

Article

Enhanced Recovery of Lithium and Cobalt from Spent Lithium-Ion Batteries Using Ultrasound-Assisted Deep Eutectic Solvent Leaching

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Abstract: This study investigates the ultrasound-assisted leaching of Li and Co from spent batteries using a deep eutectic solvent (DES) composed of polyethylene glycol and thiourea. The synergistic effect of ultrasound and DESs was explored to enhance the efficiency of Li and Co recovery. The experimental results demonstrated that ultrasound significantly accelerates the leaching process, achieving up to four times higher recovery rates compared to traditional methods. Optimal leaching conditions were identified at a solid-to-liquid ratio of 0.02 g/g, a temperature of 160 °C, and periodic ultrasound exposure. Under these conditions, the leaching efficiency reached 74% for Li and 71% for Co within 24 h. A kinetic analysis revealed that the ultrasound application shifts the rate-limiting step from a mixed control of mass transfer and chemical reactions to predominantly chemical reaction control, reducing the activation energy by approximately 27%.

Keywords: lithium cobalt oxide (LCO); ultrasound-assisted leaching; deep eutectic solvent (DES); kinetic analysis



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1. Introduction

One of the main components of mobile phones, laptops, and digital cameras is a power element, which is a lithium-ion battery, mainly a lithium–cobalt battery. The battery consists of a graphite anode and a cathode made of lithium cobaltate (LiCoO₂); the cathode material also includes aluminum foil, carbon to improve electrical conductivity, and binding additives [1,2]. The average number of charge–discharge cycles is 500–1000, which predetermines a short service life of such batteries and their significant accumulation over time [3–5]. Waste lithium–cobalt batteries are considered in two important aspects. Firstly, they are potential sources of environmental pollution with cobalt and secondly, waste batteries are promising raw materials for the extraction of cobalt and lithium [6–9]. There are a number of approaches to the processing of lithium–cobalt batteries, including pyrometallurgical [10–13], hydrometallurgical [14–16], and mechanochemical [17–19] methods, as well as their combinations [10,12]. Pyrometallurgical methods are very energy-intensive, require elevated temperatures (about 1400 °C), and are accompanied by the release of highly toxic gases. Hydrometallurgical methods are free from the above drawbacks but require a significant consumption of inorganic or organic acids and are accompanied by the formation of large quantities of wastewater; in addition, chemical precipitants must be used to isolate valuable components from the solution. Mechanochemical methods are usually used to increase the reactivity of the target components and are followed by hydrometallurgical processing under milder conditions than required for non-activated material.

In recent decades, so-called deep eutectic solvents (DESs), formed from two or three components due to complexation and charge delocalization through hydrogen bonds, have

gained increasing interest in the leaching of valuable metals [20–24]. One of the components of DESs is a hydrogen bond acceptor (quaternary ammonium salts, such as choline chloride, etc.) and the other component is a donor, which could be organic acids (malonic, citric, succinic, etc.), polyols (glycerol, ethylene glycol), urea, etc. DESs are environmentally friendly, relatively inexpensive, have a high dissolving power, and can effectively dissolve various metals and metal oxides from complex matrices [25–30]. In addition, they are less aggressive and less volatile than traditional solvents, which reduces the risk of equipment corrosion and improves operating conditions.

DESs based on choline chloride:malonic acid [31], choline chloride:urea [32], choline chloride:citric acid [33], guanidine hydrochloride:lactic acid [34], betaine hydrochloride:ethylene glycol [35], choline chloride:glyoxylic acid [36], guanidine hydrochloride:ethylene glycol:maleic acid [37], betaine hydrochloride:citric acid [38], and others have been successfully used to extract lithium, cobalt, and nickel from spent lithium batteries.

Along with significant advantages, DESs also have drawbacks, including a high viscosity, a relatively low solubility of target metals, and a long leaching time to achieve acceptable metal recovery into a solution. In 2020, Chen et al. developed a DES consisting of polyethylene glycol (PEG) and thiourea in a molar ratio of 2:1, and it was highly effective in leaching lithium and cobalt from LiCoO_2 [39]. The solubility of Co in this DES at 80 °C was found to be 2121.14 ppm, which is two and thirty-five times higher than in the p-toluenesulfonic acid/water/ CHCl_3 (1:1:1) and CHCl_3 /ethylene glycol (1:2) systems, respectively. Leaching at 120 °C increased the Co content in the solution to 3480.02 ppm. Moreover, the PEG/thiourea DES has a very low viscosity, which facilitates mass and heat transfer during leaching. At the same time, such a high cobalt content in the solution was achieved only after 24 h of leaching, which is not very convenient for industry practice.

One of the ways to intensify leaching is to use ultrasound [40]. The effect of ultrasound on the extraction of valuable metals from lithium batteries in citric, sulfuric, and hydrochloric acids [41], a mixture of sulfuric acid and hydrogen peroxide [42], a mixture of acetic and ascorbic acids [43], a mixture of lemon juice with hydrogen peroxide [44], and other systems has been studied. The mechanism of ultrasonic action in leaching lithium-ion batteries is based on the phenomenon of cavitation. Ultrasonic waves, passing through the liquid, cause the formation of microscopic bubbles; these bubbles grow rapidly and then suddenly collapse, creating local zones with a very high pressure and temperature. As a result of the collapse of the bubbles, the solid material of the battery is destroyed and the penetration of the leaching agent into its structure is improved [45].

To date, there have been no studies on the ultrasound-assisted leaching of valuable metals from spent lithium batteries into DESs. However, a combination of ultrasound and a DES may have a synergistic effect, where ultrasound not only accelerates reactions but also promotes a deeper penetration of the DES into the structure of the leached material. Moreover, the use of ultrasound in combination with a DES may lead to a decrease in the temperature and time parameters of the process. In this study, we focused on the use of a DES composed of polyethylene glycol (PEG) and thiourea in a 2:1 molar ratio, as first reported by Chen et al. [39]. This DES has shown high solubility for cobalt and lithium, making it an effective medium for leaching metals from LiCoO_2 batteries under moderate temperature conditions. While previous studies have highlighted the effectiveness of PEG-based DESs for metal extraction, our research introduces a novel approach by incorporating ultrasound to enhance leaching efficiency further. The combination of ultrasound and a DES reduces the activation energy of the process, enabling faster metal recovery while maintaining high selectivity for lithium and cobalt. This study thus provides new insights into the optimization of sustainable and efficient recovery methods for valuable metals from spent lithium-ion batteries.

