{-1} Fe^{2+}-MCB system compared to growth in the other leaching systems (Fig. 3c), which is conducive to SLBs leaching. Additionally, the lowest [TFe] appeared in the 6 g L^{-1} Fe^{2+}-MCB system (Fig. 3g) that allowed Fe to be easily removed from the leachate. Accordingly, the optimum Fe^{2+} dosage for SLBs bioleaching in the MCB system was determined to be 6 g L^{-1}. In contrast, Co and Li exhibited poor release from SLBs by chemical leaching with different dosages of Fe^{2+} with yields of only 9–15% and 4–9% (Fig. S6a–b), respectively, due to a lack of microbial action. These results indicate that the combination of Fe^{2+} and MCB exerted a synergistic effect on SLBs leaching. In contrast, the addition of 6 g L^{-1} Fe^0 into the MCB system resulted in a reduction in the recovery of Co (25%) and Li (31%) (Fig. 4c–d). This could be due to the bacteriostatic effect of Fe^0 on acidophilic bacteria and the acid consumption caused by the dissolution of Fe^0 (Ken and Sinha, 2020). Similarly, drastically lower metal leaching efficiencies (<4% Li and <0.2% Co) also occurred in the Fe^0-chemical leaching system (Fig. S6c–d). Finally, it was concluded that Fe^{2+} was highly advantageous for improving SLBs leaching compared to Fe^0 in the MCB process. Therefore, the effective leaching of metals from SLBs requires the action of both microorganisms and reductants; however, reductants must satisfy the characteristics of less acid consumption and no inhibition of bacterial growth in the leaching system.

Compared to the other results presented in Table S1, the 6 g L^{-1} Fe^{2+}-MCB process still exhibited a high metal leaching efficiency at a pulp density of 20 mg L^{-1}. At this high pulp density, the present study increased the yields of Co and Li by 27% and 11%, respectively, compared to the results reported by Niu et al. (2014). Additionally, the leaching tests in this study were performed at 30 °C, while the majority of hydrometallurgical process of leaching LIBs was operated at 70–90 °C (Lie and Liu, 2021; Meshram et al., 2015). Hence, the 6 g L^{-1} Fe^{2+}-MCB process possessing efficient and low-cost advantages can be used as an alternative technology for the recycling of SLBs.

3.4. Variation in the phase of spent $LiCoO_2$ batteries before and after leaching

To further investigate the effects of reduced iron species (Fe^{2+} and Fe^0) on SLBs bioleaching by mixed culture, the changes in the SLBs phase were evaluated using XRD (Fig. 5). According to the XRD results, the raw SLBs were primarily composed of $LiCoO_2$ and graphite (Fig. 5a). However, the $LiCoO_2$ peak in the abiotic control group was not noticeably weakened

