

Enhanced bioleaching of valuable metals from spent lithium-ion batteries using ultrasonic treatment

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Abstract—Recycling spent lithium-ion batteries is important from an environmental perspective and metals worthiness. In this study, an ultrasonic-assisted bioleaching process was developed to recycle valuable metals from spent lithium-ion batteries using bacterial supernatant of *Acidithiobacillus ferrooxidans*. The results showed that 13% Co, 42% Mn, 25% Ni, and 57% Li were extracted after 24 hours from 10 g/L pulp density without ultrasonication. Ultrasonication with a power of 203.5 W for 30 minutes with intervals of 1 hour enhanced the metal extraction and reduced bioleaching time; 19% Co, 50% Mn, 34% Ni, and 67% Li were extracted after 12 hours from 10 g/L pulp density. This study also investigated the effect of ultrasound on the growth of the pure culture of *Acidithiobacillus ferrooxidans*. Results indicated that a 10-minute daily application of ultrasonic waves with a power of 203.5 W was optimal for bacterial growth. The results of metals extraction and morphological, structural, and elemental analyses of the battery powder before and after the bioleaching process proved that the application of ultrasound effectively enhanced metal extraction and reduction of bioleaching time as well as the growth of *Acidithiobacillus ferrooxidans*.

Keywords: Lithium-ion Battery, Heavy Metals, Ultrasonic Treatment, *Acidithiobacillus ferrooxidans*, Bioleaching

INTRODUCTION

Electronic waste is one of the fastest-growing waste streams that contains large amounts of precious metals along with heavy metals and dangerous substances which can be used as secondary metal sources [1,2]. Among solid wastes, spent lithium-ion batteries (LIBs) make up a major part, due to their extensive usage in electronic devices [3]. Considering the presence of hazardous heavy metals in the composition of batteries like cathodic material of LiCoO_2 , LiMnO_4 , LiNiO_2 , and flammable toxic materials including LiPF_6 , $\text{Li}(\text{SO}_2\text{CF}_3)_2$, LiBF_4 , LiCF_3SO_3 , disposal of LIBs by improper methods would be a threat to human health and the environment [2,4]. Most of the waste materials of LIBs are disposed of as domestic waste. Heavy metals and organic electrolytes of LIBs can gradually penetrate the soil, surface, and underground water and also cause the emission of greenhouse gases [5,6]. It is reported that 4,000 tons of spent LIBs contain 1,100 tons of heavy metals and more than 200 tons of toxic electrolytes [7]. The value of one ton of LIBs is 7708 USD, 6101 dollars of which is related to their cathodes [8]. In fact, the most expensive constituent of the battery is the materials present in its cathode [9]. The average lifetime of these batteries is 2 to 5 years for electronic devices and 8-10 years for automobiles or other energy-saving systems; therefore, forecasts indicate that there is a need for 900 GWh LIBs till 2026 and this high demand means that large amounts of spent LIBs waste will be produced in near future [10,11].

One of the problems of the bioleaching process that prevents the commercialization of this process in metal recovery is its slow kinetics in comparison to other extraction methods [12]. According to the reports, ultrasound can help increase the rate of the bioleaching process and, as a result, the extent of extraction; this enhancement is achieved through the increase in metabolite production and small-scale mixing [13]. In a liquid medium, ultrasonic waves compress and stretch the molecular spacing, creating voids (or cavitation bubbles) containing liquid vapor. Once the bubbles reach their maximum size, they collapse during the next compression cycle (also known as cavitation) [14]. The bursting of the bubbles releases a tremendous amount of energy. By the tremendous impact of the broken bubbles, very high pressure is created on the interface of the solid and the liquid around the bubbles, which can help improve the leaching efficiency [15]. Each collapsing bubble can be considered as a microreactor in which temperatures of up to several thousand degrees and pressures higher than one thousand atmospheres are reported to be created instantaneously [14]. Experimental estimates of pressure and temperature are in the range of 500-1,800 atm and about 750-6,000 K, respectively [13].

In addition to temperature and pressure, the influence of free radicals has been reported in the reactions that occur in aqueous systems [16]. For example, in a bioleaching process that takes place in an aqueous system, the free radicals are very likely to play an important role. The formation of free radicals is likely to initiate chain reactions leading to an upsurge in leaching [13]. It was reported that free radicals such as $\text{OH}\cdot$ and $\text{HO}_2\cdot$ radicals can facilitate the oxidative conversion of Fe^{2+} to Fe^{3+} ion (a powerful oxidizing agent), resulting in enhanced metal extraction [17].

Chemical leaching processes are heterogeneous (solid-liquid) and

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the effect of ultrasound on them is mainly mechanical and attributed to cavitation. The waves resulting from cavitation intensify the movement of the solid particles and cause their powerful collision [13]. It has been witnessed that ultrasound enhances the chemical leaching of some metals like silver, gold, tungsten, titanium, nickel, and other rare metals [18,19]. Ultrasound can also be used in bioleaching during the growth of microorganisms or during the leaching stage. When used throughout the growth, to maintain positive effects on it, low frequencies are often utilized to have positive effects on the growth. Using ultrasound during the growth phase is advantageous only when it increases the effective metabolites in bioleaching; whenever the ultrasound does not increase the microbial growth and production of effective metabolites on bioleaching, it must be assessed in a spent culture medium. The mechanical effects of cavitation might result in the enhancement of bioleaching via decomposition of particles and microscopic mixing. However, the effect of ultrasound depends on some factors like reactions in the medium, metabolites, reactants, physical characteristics, and pH [13,20]. *Escherichia coli* was used in two-stage bacterial leaching using ultrasound, to boost molybdenum recovery from spent catalysts. Discontinuous ultrasound with 38 and 80 kHz frequencies gave rise to the molybdenum extraction from 46 to 54% [14]. Anjum et al. [21] reported that the utilization of ultrasound during the growth phase of *Aspergillus niger* for 7 min per day and with 40 kHz frequency resulted in the production of concentrated metabolites. Sukla et al. [22] carried out an experiment using ultrasound for 30 min at 43 kHz and 1.5 W/cm² on nickel ore and *Aspergillus niger*, aiming to maximize the leaching of nickel from the ore. In one-stage leaching, the maximum recovered nickel, without considering the ultrasound effect, was 92% in 20 days; however, when the ultrasound effect was taken into account, the nickel recovery had increased to 95% while the required leaching time was decreased to 14 days.