2. Materials and Methods

2.1. Materials and Reagents

The cathode material from lithium batteries containing lithium cobaltate as the active component was used for the experiments. A total of 86 spent LCO pouch batteries from smartphones were placed in a 10% Na₂SO₄ aqueous solution for 36 h to discharge. Then, with appropriate precautions, the batteries were manually disassembled and the aluminum foil with the black cathode material deposited on it was removed (Figure 1).



Figure 1. Aluminum foil with cathode material.

The aluminum foil with deposited cathode material was immersed in a hot (55–60 °C) 4 mol/L NaOH solution for 2.5 h; after that, the cathode material was separated from the aluminum foil, washed with hot distilled water, and dried up to a constant weight. Finally, the cathode material was ground up to obtain a powder of −0.074 mm. The total mass of the powder (hereafter referred as the LCO powder) was 718 g.

2.2. Preparation of DES

Polyethylene glycol 200 (PEG 200, AR) and thiourea (TU, 99.0%) were purchased from Shandong Longze Chemical Co., Ltd., Shandong, China. Both reagents were mixed at a molar ratio of 2:1 and the mixture was stirred at 60 ± 3 °C until it became a transparent liquid without solid inclusions. The resulting liquid, hereafter referred to as the DES, was used for leaching experiments.

2.3. Leaching Procedure

Typically, 250 g of the DES was placed in a glass round-bottom flask equipped with a condenser tube. The flask was placed into the ultrasonic instrument (Kunshan Ultrasonic Instrument Co., Ltd., KQ-300VDE, Kunshan, China) filled with 1 L of oil heated to a pre-determined temperature. As the desired temperature (80, 100, 120, 140, 160 °C) in the flask was reached, a pre-determined amount of LCO powder (2.5–15.0 g) was added to the DES and the formed mixture was stirred by using a mechanical stirrer (Sciogex, SCI40-S, Berlin, CT, USA). Simultaneously, an ultrasonic treatment was carried out at a frequency of 40 kHz and a power of 30 W (10% of the maximum power). The leaching duration varied from 1 to 24 h. Every 1 or 2 h, liquid samples were taken from the flask with a micropipette to determine the Li and Co content. To evaluate the efficiency of leaching, the recovery of Li and Co (α) was determined using the following equation:

$$\alpha = \frac{m_x}{m_0} \cdot 100\% \quad (1)$$

where m_x and m_0 are masses of the target metal in the solution and the initial LCO powder sample, respectively.

2.4. Analytical Techniques

The XRD patterns of the LCO powder sample were recorded by using a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with CuK α (40 kV, 40 mA) radiation.

FTIR spectroscopy was performed by using a *Shimadzu IR Prestige-21* (Shimadzu Corporation, Kyoto, Japan) IR spectrometer. UV–Vis spectroscopic studies were conducted by using a *Shimadzu UV 2600* (Shimadzu Corporation, Kyoto, Japan) spectrophotometer.

The elemental composition of the LCO powder sample and the content of Li and Co in the DES solution were determined by using atomic absorption spectrometry (AAS) on a Savant AA spectrometer GBC Scientific Equipment, Melbourne, Australia). In the case of a liquid, it was diluted with a 10% nitric acid solution (1:100, *v/v*) before analysis. In the case of a solid, its preliminary microwave digestion with a mixture of concentrated HNO_3 and H_2O_2 at 80–85 °C was performed to obtain the solution by using a system for the microwave digestion of samples, namely Tank-eco (Hanon Instruments, Jinan, China).

3. Results and Discussion

3.1. Characterization of LCO Powder Sample

The LCO powder sample was a dark gray, almost black powder, as shown in Figure 1. The elemental composition of the sample was wt.%: Li—6.86, Co—57.84. Based on the figures given, it can be assumed that the LCO powder sample consisted of 96% LiCoO_2 and 4% impurity. Heating the LCO powder sample at 800 ± 5 °C for 3.5 h in the presence of air resulted in a content of 7.09% Li and 60.18% Co, which almost exactly corresponds to the formula of LiCoO_2 . Apparently, this is due to the removal of carbon black, which is present in the cathode material as a conductive additive. At the same time, only lithium cobaltate was detected in the X-ray diffraction pattern of the LCO powder sample (Figure 2).

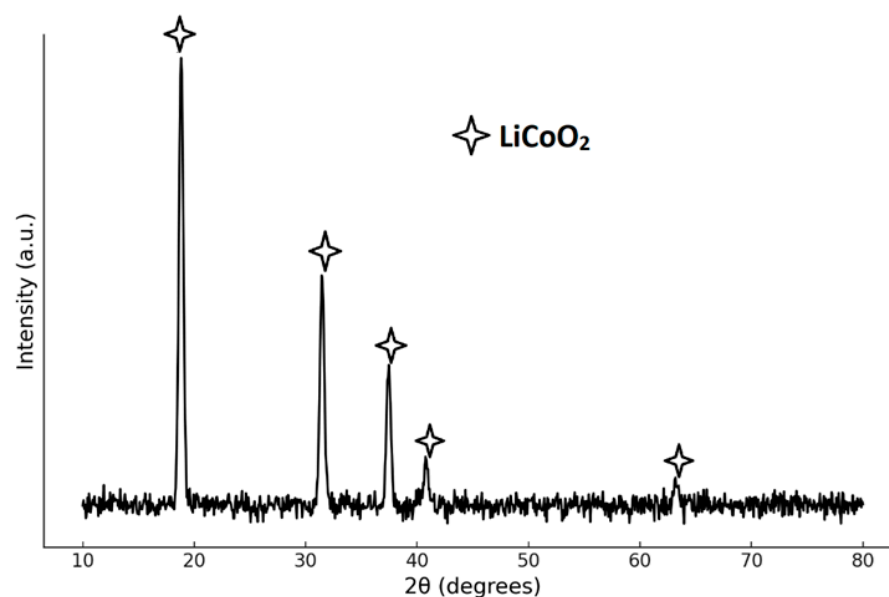


Figure 2. XRD pattern of LCO powder sample.

3.2. Leaching Experiments

3.2.1. Effect of Leaching Duration on Leaching Efficiency

The first series of experiments was devoted to identifying the effect of leaching duration on the extraction of Li and Co into the solution in the absence and presence of ultrasound exposure. The initial temperature of the oil in the ultrasonic instrument was 80 °C and had a solid-to-liquid ratio (S:L) of 0.02 g/g. The results of the Li and Co extraction into the solution are shown in Figure 3.