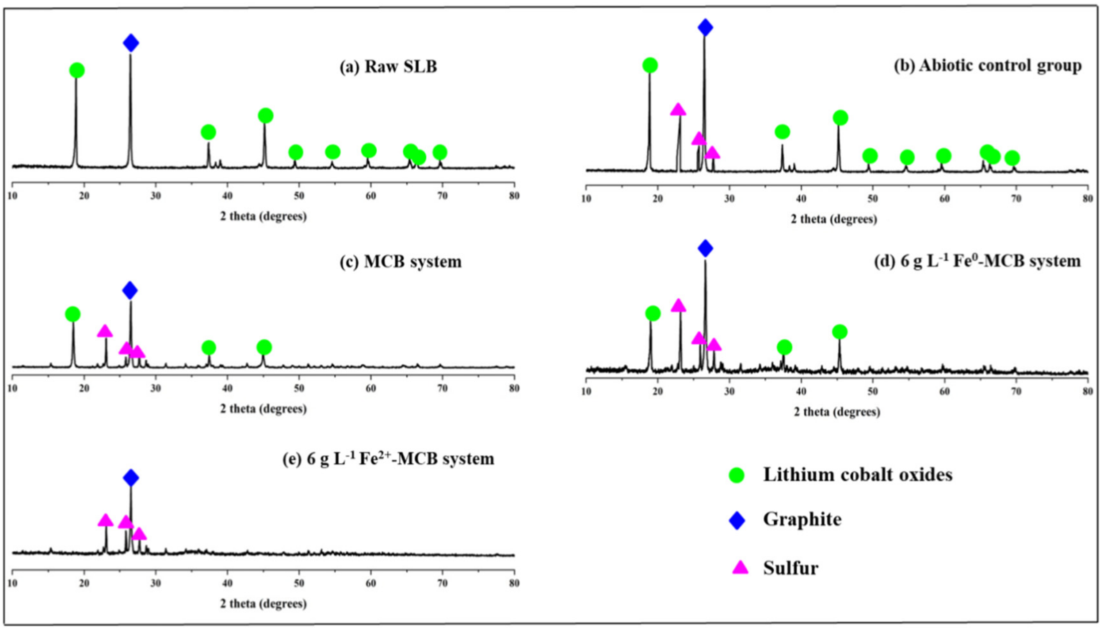

Fig. 5. The XRD results of leached residues in different leaching groups. (a) raw SLBs; (b) abiotic control group; (c) MCB system; (d) 6 g L^{-1} Fe^0-MCB system; (e) 6 g L^{-1} Fe^{2+}-MCB system.

(Fig. 5b), thereby indicating that the effect of chemical leaching on the SLBs dissolution was negligible (Fang et al., 2022). Compared to the abiotic control group, the intensity of the $LiCoO_2$ peak was markedly reduced after SLBs treatment using the MCB process (Fig. 5c), indicating that SLBs leaching was accelerated by the action of microorganisms. However, after the addition of 6 g L^{-1} Fe^0 to the MCB system, an insignificant reduction in the $LiCoO_2$ peak intensity was observed (Fig. 5d). Interestingly, the $LiCoO_2$ peak in the leached residue from the 6 g L^{-1} Fe^{2+}-MCB system disappeared (Fig. 5e), confirming the ICP-OES results that 99% Co and 100% Li were effectively bioleached. Additionally, it was observed that there was an obvious characteristic peak of elemental sulfur in the bioleached residue that indicated that the dosage of sulfur (10 g L^{-1}) in this study was sufficient for bioleaching and firmly supported the conclusion presented in Section 3.1. However, the XRD pattern of the bioleached residue exhibited no characteristic peaks related to iron compounds such as $Fe(OH)_3$ and jarosite. This was likely because $Fe(OH)_3$ with weak crystalline planes and low levels of jarosite were difficult to detect by XRD (Carrasco et al., 2021). Ultimately, it was determined that the addition of Fe^{2+} exhibits greater potential for bioleaching valuable metals from SLBs than Fe^0.

3.5. Mechanism analysis of enhanced bioleaching of spent $LiCoO_2$ batteries by Fe^{2+}

XPS analysis of the SLBs surface was performed to further illustrate the mechanism of the promotion of SLBs leaching by the Fe^{2+}-MCB process. As presented in Fig. 6a, C, O, Co, F, and other elements were present on the surface of the SLBs. The spectrum of Co 2P on the surface layer of the SLBs is presented in Fig. 6b. The Co 2p3/2 and Co 2p1/2 peaks at binding energies of 780.94 and 795.89 eV were assigned to Co(III), while Co(II) was characterized by the Co 2p3/2 and Co 2p1/2 peaks at 783.4 and 797.22 eV, respectively (Fu et al., 2020; Lie and Liu, 2021). The peaks appearing at 787.54 and 802.79 eV were ascribed to the satellite peaks of Co 2p3/2 and Co 2p1/2, respectively. Therefore, the Co in the raw SLBs powder contained two valence states that included Co(III) and Co(II). The characteristic peak of Co(III) was higher than was that of Co(II), thus indicating that Co in the SLBs was dominated by Co(III). Nevertheless, it was previously reported that the high-valence state of Co(III) is insoluble and difficult to leach under acidic conditions (Naseri et al., 2019a). After SLBs was treated using the MCB process, only the Co 2p3/2 and Co 2p1/2 peaks of Co(III) appeared in the Co 2p orbital, and they exhibited a lower intensity compared to that of the raw SLBs powder. These results imply that the acid produced by microorganisms promoted the bioleaching of Co(II) from the SLBs. Simultaneously, the bacteria-driven oxidation of sulfur powder may produce unknown intermediate reducing compounds that improve Co(III) leaching (Niu et al., 2014). Interestingly, all of the characteristic peaks of Co disappeared on the surface of the SLBs after 6 g L^{-1} of Fe^{2+} was added to the MCB system, revealing that the addition of Fe^{2+} could further promote the leaching of Co(III). However, the UV visible spectra of the leaching solution indicated that the Co present in the 6 g L^{-1} Fe^{2+}-MCB system was primarily in the form of Co(II) (Fig. S7). In summary, Fe^{2+} promoted the leaching of Co from SLBs by reducing refractory Co(III) into soluble Co(II).

