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Enhancement of Leaching Copper from Printed Circuit Boards of Discarded Mobile Phones Using Ultrasound–Ozone Integrated Approach

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Abstract: The recovery of metals from discarded mobile phones has been of interest due to its environmental and economic benefits. This work presents a simple and effective approach for leaching copper (Cu) from the printed circuit boards of discarded mobile phones by combining ultrasound and ozone approaches. The X-ray diffraction (XRD) technique and Fourier-transform infrared spectroscopy (FT-IR) were used to characterize the solid phases, and inductively coupled plasma optical emission spectrometry (ICP-OES) was utilized to determine the concentration of metals in the liquid phases. The effects of several influential parameters, including ultrasound, ozone dose, HCl concentration, liquid/solid ratio, temperature, and reaction time on the leaching efficiency were investigated. The results showed that the optimal conditions for Cu leaching included an ozone dose of 700 mg/h, HCl concentration of 3.0 M, liquid/solid ratio of 8, and temperature of 333 K. Under optimal conditions, about 99% of Cu was leached after 180 min. The shrinking core model was used to analyze the kinetics of the Cu leaching process, and the results showed that the surface chemical reaction governs this process. The activation energy of the leaching reaction, calculated using Two-Point form of the Arrhenius equation, was 10.852 kJ mol^{-1}.

Keywords: ultrasound; ozone; copper; printed circuit boards; leaching efficiency

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1. Introduction

With the rapid development of electronic technology in recent years, electronic devices such as mobile phones, computers, televisions, etc., have become more cost-effective and multifunctional. However, their life-time and life cycle significantly decrease due to their extensive use in users' work, lifestyle, and leisure activities [1,2]. Particularly, mobile phones have become the most popular electronic devices, as they can be used for multiple purposes in people's daily lives and work [3]. Consequently, mobile phone waste has grown exponentially and is becoming a challenge for environmental protection and resource sustainability. Thus, recycling mobile phone waste has been of major interest in recent years in order to provide economic advantages and prevent an environmental catastrophe [2–7].

Typical mobile phones consist of various components such as printed circuit boards (PCBs), batteries, screens, magnets, vibrators, and LED backlights. Regarding metal recycling, PCBs are the most crucial component of discarded mobile phones because they are the main metal content of mobile phones. According to the literature [3,8], the metals in mobile phone printed circuit boards (MP-PCBs) include copper (20–30%), zinc (1–3%), tin (1–2%), aluminum (0.3–0.5%), iron (1–2%), gold (0.86–1.6 g/kg), and silver (0.14–5.8 g/kg). With a high content of precious and valuable metals such as silver, gold, copper, and zinc, MP-PCBs are economic sources for recycling these metals. To recover the metals from MP-PCBs, various methods such as hydrometallurgical, pyrometallurgical, bio-metallurgical, and physical methods have been developed and applied [9]. Among these methods, hydrometallurgy has the advantages of good stability and a high leaching efficiency. Additionally, this method has been reported to be predictable, easily controlled, and environmentally friendly [9,10].

A typical hydrometallurgical process consists of two sequential steps: leaching metals from raw materials and recovering them from the solutions [9,11]. The leaching step is critical in hydrometallurgical processes and has been of significant interest [12,13]. Cu can be leached from PCBs by various solutions such as HNO_3, H_2SO_4-H_2O_2, H_2SO_4-Cl_2, HCl-Cl_2, and ammonia-based solutions [14]. However, the use of (1) HNO_3 and Cl_2 releases toxic gases such as NO_2, NO, and Cl_2, (2) ammonia-based solutions cause environmental and operational safety concerns, and (3) H_2O_2 has a high operation cost because of chemical consumption. Therefore, environmentally friendly and cost-effective alternative chemicals are in high demand [13,15,16].