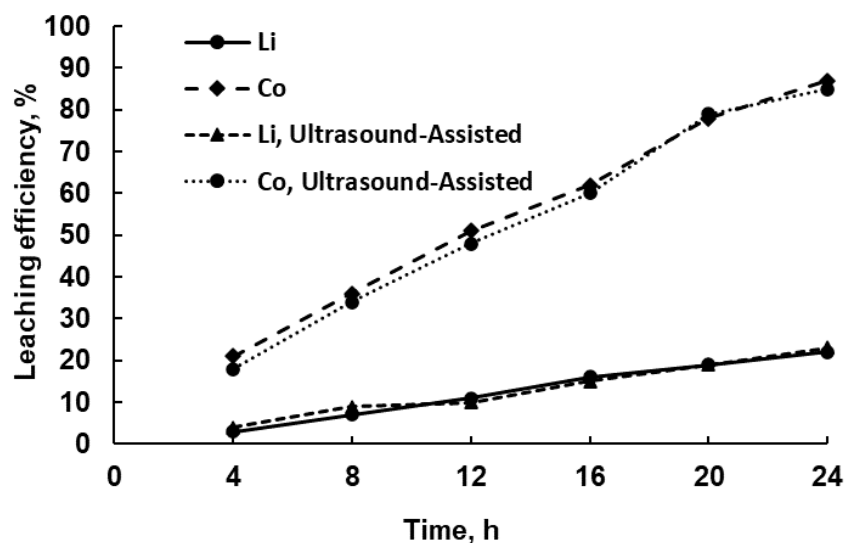


Figure 3. Effect of leaching duration on Li and Co recovery from LCO powder sample into PEG/thiourea (2:1, mol/mol)-based DES (S:L = 0.02 g/g; oil temperature in ultrasonic instrument is 80 °C).

In the absence of ultrasound, only 3 and 4% of Li and Co, respectively, passed into solution in the first 4 h. Over the next 4 h, the extraction of these metals reached 7 and 9%, while the subsequent 4 h showed an increase in extraction of 10% for both metals. After 24 h, the content of Li and Co in the solution reached 151 and 1263 ppm, respectively, at a leaching efficiency of 22% for both metals. Chen et al. [39] achieved a Co recovery of 24.8% in PEG/thiourea (2:1, mol/mol)-based DES at 120 °C, which is comparable to our results. Ultrasound-assisted leaching made it possible to significantly increase the extraction of target metals into the solution; after 24 h, the content of Li and Co in the solution was 1076 and 9481 ppm, which is almost four times higher than that achieved in the absence of ultrasound.

It should be noted that under ultrasound-assisted leaching conditions, the pulp temperature increased; the change in temperature over time is shown in Figure 4. It can be seen that the pulp temperature increased over time and the rate of increase decreased. At the end of 24 h of leaching, the temperature in the flask was already 171 °C. To determine whether the increase in the extraction of lithium and cobalt into the solution was due only to the increase in temperature, the following experiment was conducted. A flask containing the DES and LCO powder sample was placed in an oil bath at 135 °C for 8 h, at 160 °C for 8 h, and at 170 °C for 8 h. After 24 h, the Li and Co content in the solution was 324 and 2568 ppm, respectively, which is significantly lower than the values obtained under ultrasonic leaching conditions.

3.2.2. Leaching under Periodic Ultrasound Exposure

Despite the obvious positive effect of using ultrasound in leaching, continuous ultrasonic exposure of the DES:LiCoO₂ system entails significant energy costs. In 24 h, 67% of cobalt was extracted into the solution, which is 1.9 g, taking into account that the initial mass of the LCO powder sample was 5 g and the mass fraction of cobalt in the initial sample was 57.84%. Exposure of the pulp to ultrasound with a power of 30 W (i.e., 30 J/s) for 24 h (i.e., 86,400 s) leads to a consumption of 2592 kJ, which is an extremely large value. Therefore, leaching studies were carried out with periodic exposure of the pulp to ultrasound. Ultrasound was turned on for 5 min every hour, i.e., the total duration of ultrasonic exposure was 120 min. Figure 5 shows the dependence of Li and Co extraction into the solution on time under this leaching mode.

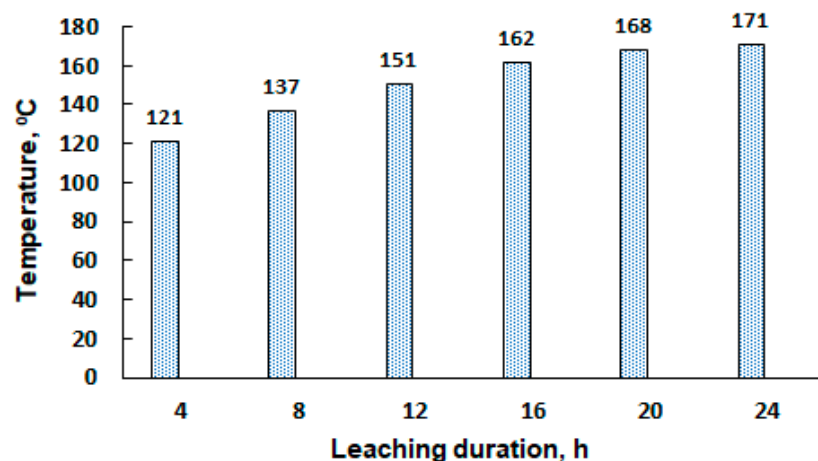


Figure 4. Effect of ultrasound-assisted leaching duration on pulp temperature (frequency of 40 kHz and a power of 30 W).

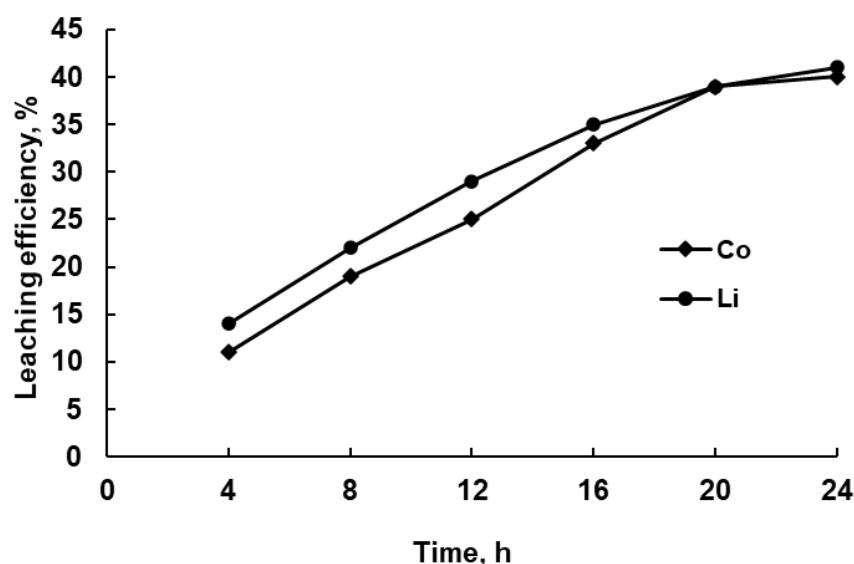


Figure 5. Effect of leaching duration on Li and Co recovery from LCO powder into PEG/thiourea (2:1, mol/mol)-based DES (S:L = 0.02 g/g; oil temperature in ultrasonic instrument: 100 °C) with periodic ultrasound exposure (5 min at the beginning of each hour).