To further elucidate the role of 6 g L^{-1} Fe^{2+} in the improvement of metal yield using the MCB system, XPS analysis of Fe 2p in the leached residue was performed as described in Fig. 6c. The analysis revealed six characteristic peaks in the Fe 2p orbital. It has been previously reported that the peak at binding energy of 724.80 eV can be attributed to the Fe 2p1/2 peak of Fe(III), while its Fe 2p3/2 spectra included three peaks at binding energies of 710.60, 712.25, and 713.36 eV (Tang et al., 2020). Additionally, the satellite peaks of Fe 2p1/2 and Fe 2p3/2 were located at the binding energies of 718.650 and 732.04 eV, respectively. According to previous reports, the peaks possessing binding energies of 710.6, 712.25 and 713.36 eV can be attributed to $Fe(OH)_3$, Fe(OH-O) and Fe (III)-SO_4^{2-}, respectively (Chen et al., 2021; Feng et al., 2018; Lin et al., 2014; Tang et al., 2020). In particular, the appearance of Fe(OH-O) and Fe(III)–SO_4^{2-} indicated that jarosite was formed on the surface of the SLBs (Chen et al., 2021). Thus, the mechanism of the Fe^{2+}-MCB process for SLBs leaching can be expressed by Eqs. (1)–(6). Specifically, when Fe^{2+} was added to the MCB system, it released electrons to attack $LiCoO_2$ (Eq. (1)), causing Co in the SLBs to convert from Co(III) to Co(II) (Eq. (2)). Additionally, the acid produced by the microorganisms drives the extraction of Co from the SLBs powder (Eqs. (3)–(4)) (Naseri et al., 2019a; You et al., 2020), thereby enhancing the Co leaching yield. Furthermore, Fe^{3+} is hydrolyzed into $Fe(OH)_3$ (Eq. (5)) or jarosite (Eq. (6)), ultimately leading to the release of hydrogen ions that could prevent a significant elevation in pH during SLBs leaching and improve the