Ozone is one of the strongest oxidants with a reduction potential of 2.07 eV, and is effective for leaching many metals from ores and PCBs [13,17–19]. During the leaching process, which can be carried out under atmospheric pressure and moderate temperatures, ozone is decomposed to form oxygen [20]. Ozone can be generated using different methods, including corona discharge, UV light, and electrolysis. In metallurgy, ozone is mainly produced by ozone generators, depending on the corona discharge method with different input gas sources [15,20–23], because this method is scalable, can generate enormous amounts of ozone, and requires little maintenance. The use of ozone in leaching metals from ores and PCBs has been intensively studied, owing to its several technical and environmental benefits [13,18,19,21,24,25]. Regarding metal leaching processes, Wang et al. [23] evaluated the effectiveness of ozone in leaching Cu from chalcopyrite and found that 100% of Cu was leached after 48 h without the addition of ferric ions. Another study by Rodríguez et al. (2014) [18], about the use of ozone, showed that 80% of silver could be dissolved from pyrargyrite under optimum conditions. Although ozone is a highly effective oxidant for recycling metals from various sources, its use for leaching Cu from MP-PCBs is still limited. Previously, ozone has been used for leaching metals from MP-PCBs by dissolving in HCl and H_2SO_4 solutions at 298, 313, and 353 K [13]. Results have shown that 79% of Cu was leached after 4 h at 353 K, which was similar to HCl-H_2O_2 solution. Therefore, O_3-HCl solution is an effective solution for leaching Cu from MP-PCBs. However, the effects of other parameters, such as HCl concentration, zone dose, and kinetics of the process, were not investigated in this study. Moreover, the leaching time was prolonged, and the time for complete leaching was not reported. Thus, the leaching of Cu from MP-PCBs in O_3-HCl solution requires further study for application in practice.

Ultrasound is considered one of the most effective techniques for improving the metal leaching efficiency from various sources [26]. Under ultrasound conditions, the cavities in the liquid form, grow, and collapse rapidly, causing the dissolution, cracking the layers on the solid surface, and accelerating the penetration of leaching reagents into the pores and cracks of the solid [22,26–28]. In a previous study by Zhang et al. (2016) [29], ultrasound-assisted system was used for leaching germanium from the by-product of zinc metallurgy, and the leaching time was reduced by 60% in the presence of ultrasound. Chen et al. [27] found that the application of ultrasound can enhance the vanadium extraction from low-grade vanadium-bearing shale. Thus, ultrasound may be a potential and sustainable technique in enhancing the leaching efficiency of Cu from MP-PCBs.

The combination of ozone and ultrasound shows promise in enhancing the leaching efficiency of metals. The synergistic effects of ozone and ultrasound have been demonstrated in improving the leaching percentages of Au, Cu, and Ag. Gui et al. [27] used this combination to leach gold and silver from the refractory gold ore, resulting in an increased leaching efficiency from 49.12% to 93.52% and from 4.01% to 61.25% for gold and silver, respectively, after 4 h. Liu et al. [30] found that 98.46% of Cu can be leached from Cu anode slime using the combination of ozone and ultrasound. Although the combination of ozone and ultrasound can significantly enhance the leaching of metals, this combination also shows disadvantages, such as high initial investment and maintenance costs [31] and operational challenges; both ozone and ultrasound technologies require careful control and monitoring to optimize their effects [30]. Therefore, the process parameters need to be optimized to achieve the desired leaching outcomes and ensure a consistent and reliable operation. To the best of our knowledge, the combination of ozone and ultrasound for leaching Cu from MP-PCBs, and the effects of the process parameters, have not been studied or reported.

After the leaching process, there are leachates and solid residues that need to be further processed. For leachates, several methods, such as cementation, crystallization, precipitation, and electrowinning, can be applied to recover the metals [32]. Solid residues can be used as additives for rubber and construction materials [13,32]. However, in previous studies, MP-PCBs were often converted into a fine powder before leaching, leading to extra costs for the operation and investment of machines, and to difficulty in separating the leached solution from the residues. Hence, efficient and economical approaches need to be studied and developed.

In this work, we utilize a simple but effective process for leaching Cu from MP-PCBs. The plates of MP-PCBs are used directly for leaching without grinding and we investigate the synergistic effect of ultrasound and ozone on Cu leaching. The effects of various parameters, including ultrasound, ozone dose, HCl concentration, liquid/solid ratio, reaction time, and temperature, are investigated in detail. To further understand the enhancement mechanism of ultrasound and ozone, the kinetics of the process are investigated using the shrinking core model and the corresponding kinetic equation is established.

2. Materials and Methods

2.1. Materials

Discarded mobile phones from various brands were purchased from the local mobile phone service centers in Thai Nguyen city, Vietnam. The MP-PCBs were manually separated from other components, washed thoroughly and air-dried. They were cut into small plates of about 1 cm in size using scissors and directly used for leaching without any further griding.