The general trend of increasing recovery with time was maintained for both metals throughout the time interval studied (0–24 h). The maximum recovery was achieved at 24 h and amounted to 40–41%; the Li and Co content in the solution was 539 and 4817 ppm, respectively. The pulp temperature was increased to 86 ± 1 °C during each ultrasound exposure and then lowered to the oil bath temperature (80 °C) over 15–20 min. Subsequent leaching experiments were carried out with periodic ultrasound exposure as described above.

3.2.3. Effect of Temperature on Leaching Efficiency

Figure 6a,b shows the dependence of Li and Co extraction into the solution under periodic ultrasound exposure (for 5 min at the beginning of each hour) on temperature.

At 100 °C, Li recovery increased from 11% to 40% when the leaching time was increased from 4 to 24 h; at 160 °C, the recovery value reached 74% over the same period. Similarly, at 120 °C, Li recovery increased from 16% to 59% and at 160 °C from 29% to 74%. A similar trend is observed for Co. At 100 °C, its value increased from 8% to 37% over 24 h, while at 160 °C, it reached 71%.

The leaching of the LCO powder sample at 160 °C for 24 h in the absence of ultrasound allowed us to extract 46% Li and 43% Co into the solution.

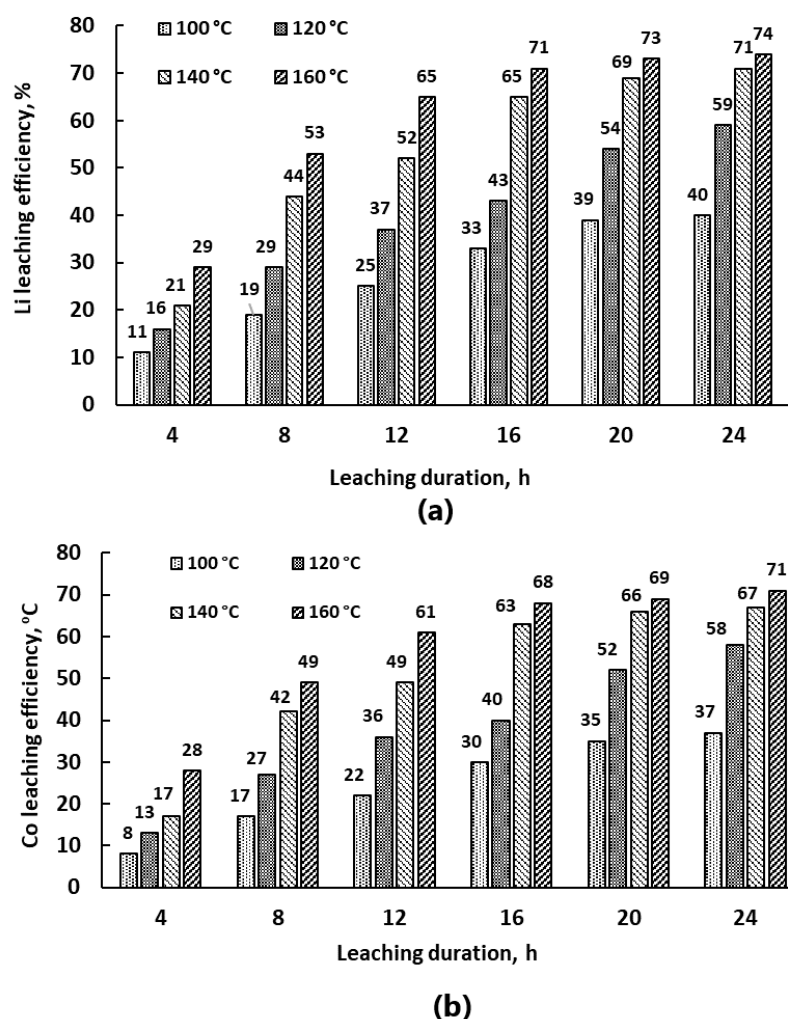


Figure 6. Effect of temperature and leaching duration on Li (a) and Co (b) recovery from LCO powder into PEG/thiourea (2:1, mol/mol)-based DES (S:L = 0.02 g/g) with periodic ultrasound exposure (5 min at the beginning of each hour).

3.2.4. Effect of S:L Ratio on Leaching Efficiency

The S:L ratio plays an important role in the industrial implementation of the leaching process of solid raw materials. As a rule, high S:L values allow the obtainment of richer solutions after leaching, which are relatively convenient to process. Therefore, leaching is usually carried out at the highest possible permissible S:L. On the other hand, too high S:L values decrease leaching efficiency due to insufficient contact between the liquid and solid phases; this may necessitate an increase in leaching time or an increase in the process temperature to achieve the desired level of extraction of the target components.

Figure 7a,b shows the dependence of Li and Co extraction over time on the S:L ratio (0.01, 0.02, 0.04, and 0.06 g/g) with periodic ultrasonic exposure (5 min at the beginning of each hour) at 160 °C.