The main purpose of this study was to investigate the effect of ultrasound on the extraction of four metals, including manganese, cobalt, nickel, and lithium, and on the required bioleaching time using bacterial supernatant of *A. ferrooxidans*. To the best of our knowledge, there is no report on sonobioleaching of LIBs using bacterial supernatant of *A. ferrooxidans* up to now. Moreover, for the first time, the effect of ultrasound on the growth of a pure culture of *A. ferrooxidans* was investigated in this study.

MATERIALS AND METHODS

1. LIBs Powder Preparation

The spent batteries used in this research were all lithium-ion types that were collected from cell phone stores. First, all the batteries were discharged to prevent fire or short circuits and then were dismantled to their components like anode, cathode, plastic divider, and metallic frame. The cathode, which contains Al foil collector and cathode active materials, was dried in an oven for 24 hours at 60 °C and then cut into pieces of about 1 cm² area. A planetary ball mill and a mill were used simultaneously to reach the cathode powders. When the powdered sample was screened with a mesh number 200, a homogeneous powder with particle size less than 75 μm was obtained.

2. Characteristics of LIBs Powder

The alkaline fusion method was used to determine the constit-

uents of LIBs powder. In this method, 0.25 g of the powder was placed in a platinum crucible with a mixture of sodium-potassium carbonate and boric acid with a 4:3 ratio. This mixture was melted first on a flame and then in an electric furnace working at 950 °C for 15 min. The melted materials were dissolved in HCl (1:1) and aqua regia (5 mL). Then, 100 mL of deionized water was used to prepare the filtered digestion. The inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized to measure metal concentration in the solution.

To determine the primary pH of the LIBs powder, 1 g of the powder was mixed with 50 mL of deionized water in a flask. The flask was put in a shaking incubator at 160 rpm for 24 hours [23]. The primary pH of the powder was 8; it indicates the alkaline nature of the battery powder due to the presence of alkaline components like lithium compounds. The metallic lithium belongs to the alkaline metals family and is highly reactive with water. Lithium produces an aqueous solution of strong basic hydroxides when reacting with water.

3. Microorganism and the Growth Condition

One of the most important parameters affecting bioleaching is the selection of the proper strains. The mesophilic *A. ferrooxidans* strain No.: 1647 PTCC, purchased from the Iranian Research Organization for Science and Technology (IROST), was used for the extraction of metals like lithium, manganese, cobalt, aluminum, and nickel from LIBs powder, and also the investigation of ultrasound effect on bioleaching. This strain was a domestic strain separated from the Sarcheshmeh copper mine in Kerman province with an optimal growth temperature of 30 °C. The composition of the required material for the preparation of this strain culture medium, which is called a 9 K culture medium, is: 0.01 g Ca(NO₃)₂, 0.1 g KCl, 0.5 g MgSO₄·7H₂O, 0.5 g K₂HPO₄, 3 g (NH₄)₂SO₄, and 44.22 g Fe₂SO₄·7H₂O per 1 L distilled water. The 9 K culture medium does not need to be sterilized due to acidic conditions for culturing of *A. ferrooxidans* [24]. To culture the bacteria, the 9 K culture media was first inoculated with 5% (v/v) of seed culture in a 250 mL Erlenmeyer flask containing 100 mL of the culture medium, and then it was placed in a shaking incubator at 30 °C and 160 rpm. Since the proper pH for bacterial growth is about 2, concentrated sulfuric acid (98%) was used for the perfect adjustment of pH.

4. Sonobioleaching Experiments

We selected lithium, manganese, nickel, and cobalt as the main elemental targets to be investigated; the reason for this selection is their abundance, high value, and toxicity. There are three different methods in a bioleaching process: i) one-step, ii) two-step, and iii) spent medium bioleaching [25]. In the present study, due to the high toxicity of the LIBs powder, the spent medium bioleaching with and without ultrasonic treatment was examined. The low reaction rate of the bioleaching process is one of the main issues that prevent its widespread commercialization. Reports indicate that the application of ultrasound in bioleaching results in enhancing metal extraction [13].

To conduct the bioleaching process without the assistance of ultrasonic (conventional bioleaching), Erlenmeyer flasks (250 mL) of 9 K medium (100 mL) were prepared, and then 5% (v/v) inoculum was added into the culture medium. After the maximum conversion of ferrous ions into ferric ions by a pure culture of *A.*

ferrooxidans (which occurs after three days), the medium was centrifuged (10,000 ×g for 20 min at 4 °C) to gain the spent cell-free medium (The 9 K culture medium contains 44.22 g/L FeSO₄·7H₂O which is equal to 9 g/L ferrous ions. When all the ferrous ions are converted to ferric ions by the action of bacteria, nearly 9 g/L of ferric ions is present in the culture medium. By monitoring the amount of available ferric ions in the media, the maximum conversion of ferrous ions into ferric ions and the time of reaching nearly 9 g/L of ferric ions can be defined). Then, 1 g battery powder was added to the 100 mL of spent medium for 24 hours at 30 °C and 160 rpm.

The procedure was the same as the conventional bioleaching, which was described in the previous paragraph, but in the growth period of *A. ferrooxidans*, the ultrasonic wave was applied for 10 min (40 kHz) per day upon the flasks because the ultrasound can enhance the speed of oxygen and nutrient transfer to the microorganisms. In addition, after centrifuging the medium and adding the powder to the spent medium, the bioleaching medium was sonicated for 30 min in an ultrasonic bath every 1 hour. The conditions for the ultrasound-assisted bioleaching were: a temperature of 30 °C and a power of 203.5 W. Due to working with a biological system, the bath temperature was monitored using a thermometer and maintained at 30 °C. A power of 203.5 W was selected based on a literature study [13,14,21,26,27] and our preliminary experiments to find the most suitable power (data not shown). During the bioleaching process with and without ultrasonic treatment, the pH and Eh variations were measured. After a desired time of bioleaching, the concentration of metals was determined using ICP-OES.