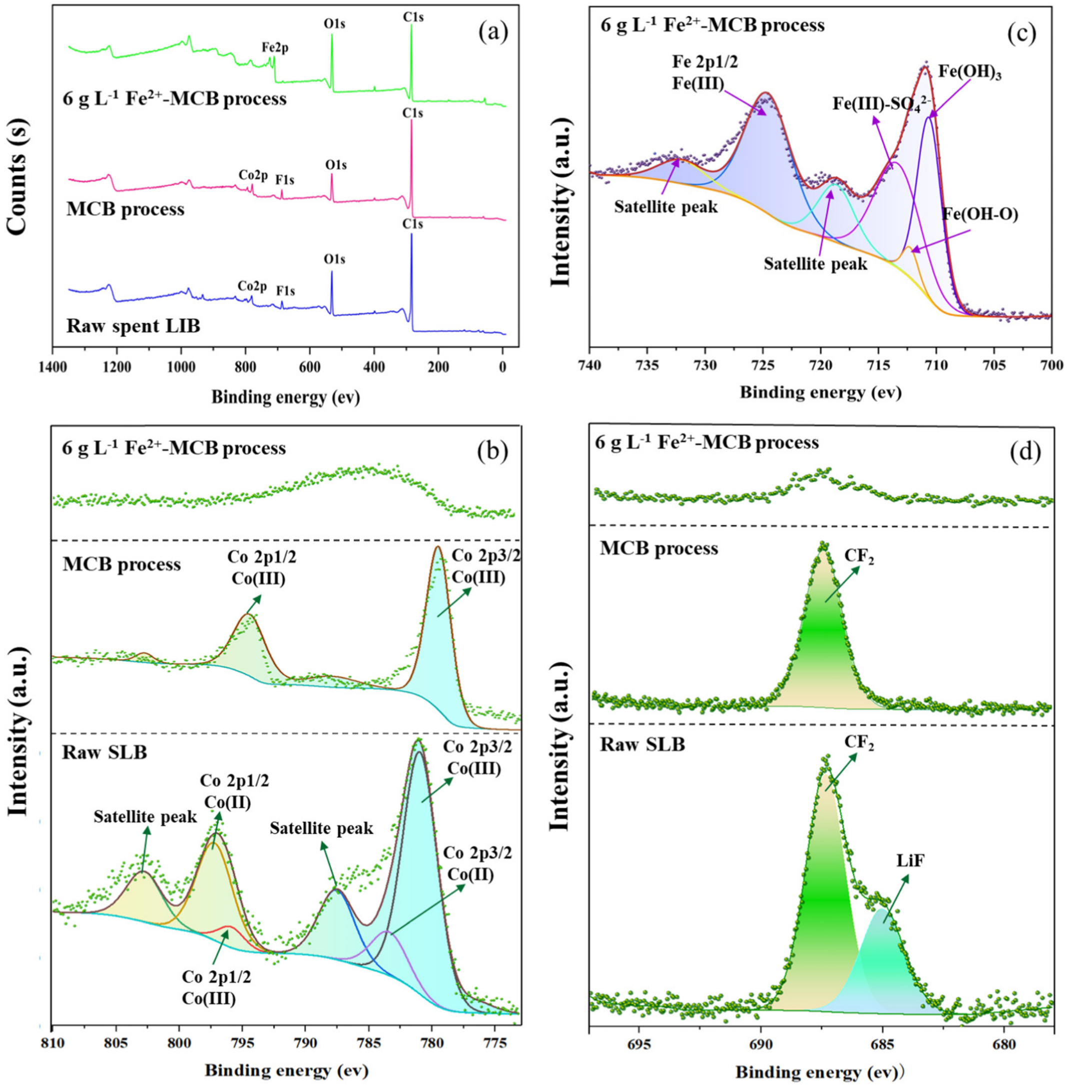

Fig. 6. The XPS results of SLBs before and after disposal by MCB and 6 g L^{-1} Fe^{2+}-MCB processes: (a) full-scan spectrum; (b) Co 2p; (c) Fe 2p; (d) F 1s.

dissolution of metal ions from the SLBs (Naseri et al., 2019a; Silva et al., 2020). Simultaneously, the precipitated Fe^{3+} facilitated the subsequent removal of Fe^{3+} from the leachate.

$$Fe^{2+} - e^{-} \rightarrow Fe^{3+} \tag{1}$$

$$Co^{3+} + e^{-} \rightarrow Co^{2+}\ (CoO) \tag{2}$$

$$2S^{0} + 3O_2 + 2H_2O \overset{\text{Bacteria}}{\rightarrow} 4H^{+} + 2SO_4^{2-} \tag{3}$$

$$CoO + 2H^{+} \rightarrow Co^{2+} + H_2O \tag{4}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+} \tag{5}$$

$$3Fe^{3+} + K^{+} + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^{+} \tag{6}$$

As can be observed from Fig. 6d, the F1s peaks in the raw SLBs powder were located at binding energies of 685.02 and 687.34 eV and were attributed to LiF and CF_2, respectively (Gauthier et al., 2020). Overall, these results confirmed that the SLBs residue contained the binder polyvinylidene fluoride (PVDF) and the electrolyte $LiPF_6$ salt that presents a toxic hazard to the environment once they leak from the SLBs (Guo et al., 2021; Sethurajan and Gaydardzhiev, 2021). After the treatment of SLBs by mixed culture, the characteristic peak of LiF disappeared, likely due to $LiPF_6$ becoming hydrolyzed into HF that is harmful to the growth of bacteria (Roy et al., 2021a). Furthermore, the PVDF peak also disappeared from the surface of the SLBs after treatment with the Fe^{2+}-MCB process, revealing that PVDF was degraded. Therefore, the Fe^{2+}-MCB process can effectively reduce the hazards posed by organic matter present in the SLBs to the environment.