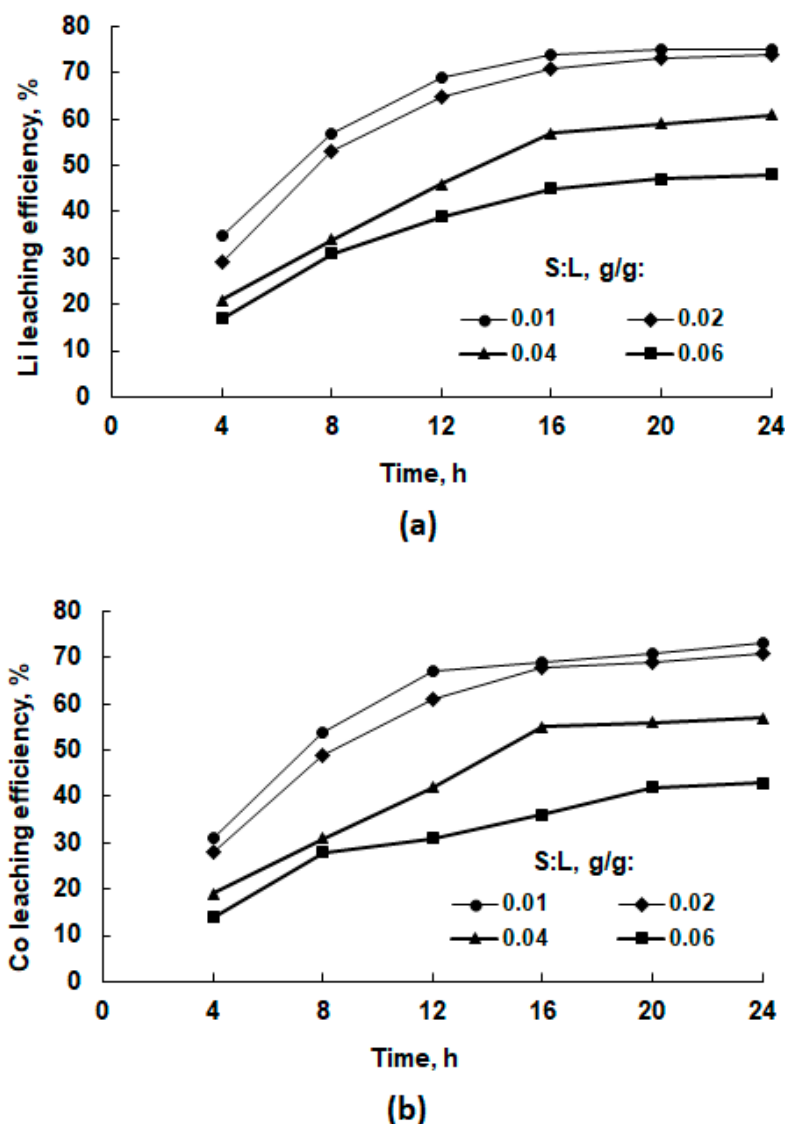


Figure 7. Effect of L:S ratio and leaching duration on Li (a) and Co (b) recovery from LCO powder into PEG/thiourea (2:1, mol/mol)-based DES (S:L = 0.02 g/g) at 160 °C with periodic ultrasound exposure (5 min at the beginning of each hour).

In general, decreasing the S:L value increased the recovery of both metals into the solution; at S:L = 0.01 g/g, the recovery of Li and Co in 24 h was 75 and 73%, respectively, while at S:L = 0.06 g/g, these values were only 48 and 43%. At the same time, no significant difference was observed in the recovery of metals at 0.01 and 0.02 g/L at significant (16 h or more) leaching durations. Increasing the leaching duration increased the metal extraction into the solution, but after some time, the extraction values reached a plateau. In the case of S:L = 0.02 g/g, the extractions of Li and Co reached their almost maximum values in 20 h.

Based on practical considerations, the following conditions are recommended for Li and Co extraction from the LCO powder sample into a PEG/thiourea (2:1, mol/mol)-based DES: S:L = 0.02 g/g, 20 h, 160 °C, and ultrasound exposure (frequency of 40 kHz and a power of 30 W) of 5 min at the beginning of each hour.

The color change during the leaching of the LCO powder sample under the specified conditions over time is shown in Figure 8. The initial DES was an almost transparent liquid; LCO powder was placed into it (Figure 8a). After the first few hours of leaching, the solution already acquired a bluish color, indicating the dissolution of Co (Figure 8b). After 8 h of leaching, the solution acquired a rich blue color (Figure 8c) which turned into an almost black color after 20 h of leaching (Figure 8d).