5. Analytical Methods

Ferrous sulfate is one of the major salts of *A. ferrooxidans* culture media. Ferrous ions are converted into ferric ions by this microorganism, and this way, the strain gains its required energy [28]. The amount of available ferric ions in the media can be a good indication of how far the bioleaching process has progressed. To measure the concentration of ferric ion, 3 mL of 10% 5-sulfosalicylic acid was added to 100 μL of the sample in a 100 mL volumetric flask, and the resultant solution was made up to 100 mL with deionized water. The appearance of purple color in the solution is a hint of ferrous ion consumption by microorganisms and, therefore, the formation of ferric ions. The absorption of ferric ions was measured by an optical spectrometer device (Optizen; 3200-UV; South Korea) at the wavelength of 500 nm. For the investigation of the chemical structure, functional groups, and bonds of the battery powder before and after bioleaching, Fourier transform infrared spectroscopy (FTIR) (Perkins-Elmer; USA) was carried out in the range of 500–4,000 cm⁻¹ and ambient temperature. The solid sample was mixed with potassium bromide and was shaped in the form of a pellet under five tons of weight press. Then the prepared sample was placed in the device to obtain its spectrum. To determine the constituent phases of battery powder, X-ray diffraction (XRD) (X'Pert MPD; Philips; the Netherlands) was used to show the amorphous or crystalline structure of the sample. The XRD patterns were obtained using an optical spectrometer with Kα, Co anode and wavelength of 1.78901 Å, accelerator voltage of 40 kW, amperage of 40 mA, and in the range of 2θ from 10 to 90° with 0.02 step size in each second. pH was measured by a pH meter (p25; Istek; South

Korea). Eh was measured by an Eh meter (691; Metrohm; Switzerland) with a platinum reference electrode. An optical microscope (standard25; Zeiss; Germany) was utilized for cell counting. The concentration of different metal ions in a sample was assessed by an ICP-OES (Spectro Arcos, Germany). To determine the size and morphology of the battery powder particles before and after bioleaching, we used field emission scanning electron microscopy (FESEM) (S-4160; Hitachi; Japan). The samples were placed on sticky carbon tape and were coated with a 30 nm thick gold layer to enhance the electric conductivity of their surfaces and the resolution of the pictures; then the prepared sample was tested under 30 kW accelerator voltage and high vacuum. For the ultrasound-assisted bioleaching, the ultrasonic bath (Daihan Scientific; Wise clean D10H; South Korea) operated at a frequency of 40 kHz and a maximum power of 407 W. The used ultrasonic bath had a microprocessor control containing: a timer (0 to 60 min), temperature (ambient to 80 °C), and changeable power output from 20 to 100% watt.

To calculate the metal extraction, Eq. (1) was employed, in which C_s corresponds to the concentration of the metal in bacterial leaching solution (mg/L), C_f is the concentration of the metal in the battery powder (mg/g), M_f is the amount of battery powder used in bacterial leaching (g), and V_s is the culture volume used for bacterial leaching (L) [29].

$$\text{Metals Extraction} = \frac{C_s \times V_s}{C_f \times M_f} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

1. Morphological Characterization and Analysis of Metal Content in LIBs

According to ICP analysis, manganese (23.65%), cobalt (20.46%), aluminum (6.14%), nickel (3.45%), and lithium (3.74%) had the highest amount in the cathode powder of LIBs. Other elements like iron, magnesium, and silica are negligibly present in the battery cathode powder. The morphology of the LIBs powder is presented in Fig. 1, where Fig. 1(a) shows the camera image of LIBs powder. FESEM micrograph in Fig. 1(b) demonstrates the presence of numerous disordered particles that are randomly distributed throughout the surface of the powdered battery. In a closer view (Fig. 1(c)), the surface of LIBs powder before the bioleaching process appears fairly smooth. Based on the EDX and mapping images (Fig. 1(d)-(e)), it can be concluded that the main metallic elements of LIBs were Mn, Co, Al, and Ni, excluding Li due to its well-known impossibility of detection by this technique.

2. Effect of Ultrasound on Culture Medium

2-1. Effects on the *A. ferrooxidans* Growth

Fig. 2 shows the cell density changes of *A. ferrooxidans* in the presence and absence of ultrasound. According to Fig. 2, when ultrasound was used for 10 min in a day at 203.5 W power and 40 Hz frequency during the growth, and at the bacterial growth temperature, the logarithmic growth phase of *A. ferrooxidans* elongated, and the logarithmic growth phase increased from three to five days. Without ultrasonic treatment, the bacteria entered the stationary phase after the third day, while using ultrasonic treatment, the cell

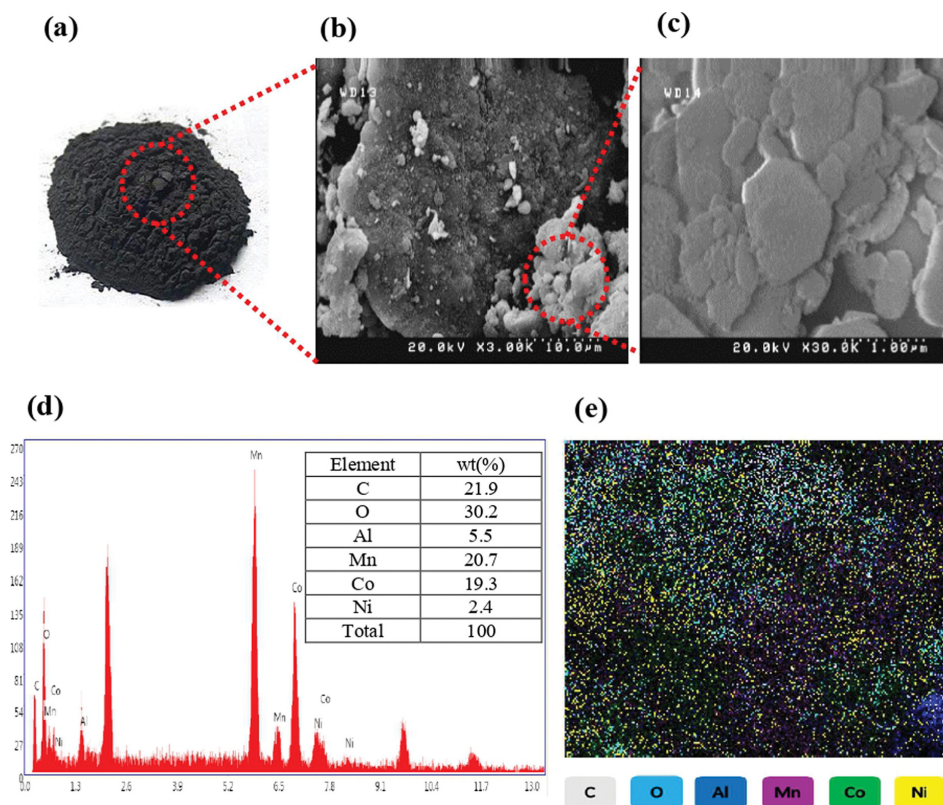


Fig. 1. (a) Photograph of the original LIBs powder, (b) low-magnification SEM image, (c) high-magnification SEM image, (d) EDX spectrum before bioleaching, and (e) EDX mapping before bioleaching.