3.6. Environmental implications

Metal recovery from SLBs is essential to address the increasing gap between market demand and depletion in available reserves. However, it remains challenging to leach >90% of Co and Li from LIBs using bioleaching at a pulp density of 20 g L^{-1} (Niu et al., 2014). In this study, Co and Li of >99% were leached from SLBs by the 6 g L^{-1} Fe^{2+}-MCB process, allowing the metals to be easily recycled by precipitation and extraction. However, Fe^{0} suppressed metal extraction from SLBs in MCB system. Finally, this study revealed that the different effects of Fe^{2+} and Fe^{0} on SLBs leaching were related to their acid consumption and toxicity characteristics toward bacteria.

The TCLP results indicated that the Co leaching concentration (591.47 mg L^{-1}) from the raw SLBs significantly surpassed the specified threshold of 85 mg L^{-1} (Table 2), highlighting the risk of leaching toxicity

Table 2
Results of toxicity assessment of SLBs before and after leaching.

Elements	Metal concentrations in the acetic acid during TCLP test (mg L^{-1})				
	Raw SLBs	Bioleached residue A	Bioleached residue B	Bioleached residue C	Threshold value
Co	591.47	5.19	178.71	1.62	85[a]
Li	102.08	0.83	12.69	0.12	–

Note: the bioleached residues A, B and C were obtained after SLBs treatment by MCB, 6 g L^{-1} Fe^0-MCB and 6 g L^{-1} Fe^{2+}-MCB processes, respectively.

[a] The threshold limit value of california regulatory.

(Heydarian et al., 2018). Currently, SLBs are considered hazardous waste by the US Environmental Protection Agency, and require proper disposal (Bahaloo-Horeh and Mousavi, 2017). After bioleaching treatment of SLBs with the mixed culture, the Co leaching concentration from the bioleached residue was reduced to an acceptable level (5.19 mg L^{-1}). Thus, biological oxidation is conducive to the transformation of SLBs from hazardous waste to non-hazardous waste (Liao et al., 2021). Moreover, the addition of 6 g·L^{-1} of Fe^{2+} to the MCB system further reduced the leaching toxicity of Co (1.62 mg L^{-1}). This is because the greater amount of Co leached from SLBs by the synergistic effect of 6 g L^{-1} Fe^{2+} and the mixed culture, reduced its content in SLBs. However, after SLBs treatment by the MCB process with 6 g L^{-1} of Fe^0, the Co leaching concentration was 178.71 mg L^{-1} from the bioleached residue and remained above the standard threshold value, revealing that the bioleached residue still poses a hazard to the environment. Hence, Fe^{2+} performed better than did Fe^0 in regard to reducing SLBs leaching toxicity during the MCB process. Briefly, this study developed a high-efficiency process to leach metals from SLBs and reduce the leaching toxicity of SLBs. A flow chart of the processes used in this study is presented in Fig. 7 to highlight the research objectives and significance of this study.

4. Conclusions

In this study, a MCB process involving *A. caldus* and *S. thermosulfidooxidans* was used to extract 66% of Li and 41% of Co from SLBs. Significantly, this MCB process coupled with 6 g L^{-1} of Fe^{2+} achieved 100% Li and 99% Co yields, while Li and Co yields were both <15% when Fe^{2+} chemical leaching was used. The XPS results revealed that the effective metal recovery from SLBs by the Fe^{2+}-MCB process was attributed to the release of electrons from Fe^{2+}, thus reducing insoluble Co(III) to the easily bioleachable Co(II). Finally, this coupled process markedly reduced the leaching toxicity of Co from 591.47 to 1.62 mg L^{-1}, which is below the acceptable level. However, the addition of Fe^0 inhibited the extraction of metals from SLBs by the MCB process, as Fe^0 caused bacterial apoptosis and an increase in pH. The XRD results also confirmed that Fe^{2+} exhibits an advantage over Fe^0 in regard to improving metal recovery from SLBs by the MCB process. Thus, in industrial applications, when a reductant is added to the bioleaching system to improve SLBs leaching, the selected reductant should exhibit low acid consumption and be non-toxic to bacteria.