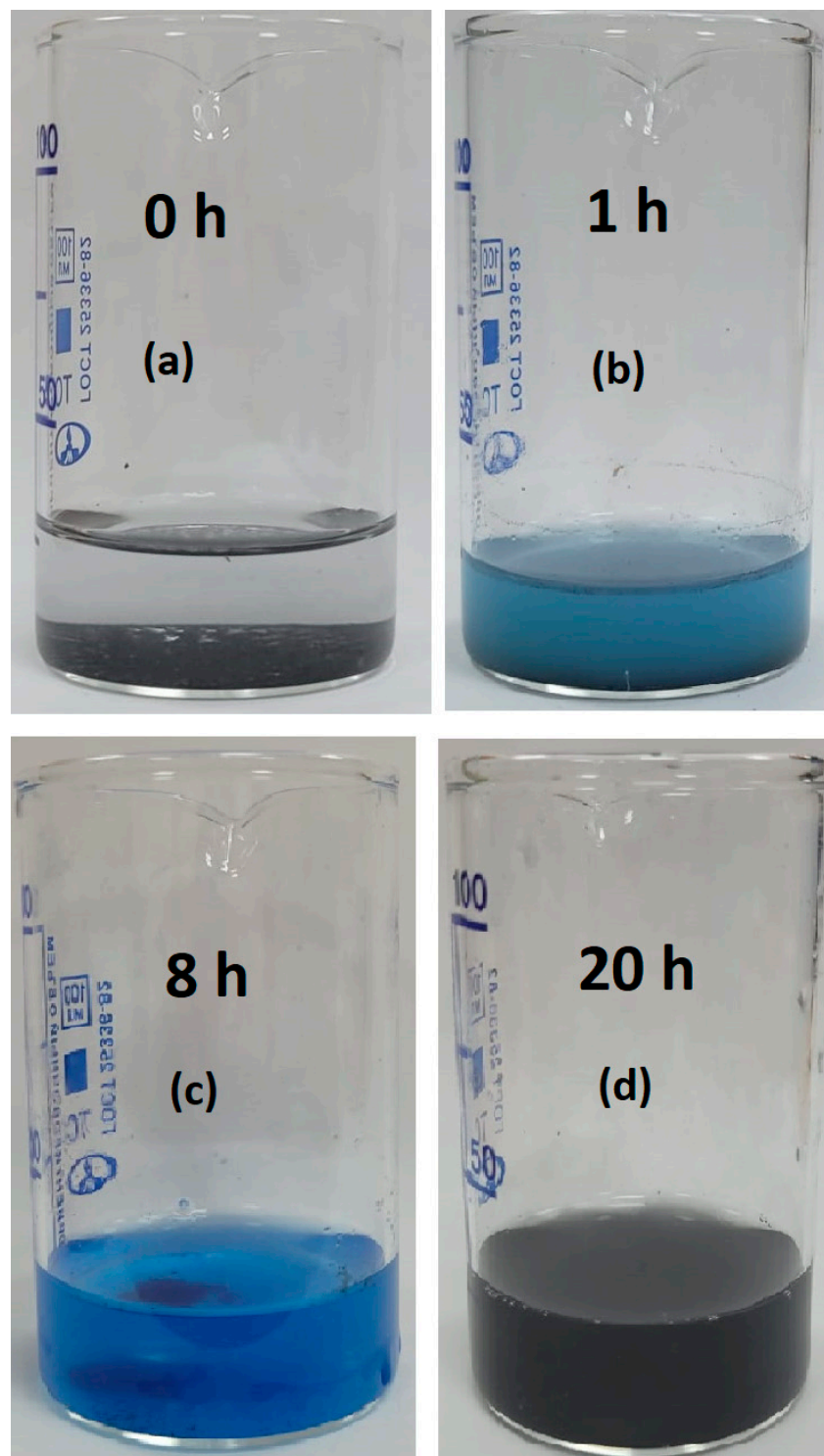


Figure 8. Color change of the liquid under the conditions of LCO powder leaching with PEG/thiourea (2:1, mol/mol)-based DES (S:L = 0.02 g/g) at 160 °C with periodic ultrasound exposure (5 min at the beginning of each hour) before leaching (a) and after 1 (b), 8 (c) and 20 (d) hours of leaching.

3.3. Leaching Kinetics Study

The shrinking core model was used to reveal the rate-limiting stage of leaching LCO powder with the PEG/thiourea DES under ultrasound and for comparison, without ultrasound. Depending on which stage is limiting, the dependence of the target metal

fraction transferred into the solution on the leaching time can be described by the following equations [46,47]:

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k\tau \quad (2)$$

$$1 - (1 - X)^{\frac{1}{3}} = k\tau \quad (3)$$

$$\frac{1}{3}\ln(1 - X) - 1 + (1 - X)^{-\frac{1}{3}} = k\tau \quad (4)$$

where X_{Me} is the fraction of the target metal recovered, k is the rate constant of the chemical reaction of leaching, and τ is the time in which the recovery of X is achieved.

If mass transfer phenomena limit the leaching rate, model (2) applies. The relationship between the fraction of metal transferred into the solution and the leaching duration when the rate-limiting step is a chemical reaction is described by Equation (3). When both the mass transfer rate and the chemical reaction rate simultaneously influence the process, model (4) is applicable.

To determine the rate-limiting step in the LCO powder leaching, the left-hand sides of Equations (2)–(4) were plotted against the leaching duration at three different temperatures; for ultrasound-assisted leaching, the data from Figure 6 were used. Since the recoveries of Li and Co were correlated, the average recovery of both metals was used as X . To obtain data on the recovery of Li and Co in the absence of ultrasound, appropriate experiments were carried out at S:L = 0.02 g/g and temperatures of 120, 140 °C, and 160 °C. The coefficients of determination for these plots are provided in Table 1.

Table 1. Coefficients of determination (R^2) for linear dependencies according to Equations (2)–(4), obtained from the data in Figure 6.

Equation	Conditions	Temperature, °C		
		120	140	160
2	No ultrasound	$R^2 = 0.5873$	$R^2 = 0.6438$	$R^2 = 0.6271$
	Ultrasound	$R^2 = 0.6942$	$R^2 = 0.7115$	$R^2 = 0.7009$
3	No ultrasound	$R^2 = 0.7065$	$R^2 = 0.6794$	$R^2 = 0.4951$
	Ultrasound	$R^2 = 0.9792$	$R^2 = 0.9875$	$R^2 = 0.9817$
4	No ultrasound	$R^2 = 0.9898$	$R^2 = 0.9443$	$R^2 = 0.9685$
	Ultrasound	$R^2 = 0.7463$	$R^2 = 0.7738$	$R^2 = 0.7916$

The coefficients of determination show that the leaching of both metals in the absence of ultrasound is limited by both mass transfer and the chemical reaction (mixed control), whereas the presence of ultrasound eliminates diffusion limitations and the leaching rate is limited only by the rate of the chemical reaction.

To determine the kinetic parameters of the Li and Co leaching process, the data on the metals' leaching were used in combination with Equation (3) (for ultrasound-assisted leaching) and 4 (for the leaching without ultrasound); the resulting plots are presented in Figure 9.

According to the slope coefficients of the straight-line equations, the rate constants of the chemical reaction of Li and Co leaching under the ultrasound treatment are h^{-1} : 0.0107 (120 °C), 0.0183 (140 °C), and 0.0216 (160 °C). In the absence of ultrasonic exposure, these values are h^{-1} : 0.0012 (120 °C), 0.0039 (140 °C), and 0.0062 (160 °C). It can be seen that the effect of ultrasound increases the leaching reaction rate constants by 8.9, 4.69, and 3.48 times at 120, 140, and 160 °C, respectively. With increasing temperature, the degree of influence of ultrasound on the increase in the reaction rate constant decreases, although it remains quite high.