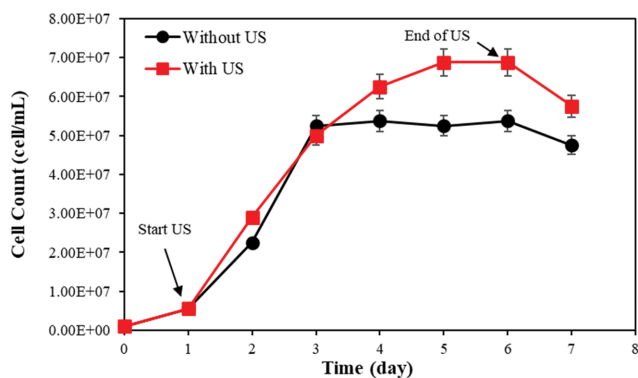


Fig. 2. The cell density curve of *A. ferrooxidans* growth in two modes of with and without ultrasound sonication (US) treatment.

density continued its increasing trend until the fifth day and then entered the stationary phase on the sixth day. Therefore, the *A. ferrooxidans* had a longer logarithmic growth phase and shorter stationary phase *via* ultrasound treatment. This might be because ultrasonic treatment increases the rate of oxygen and nutrient transfer to the cell and the rate of waste material rejection from the cell, and thus increases bacterial growth [30]. In general, cell growth increases at low ultrasound intensity due to the strengthening displacement power and transport of small molecules in the solution. Furthermore, previous researches indicated that the utilization of low-power ultrasound stimulates microorganisms' growth and

helps their rapid growth [14,21,31].

2-2. Effects on the Ferric Ions

At the power of 203.5 W, the concentration of ferric ion after 72 hours was 9,000 mg/L which was higher than the case cultured without ultrasonic treatment (8,300 mg/L). The reason for this enhancement in ferric ion concentration, especially in a suitable power, is the ease of oxidative conversion; so that sharp changes in temperature and pressure conditions (sharp temperature rise to 750-6,000 K and pressure increase to 500-1,800 atm [13]) result in a burst of bubbles due to the cavitation phenomenon and production of $\text{OH}\cdot$ radical as a strong oxidative agent. The occurrence of this phenomenon in an acidic environment makes the conversion of ferrous ions to ferric ions easier. However, this oxidation is not just due to the formation of $\text{OH}\cdot$ radicals since the production of $\text{HO}_2\cdot$ radicals, H_2O_2 molecules, and H atoms under ultrasonication results in the occurrence of cavitation. The enhancement of ferric ion concentration increases the bioleaching rate [17].

2-3. Effects on the Eh

Eh indicates changes in oxidation-reduction potential. Eh increases when ferrous ion converts to ferric ion in a medium and vice versa. Fig. 3 illustrates the changes in Eh for the without and with ultrasonic treatment cases at 203.5 W. When ultrasound was used, the Eh reached about 600 mV after 72 hours, while Eh was about 500 mV without ultrasonic treatment. The utilization of ultrasound with 203.5 W power causes an enhancement in the production of free ions in the media. As discussed before, ultrasonication increases the concentration of ferric ions [17]; this enhancement

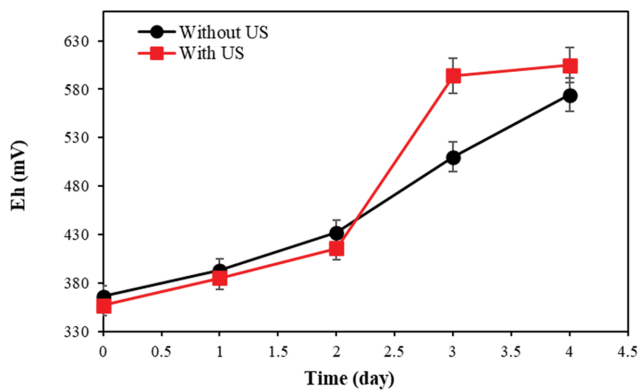


Fig. 3. Changes in Eh with and without ultrasound sonication (US) treatment during the growth of *A. ferrooxidans*.

affects Eh.

3. Effect of Ultrasound on Bioleaching Process

Considering the high toxicity of LIBs powder (containing 23% manganese and 20% cobalt), the approach of spent medium bioleaching was conducted. Bioleaching was done with and without ultrasonic treatment. Furthermore, the effect of ultrasound was investigated on Eh, Fe^{3+} ion concentration, and pH during the bioleaching process. The percentage of Co, Mn, Ni, and Li extraction was also studied in the two mentioned modes.

3-1. Effect of Ultrasound on pH during the Bioleaching Process

A proton is consumed in the culture media according to reaction (2) when bacteria exist, and it is produced in the media according to reactions (3) to (5) [32-34]. When the production rate of H^+ ion in the media is greater than its consumption rate, pH decreases, but if the rate of H^+ ion consumption is greater than its production rate, the pH of the media increases [34].

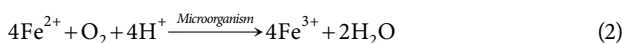


Fig. 4(a) displays the changes in pH during the bioleaching process. The increasing trend, which is observed after the addition of the powder, indicates the consumption of acid in the media and the dissolution of some alkali metals like lithium [35]. Since there are no bacteria in the spent culture media, H^+ ion production has stopped and there is just H^+ ion consumption that results in metal extraction; therefore, pH continuously increases with time, both in the presence or absence of ultrasound. Considering Fig. 4(a), when ultrasonic treatment is done during bioleaching, the final pH increases by about 0.15 compared to the absence of ultrasound. The graphs in Fig. 4(a) establish that after 12 hours (In the following, in section 3.3.3, is provided that the maximum extraction is achieved after 12 hours from the beginning of the bioleaching process), in the case of ultrasonic treatment, pH is about 0.45 higher than the case that no ultrasound is utilized. This pH enhancement is due to the effect of ultrasound on the enhancement of the reaction rate [18,21]. Actually, the energy from the ultrasound can increase the