CRediT authorship contribution statement

Xiaojian Liao: Conceptualization, Investigation, Methodology, Formal analysis, Software, Roles/Writing - original draft. **Maoyou Ye**: Methodology, Validation, Writing - review & editing. **Jialin Liang**: Methodology, Writing - review & editing. **Zhijie Guan**: Writing - review & editing. **Shoupeng Li**: Conceptualization. **Yanghong Deng**: Data curation. **Qiaowei Gan**: Investigation. **Zihang Liu**: Investigation. **Xiaodi Fang**: Validation. **Shuiyu Sun**: Conceptualization, Funding acquisition, Project administration, Resources, Supervision.

Declaration of competing interest

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

Acknowledgements

This work was supported by the GuangDong Basic and Applied Basic Research Foundation (2021A1515110662), the National Key R&D Program of China (No. 2018YFD0800700), the Natural Science Foundation of Guangdong Province (No. 2015A030308008) and the Science and Technology Planning Project of Guangdong Province (No. 2016A040403068).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.154577.

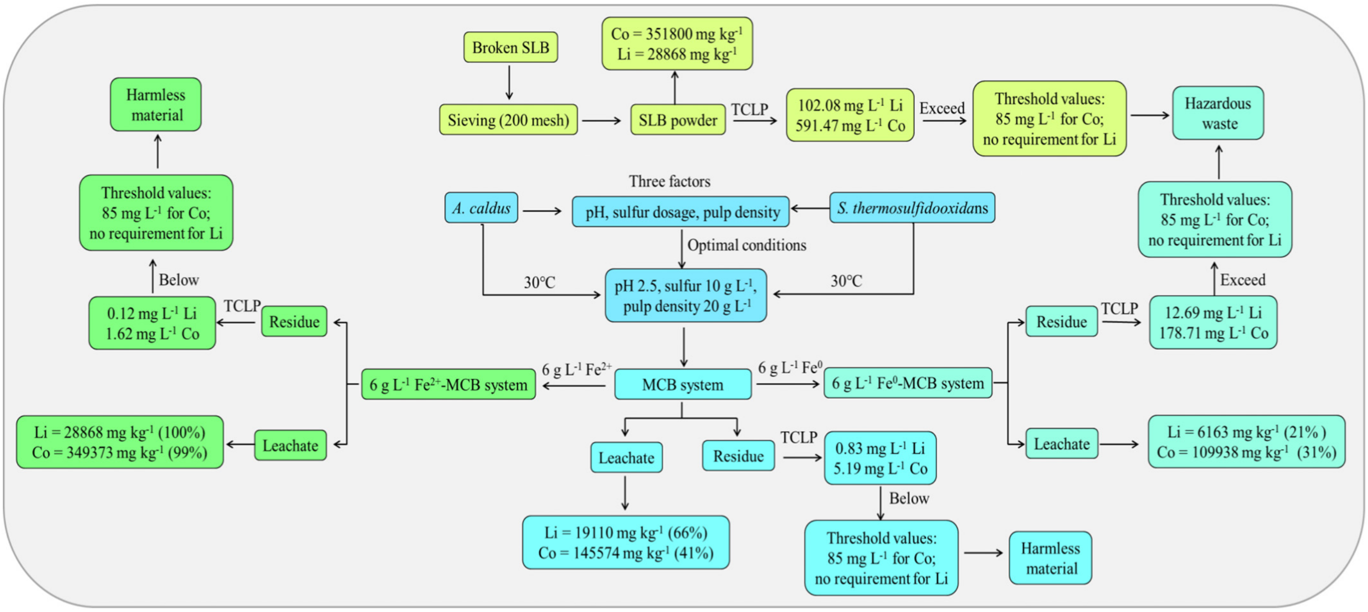

Fig. 7. The flow chart about the processes of recovery metal from SLBs in this study.

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