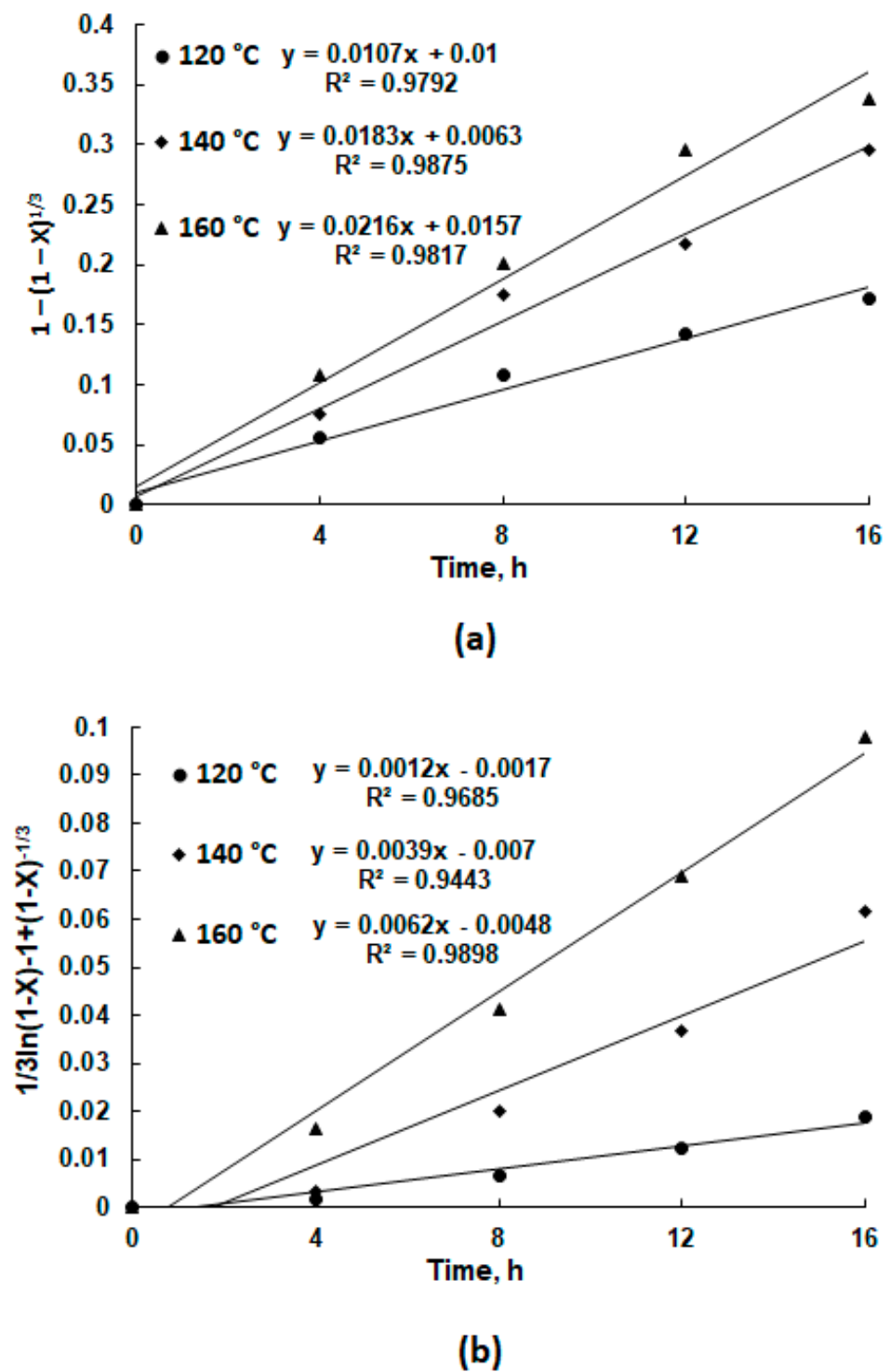


Figure 9. Kinetic analysis during the leaching of LCO powder sample into PEG/thiourea-based DES with (a) and without (b) ultrasound treatment by using a shrinking core model. Conditions: S:L = 0.02 g/g, ultrasound exposure (frequency of 40 kHz and a power of 30 W) of 5 min at the beginning of each hour.

Arrhenius plots for Li and Co recovery from the LCO powder were created by using these calculated rate constants (Figure 10).

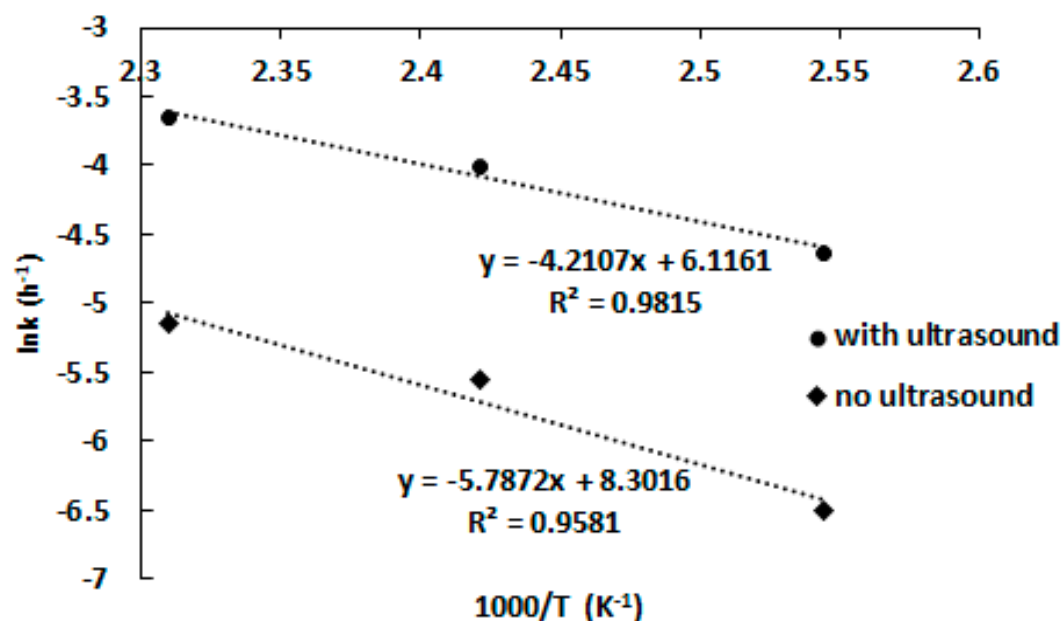


Figure 10. Arrhenius plot for Li and Co recovery into PEG/thiourea-based DES with and without ultrasound treatment. Conditions: S:L = 0.02 g/g, ultrasound exposure (frequency of 40 kHz and a power of 30 W) of 5 min at the beginning of each hour.

The activation energy (E_a) of the overall chemical reaction determining the Li and Co recovery into the solution was determined using Arrhenius's law (Equation (5)) [47]:

$$\ln k = -\frac{E_a}{RT} \quad (5)$$

where k is the rate constant of the chemical reaction (h^{-1}), R is the universal gas constant ($\text{J}/(\text{mol}\cdot\text{K})$), and T is absolute temperature (K).

The calculated values of E_a were 35.01 kJ/mol for ultrasound-assisted leaching and 48.11 kJ/mol for Li and Co recovery without ultrasound. The comparison of these values highlights the efficiency-enhancing effect of ultrasound. The lower E_a with ultrasound indicates reduced energy barriers, primarily due to improved mass transfer and the disruption of passivating layers, making the reaction process more efficient. Without ultrasound, the higher E_a reflects the greater energy required to overcome the intrinsic barriers of the process, likely due to combined mass transfer and chemical reaction limitations.

3.4. FTIR and UV-Vis Spectra Analysis

The spectrum of the original DES (Figure 11) was characterized by the presence of a strong broad band at $3200\text{--}3400\text{ cm}^{-1}$ corresponding to hydrogen bonds and free hydroxyl groups. The band in the region of $1600\text{--}1650\text{ cm}^{-1}$ is associated with deformation vibrations of the N-H groups of thiourea. C-O-C vibrations of the ether group of polyethylene glycol cause the formation of a band in the region of $1100\text{--}1150\text{ cm}^{-1}$. The band in the region of about $650\text{--}700\text{ cm}^{-1}$ is caused by vibrations of the C-S group of thiourea.