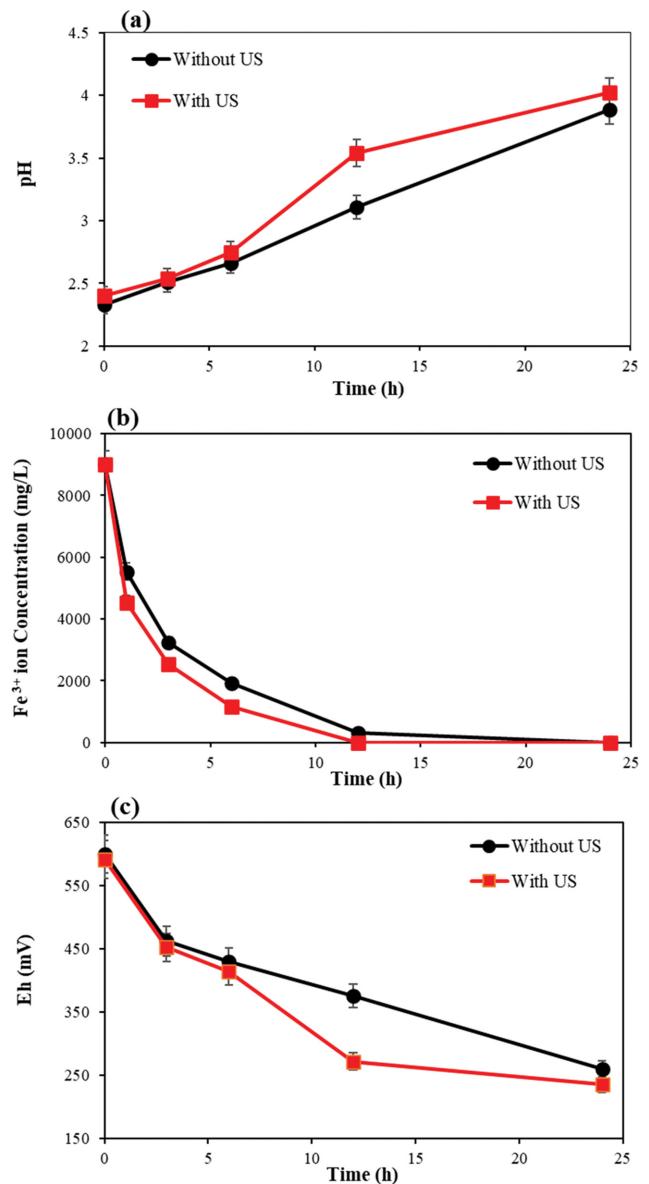


Fig. 4. Changes in (a) pH; (b) Fe^{3+} ion concentration and (c) Eh during bioleaching with and without ultrasonication.

rate of reaction or stimulate chemical reactions due to the formation of very reactive radicals during cavitation [36]. This enhancement in reaction rate and the formation of H_2O_2 and free radicals like $\text{HO}_2\cdot$ and $\text{OH}\cdot$ increases the consumption of H^+ ion and the formation of OH^- ion in the medium and, as a result, increases the pH [13].

3-2. Effect of Ultrasound on Ferric Ion Concentration and Eh during Bioleaching

The ferric ions and Eh changes are shown in Fig. 4(b) and 4(c). As seen, the descending trend in ferric ion concentration is obvious in both cases with and without ultrasound treatment.

After the addition of LIBs powder, ferric ion attacks the particles of solid powder and is reduced to ferrous ion and causes the dissolution of metals [34]. Considering that a spent culture media was utilized in this research, there are no bacteria in the medium

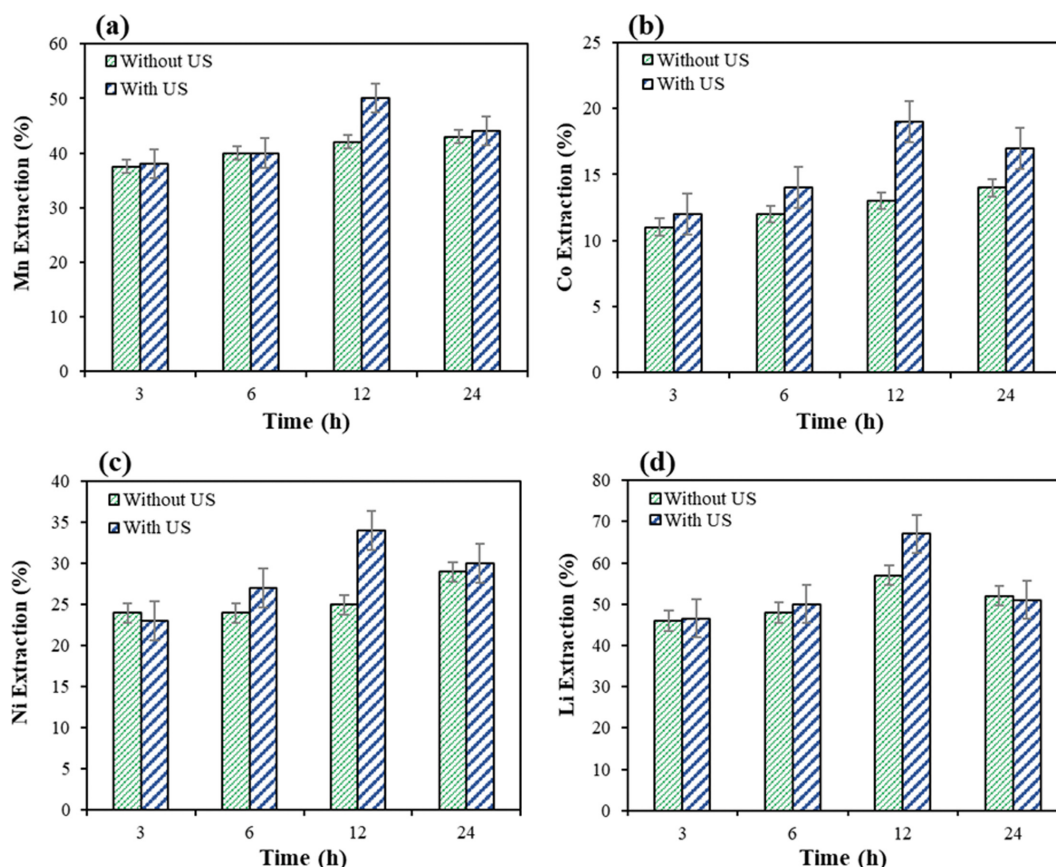


Fig. 5. Changes in metals extraction during bioleaching with and without ultrasonication (a) Mn, (b) Co, (c) Ni, and (d) Li.

that can continuously produce ferric ions by the oxidation-reduction; therefore, the ferric ion is continuously consumed through the reaction with metals, this causes the reduction of Eh with time in both cases of with and without ultrasonic treatment.