Lithium cobaltate leaching leads to changes in the spectrum. There is an increase in the intensity of the band in the $1600\text{--}1650\text{ cm}^{-1}$ region and its shift to lower frequencies, which can be caused by the interaction of dissolved cobalt ions with the C=O groups of thiourea. The change in the position and intensity of the band in the $1600\text{--}1650\text{ cm}^{-1}$ region is associated with the possible formation of a Co^{2+} -thiourea complex. A wide band at $3200\text{--}3400\text{ cm}^{-1}$ is preserved, indicating the preservation of free hydroxyl groups of polyethylene glycol. The increase in the intensity of the bands in the $1600\text{--}1650$ and $650\text{--}700\text{ cm}^{-1}$ regions under the influence of ultrasound is caused by an increase in the concentration of Co^{2+} -thiourea complexes.

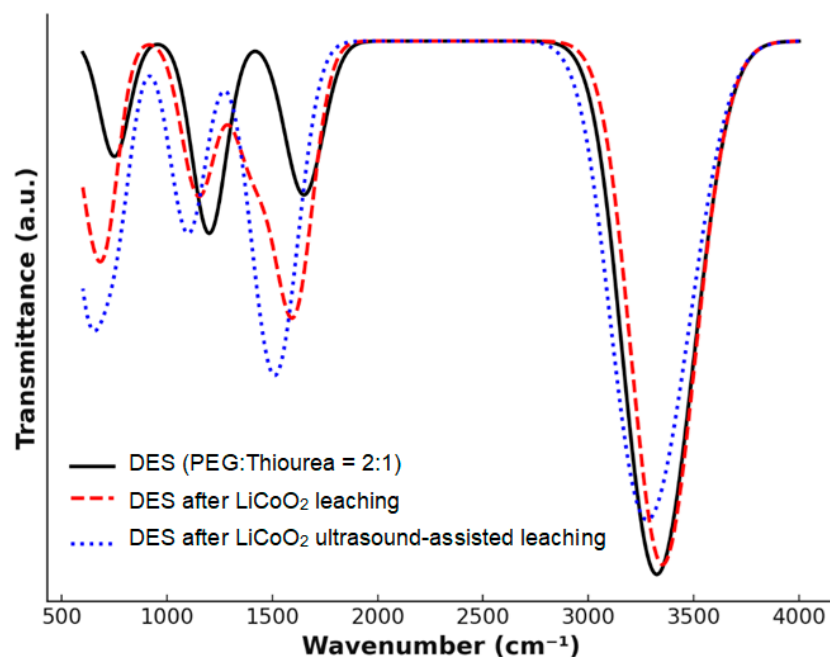


Figure 11. FTIR spectra of PEG/thiourea (2:1, mol/mol)-based DES as well as DES after LCO powder leaching with/without ultrasound.

In the UV–Vis spectrum of the pure DES, several absorption peaks are observed, associated with the electronic transitions of thiourea and polyethylene glycol (Figure 12).

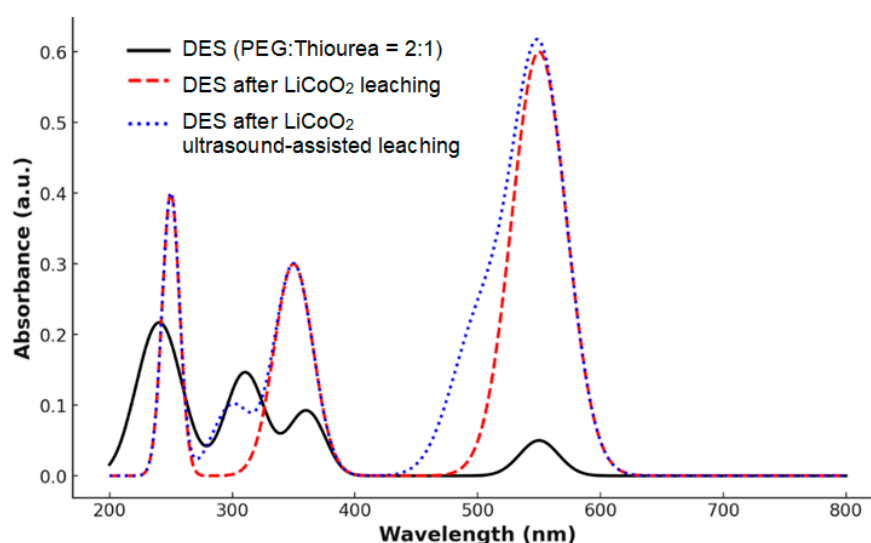


Figure 12. UV–Vis spectra of PEG/thiourea (2:1, mol/mol)-based DES as well as DES after LCO powder leaching with/without ultrasound.

The first peak around 240 nm indicates $\pi \rightarrow \pi^*$ transitions associated with the C=O groups of thiourea. The second peak around 310 nm is associated with $n \rightarrow \pi^*$ transitions. A weak peak is also observed in the 360 nm region, which may be associated with interactions of the DES components. An additional weak peak in the 550 nm region indicates the presence of minor impurities or weak electronic transitions characteristic of complexes in the system. After the leaching of lithium cobaltate, a sharp increase in the absorption bands at 240 and 550 nm occurs, which is associated with the complexation of cobalt ions with the DES components. The action of ultrasound significantly broadens the peak at 550 nm, which may be an uneven distribution of cobalt ions in the solution due to cavitation effects.

4. Conclusions

The study shows the potential of ultrasound-assisted leaching in a deep eutectic solvent (DES) based on polyethylene glycol (PEG) and thiourea for the recovery of Li and Co from spent lithium cobalt oxide (LiCoO₂) batteries. The combination of ultrasound with the DES significantly enhanced the leaching efficiency of both metals. The application of ultrasound improved mass transfer and accelerated the chemical reaction rates, as confirmed by a lower activation energy compared to non-ultrasound-assisted processes.

The following optimal conditions for leaching were identified: solid-to-liquid ratio (S:L) of 0.02 g/g, a temperature of 160 °C, and periodic ultrasound exposure. Under these conditions, the leaching efficiency reached up to 74% for Li and 71% for Co within 24 h. The rate-limiting step in the absence of ultrasound was a mixed control involving both mass transfer and a chemical reaction, while in the presence of ultrasound, the leaching process was primarily limited by the chemical reaction rate.

Future research could focus on optimizing the DES composition by exploring other hydrogen bond donors and acceptors to enhance efficiency and reduce processing times. Additionally, the recyclability of the DES after metal extraction should be studied to minimize waste and solvent use.

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