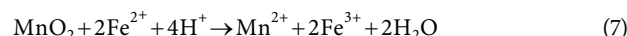
The ferric ion concentration and Eh are much decreased when ultrasound is utilized, maybe because of the influence of ultrasound on the enhancement of reaction rates by the formation of very reactive radicals during cavitation [36]. This enhancement might increase the rate of reaction of ferric ions with other metal species in the medium, so more ferric ions will convert to ferrous ions.

3-3. Mechanisms and Effect of Ultrasound on Metals Extraction

The extractions of Co, Mn, Ni, and Li, with and without ultrasonic treatment, during 24 hours were compared to one another. The results of these experiments are presented in Fig. 5(a) to 5(d). Evidently, the maximum extraction of all four metals is reached after 12 hours from the beginning of the bioleaching process, when using the ultrasonic treatment is on course. These extractions from a 10 g/L pulp, without ultrasonication, were 13%, 42%, 25%, and 57% for Co, Mn, Ni, and Li, respectively. When ultrasonic treatment was used (for 30 min at 203.5 W power with 1-hour intervals for 24 hours and at 30 °C in a 10 g/L pulp) to enhance the metal extraction, the obtained extraction was 19%, 50%, 34%, and 67% for Co, Mn, Ni, and Li that show 6%, 8%, 9%, and 10% enhancements, respectively.

The Mn and Co exist in the forms of LiMn_2O_4 and LiCoO_2 in LIBs powder. According to reactions (3) to (5), the released pro-

ton in the medium is consumed by LiMn_2O_4 and produces insoluble MnO_2 , according to reaction (6). MnO_2 produces Mn^{2+} ions according to reaction (7) [34,37].



The insolubility of MnO_2 makes the extraction of Mn harder. After the conversion of LiMn_2O_4 to MnO_2 in the medium, a very strong reducing agent like ferrous ion (Fe^{2+}) is needed to convert Mn^{4+} into Mn^{2+} ion. According to reaction (8), ferric ions might form jarosite instead of ferrous, and therefore there is no Fe^{2+} ion in the spent culture medium and there is not any source to supply this ion. As a result, the extraction of the Mn decreases due to the lack of a reducing agent. The precipitation of insoluble jarosite, which is an acid production process, occurred simultaneously with the hydrolysis reactions (reactions 3 to 5) [34, 38].



where $\text{M} = \text{K}^+, \text{Na}^+, \text{Ag}^+, \text{NH}_4^+, \text{or } \text{H}_3\text{O}^+$.

The extraction process of Co is a combination of acid dissolution and oxidation-reduction processes. Cobalt exists in a trivalent oxidation state in the structure of LiCoO_2 which is difficult to dissolve in an acid solution. Thus, reducing agents are required to reduce Co^{3+} to Co^{2+} because Co^{2+} is more readily dissolved than Co^{3+} in an aqueous solution, thereby increasing the dissolving rate

(reactions (9)) [39]. As a result of the reduction of LiCoO_2 by ferrous ions (as a strong reducing agent), Li_2O and CoO can be produced as a reducing product [34,40]. Moreover, it was reported that the cathode materials contain a small amount of CoO which originated from the transformation of LiCoO_2 [41]. The dissolution of CoO can occur by the attack of protons according to reaction (10) [42].



The low percentage of Co extraction is probably due to the lack of sufficient acid in the medium. Additionally, Co, like Mn, also needs a strong reducing agent like a ferrous ion.

Considering the formation of jarosite according to reaction (8), it can be said that there is no source of ferrous ion production in the spent culture media, and accordingly, the acid dissolution and oxidation-reduction reactions do not proceed completely and Co extraction is negligible and hard. The process for Ni extraction is similar to Co and a similar reaction can be considered for Ni, too. Ni extraction depends on a combination of acid dissolution and oxidation-reduction processes. Ni does not exist in the form of a complex in the primary LIBs powder; therefore, it might exist in the form of insoluble Ni^{3+} and needs to be converted into Ni^{2+} to be recovered [34,42].

Fig. 5(d) depicts the amount of Li extraction in different modes. A 57% Li extraction was achieved without ultrasonic treatment. Li is a highly reactive metal that needs to gain a proton to be converted from the oxide (or metallic) form into the ionic form. Since the release of Li in the media can be attributed to the gain of a proton, it can be expressed that generally the dissolution of Li directly depends on the acidity of the medium. The release of Li proceeds according to reaction (11) and consumes protons that prevent the reduction of pH in the medium [34,43-45].



When ultrasound was conducted under the explained conditions, the extraction of the target metals was enhanced and the Co, Mn, Ni, and Li extraction increased by 6%, 8%, 9%, and 10%, respectively. The lack of enough acid in the medium and the formation of iron precipitates such as jarosite are the two main reasons for the reduction in Mn, Co, Ni, and Li extraction when ultrasound treatment was not used [21,34,42]. On the other hand, the use of low-power ultrasound increases acid production, enhances microscopic mixing in the bioleaching system, and therefore decreases the required time for bioleaching [21]. Furthermore, using ultrasound leads to temperature and pressure increase in the reactions and intensifies the reactions due to the occurrence of cavitation [46,47]. The results of the EDX test in Fig. 9 indicate that when ultrasound is used, the amount of the iron precipitates such as jarosite decreases compared to the case where ultrasound is not used. Consequently, ultrasound treatment increases the extraction of Mn, Co, Ni, and Li by increasing acid production and reducing the formation of iron precipitates such as jarosite.

Since ultrasonic treatment increases the acidity, lithium extraction will be enhanced when using ultrasound [21,34]. Another important

reason for enhanced metal extraction by ultrasound treatment is the formation of very reactive radicals during cavitation that increases the reaction rate or stimulates the reaction [36]. This reason is so important in the reactions of bioleaching since the bioleaching process proceeds in aqueous systems and, therefore, it can be said that the free radicals play role in the influence of ultrasound on the bioleaching process. Reactions (12) to (15) express the formation of free radicals [13,16].



After the attack of ferric ion to the surface powder and the conversion of ferric ion to ferrous ion, the formed H_2O_2 , $\text{HO}_2\cdot$, and $\text{OH}\cdot$ in reactions (12) to (15) will again react with the ferrous ion according to reactions (16) to (18) and ferrous ions convert to ferric ions; this causes the formation of ferric ion in the media. On the other hand, the enhanced concentration of ferric ions in the medium results in an enhancement in the rate of the bioleaching process [17].



In general, ultrasound can affect bioleaching in four ways: (1) increased convective penetration in the culture media and the fragmentation of particles due to the ultrasonic treatment that accelerates bioleaching reactions; (2) the occurrence of cavitation as a result of ultrasonication that increases the temperature and pressure of the reactions; (3) the ultrasound amplifies the homogeneous and heterogeneous reactions (containing metals as the catalysts or reactants); and (4) the formation of very reactive radical species during cavitation that results in an enhancement of reaction rate or stimulates the reaction [13].

4. Changes in Structural Analyses of Powder

4-1. XRD Analysis

The patterns of XRD analysis, before bioleaching and after bio-

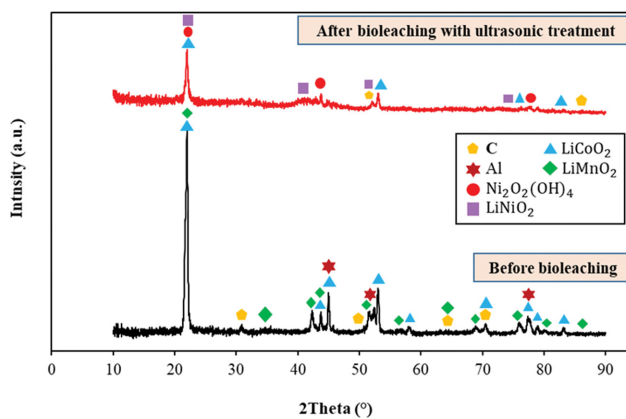


Fig. 6. The XRD of battery powder before bioleaching and after bioleaching with ultrasonic treatment.

leaching with ultrasonic treatment, are shown in Fig. 6. The crystalline phases of the cathode powder were determined by the XRD test. As shown in Fig. 6, the crystalline phases of lithium cobalt oxide (LiCoO_2) and lithium manganese oxide (LiMn_2O_4) are apparent in the powder sample before bioleaching. After bioleaching, the intensity of the LiCoO_2 peaks has decreased compared to the powder before bioleaching. Besides, the XRD analysis did not show any Mn in the resultant phases after bioleaching; it might be due to the transformation of the Mn structure to amorphous after this reaction. Amorphous structures do not show diffraction due to their low amplitude atomic order. Nickel oxide is another phase that is observed in the XRD test after bioleaching.

4-2. FTIR Analysis

The FTIR spectrum of the spent battery powder is presented in Fig. 7. In this spectrum of the spent battery powder after bioleaching, the observed peak at 500 cm^{-1} to 600 cm^{-1} belongs to the asymmetric tension of M-O (that M corresponds to Ni, Co, and Mn). The peak at 875 cm^{-1} corresponds to Al-O [42]. The other peak at $3,400\text{ cm}^{-1}$ relates to the adsorbed water and inner-hydroxyl group [48]. According to the FTIR spectrum of the sample after bioleaching, the peak at 610 cm^{-1} , which corresponds to the vibrating bonds of metal oxide structures, has lower intensity compared with the FTIR spectrum before bioleaching. This could indicate the dissolution of elements from battery powder. The peak at $1,115\text{ cm}^{-1}$ can be related to the vibration of SO_4 which can confirm the presence of jarosite [49]. It was reported that the peak at 435 cm^{-1} could be ascribed to the asymmetric stretching vibration of a metal oxide such as Fe-O [50]. Furthermore, the peak at $1,623\text{ cm}^{-1}$ that its intensity increased in the bioleached powder corresponds to the bending vibration of the O-H groups of the hydrated compounds that could be related to the hydroxyl and H_2O group of the jarosite [51]. After the bioleaching, a wide peak appears at $3,218\text{ cm}^{-1}$ indicating the tensile and vibrating absorption of O-H, indicating the formation of jarosite during the bioleaching process [49].

4-3. FESEM Analysis

The study of the surface morphology of battery powder is another efficient test for the investigation of the effect of the bioleaching process. For that reason, this test was carried out under three different conditions: (a) before bioleaching (Fig. 8(a)), (b) after bioleaching without ultrasonic treatment (Fig. 8(b)), and (c) after bioleaching

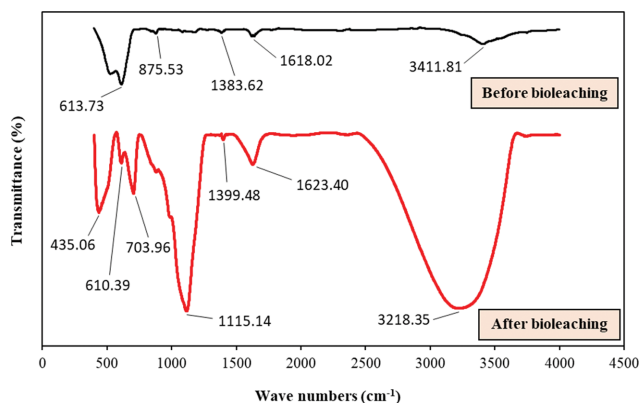


Fig. 7. The FTIR spectroscopy of the battery powder before bioleaching and after bioleaching with ultrasonic treatment.

with ultrasonic treatment (Fig. 8(c)).

According to Fig. 8(a), the primary battery powder has a smooth surface. Fig. 8(b) indicates that some cracks are formed after bioleaching without ultrasonication and the surface has become coarse, which is due to the reaction of ferric ions with the surface of the powder [34]. Fig. 8(c) displays an image of the powder surface after bioleaching with ultrasonic treatment. As observed, the size of particles has reduced compared to the preliminary battery powder and the surface of the powder has become coarser and perforated compared to the case without ultrasonication. The released energy by ultrasonication might have crushed the LIBs powder particles and reduced their sizes compared with conventional bioleaching [52]. The reduction of particle sizes after ultrasonication is due to the produced temperature and pressure as the result of the burst of the cavitation bubbles that destructs the solid surface and simplifies chemical reactions [53]. As mentioned, the mechanical effects of cavitation might amplify the bioleaching process through the decomposition of particles and microscopic mixing at the solid surface [20].

4-4. EDX Analysis

The results of EDX and mapping tests of the powder are presented in Fig. 9 for the two cases of using ultrasonic treatments and without ultrasonic treatment. The EDX analysis indicates that the

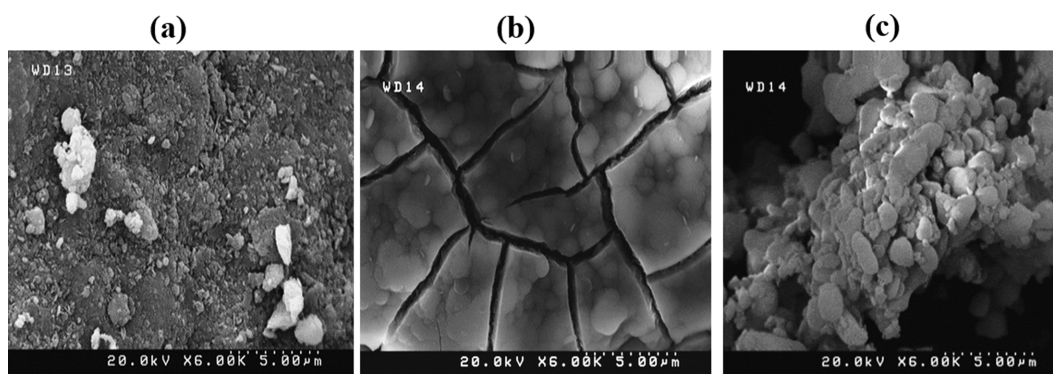


Fig. 8. FESEM images of battery powder (a) before bioleaching, (b) after bioleaching without ultrasonic treatment, and (c) after bioleaching with ultrasonic treatment.

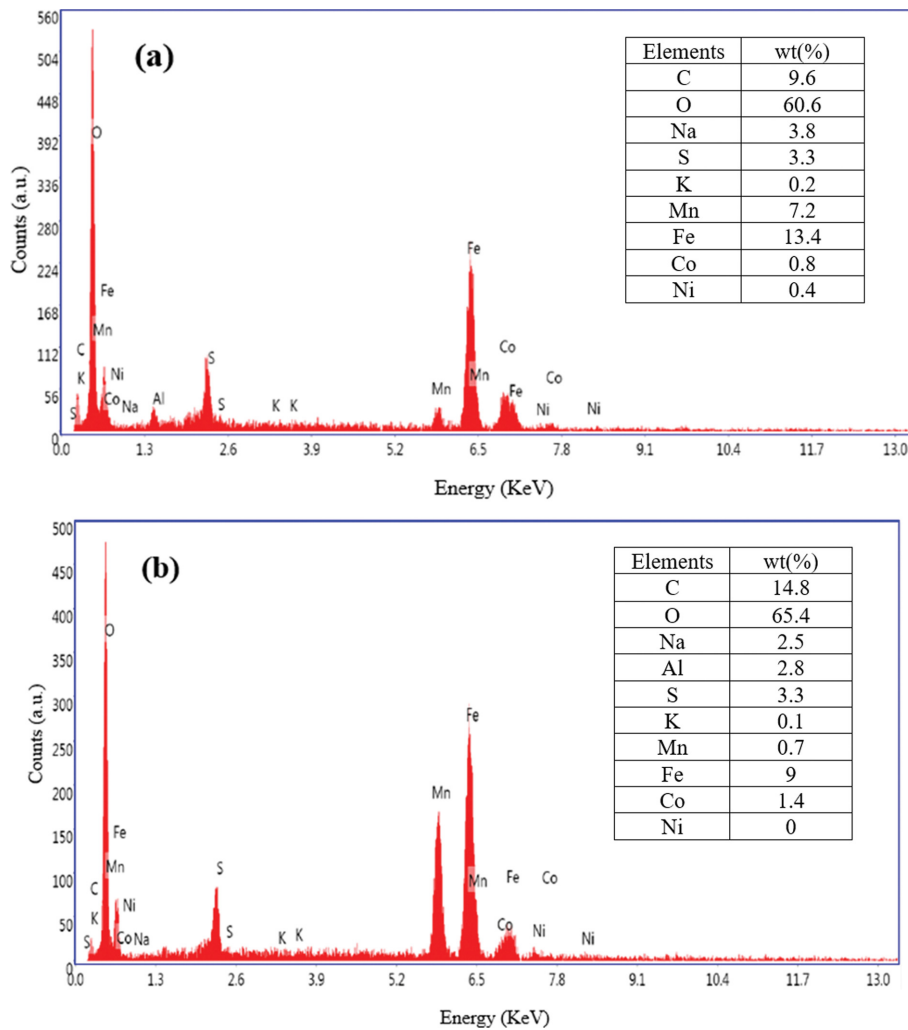


Fig. 9. EDX test (a) after bioleaching without ultrasonic treatment and (b) after bioleaching with ultrasonic treatment.

residual powder was covered with elements of S, Fe, K, Na, and O, the forming elements of jarosite. However, the stoichiometric ratios of S, Fe, K, Na, and O shown by EDX analysis indicate that jarosite is not the only form of iron precipitate.

Albeit, no iron precipitates such as jarosite compound were observed in the XRD pattern after bioleaching; it might be due to the amorphous structure of iron precipitates. The amorphous materials do not show diffraction due to their low amplitude of atomic order.

A comparison between the Fig. 9(a) and Fig. 9(b) reveals that the amount of Fe, K, and Na is higher in the absence of ultrasound compared to the case that was treated with ultrasound; therefore, considering that iron precipitates affect the bioleaching process through oxidation of iron and decrease of the extracted metals [42], the lower amount of iron precipitates can be another reason for the enhanced metal extraction by ultrasonic treatment.

CONCLUSIONS AND FUTURE DIRECTION

The variation of different parameters, such as ferric ion concentration, cell density, Eh, and pH, was first monitored during the growth of *A. ferrooxidans* with and without ultrasonic treatment.

Investigation of these parameters indicated that ultrasound affects the growth of *A. ferrooxidans*. Then, the effect of ultrasound on the bioleaching of Mn, Ni, Co, and Li from LIBs in a spent culture media was studied. Results reveal that bioleaching along with ultrasonic treatment has a positive effect on the rate of metal extraction; in a way that the rate of extraction of Co, Mn, Ni, and Li under 203.5 W, 30 °C, and ultrasonication of 30 min at each hour during 24 hours of the day were enhanced by 6%, 8%, 9%, and 10%, respectively, compared to the case with no ultrasonic treatment. The maximum extraction of metals occurred at a leaching time of 12 hours when using the ultrasonic treatment. EDX analysis showed that iron precipitates are formed on the surface of the powder after bioleaching that this amount of iron precipitates is lower compared to the case where no ultrasonic treatment was used. Therefore, according to the results obtained, ultrasound led to an increase in the extraction of target metals and also a reduction in bioleaching time and thus increasing the rate of reaction. In the future, it would be interesting to investigate the effect of ultrasound on other microorganisms that are effective in bioleaching, especially microorganisms that have a long growth period and a long leaching period. It is also recommended to use a probe ultrasonic device and investigate other vari-

ables such as temperature and frequency for new studies.

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