2.2. Characterization and Analysis

The small plates of MP-PCBs were ground into fine powder and the phases of the materials were examined using an X-ray diffractometer (D2-Phaser, Brucker) with CuKα radiation of 0.154 nm with a scan rate of 0.01°/step. The FT-IR analysis was recorded on a Spectrum Two spectrometer (Perkin Elmer) with a wavenumber in the range of 4000–400 cm^{-1} using an attenuated total reflectance (ATR) accessory. To determine the metallic contents of MB-PCBs, the samples were completely leached in aqua regia, and the analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima Expert, Horiba). The absorbance spectra of the leaching solutions were recorded on a V-770 spectrophotometer (Jasco).

2.3. Leaching Study

2.3.1. Leaching System

The leaching system includes a glass reactor, an ozone generator (D1, Dr. Ozone), and an ultrasound bath (S-100H, Elma) with a frequency of 40 kHz (Figure 1). The reactor was placed in the bath, and the water level in the bath was equal to the level of the solution in the reactor. Ozone was introduced into the reaction system through an ozone diffuser to form small ozone bubbles. To prevent the evaporation of the solution, a water condenser was plugged into the system. In each experiment, 20 g of plates of MP-PCBs and a specific volume of HCl solution were added into the reactor. Simultaneously, the ozone gas and ultrasound were applied to the reaction system under a particular temperature. After 30, 60, 90, 120, 150, and 180 min, 1 mL of the leaching solution was withdrawn and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima Expert, Horiba). Each leaching experiment was repeated three times and the accepted errors were below 5%.

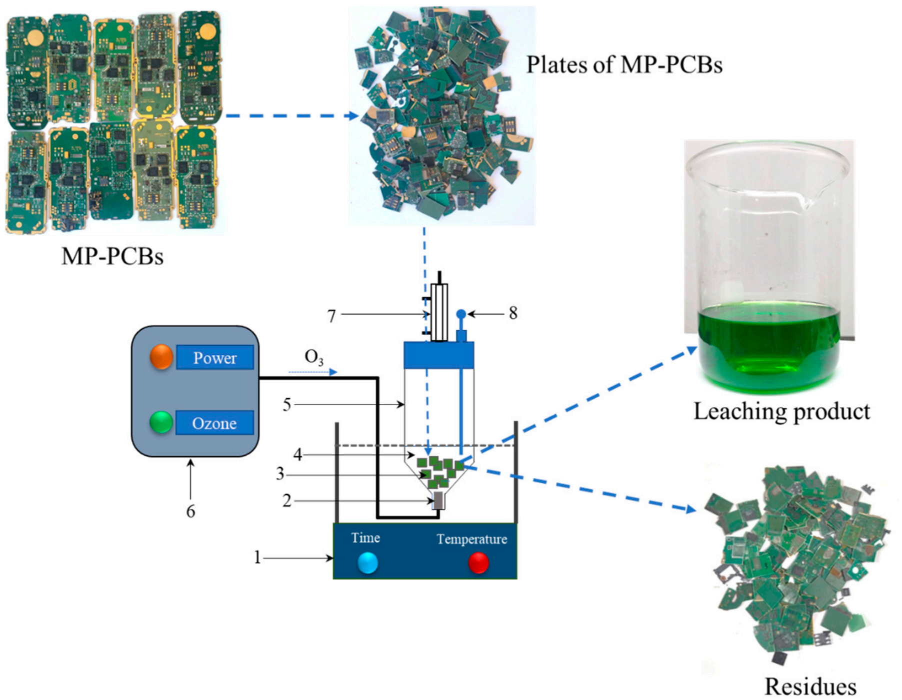

Figure 1. Experimental leaching apparatus: 1—ultrasonic bath; 2—ozone diffuser; 3—plates of MP-PCBs; 4—HCl solution; 5—reactor; 6—ozone generator; 7—condenser; 8—thermometer.

2.3.2. Parameter Effect Study

The effects of ultrasound, ozone dose, HCl concentration, liquid/solid ratio (*w*/*w*), reaction time, and temperature on the leaching efficiency were studied to find out the optimal conditions for the Cu leaching process. To investigate the effect of ultrasound, the experiments were carried out with and without ultrasound under the experimental conditions of ozone dose of 900 mg/h, HCl concentration of 4.0 M, temperature of 323 K, and liquid/solid ratio of 10. For investigating the effect of ozone dose, the experiments were conducted with the presence of ultrasound, ozone doses ranging from 300 to 900 mg/h, HCl concentration of 4.0 M, and liquid/solid ratio of 10 at 323 K. The effect of the concentration of HCl solution was studied by changing HCl concentration from 0.5 to 4.0 M with ozone dose of 700 mg/h, temperature of 323 K, and liquid/solid ratio of 10. The effect of the liquid/solid ratio was varied from 2 to 10 to investigate the effect of this ratio on the leaching efficiency under conditions: 323 K, HCl concentration of 3 M, and ozone dose of 700 mg/h. To study the effect of the temperature, the reactions were carried out at 323, 333, 343, and 353 K with a HCl concentration of 3M, ozone dose of 700 mg/h, and liquid/solid ratio of 8. The Cu leaching efficiency (LE, %) was calculated according to the following equation:

$$LE = \frac{m_o - m_t}{m_o} 100 \quad (1)$$

where m_o and m_t are the mass of copper in the MP-PCBs and the leaching solution after t minutes, respectively.

3. Results and Discussion

3.1. Characterization of MP-PCBs

The results from the XRD analysis of the phase composition of the MP-PCBs are presented in Figure 2. The most obvious metallic phase in the MP-PCBs is copper, which is characterized by the diffraction peaks at 2θ angles of 43.26, 50.27, and 73.84° corresponding to the reflections of the (111), (200), and (220) planes in the crystal lattice of copper (PDF 01-071-4611).

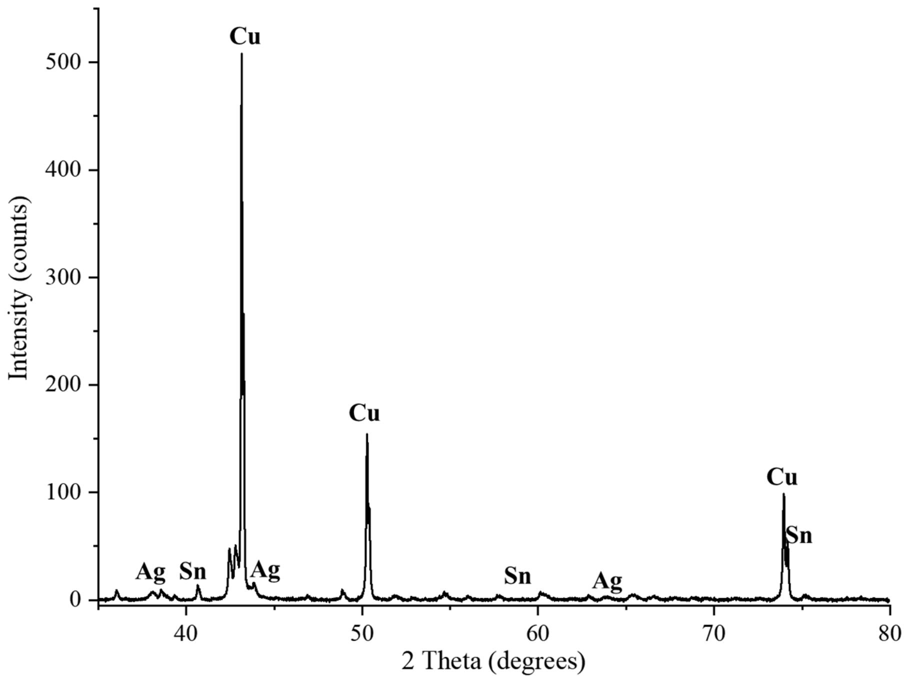

Figure 2. XRD pattern of MP-PCBs.

The characteristic diffraction peaks of Sn (PDF-01-083) can also be observed at about 40.7, 58.9, and 74.5°, and the peaks of Ag (PDF 01-089-3722) are at about 38.1, 44.3, and 64.2°. The low intensity of these peaks may be due to the low content of Sn and Ag in the MP-PCBs. The presence of Fe (PDF-01-081-8874) and Au (PDF 01-086-5575) are difficult to recognize, owing to the overlap of the diffraction peaks of these elements with those of Cu.

The organic contents of MP-PCBs were analyzed by the FT-IR method and the results are illustrated in Figure 3. A strong and broad band at around 3380 cm^{-1} can be assigned to the phenol O–H stretching. The existence of C-H stretching vibration is confirmed by the bands at 2928.2 and 2859.8 cm^{-1}. The bands at about 1726, 1600, 1181, and 1069 cm^{-1} can be attributed to the stretching vibrations of the C=O, C=C, and C-N groups. The stretching vibrations of the C-H groups in the aromatic rings are observed at 803, 636, and 603 cm^{-1}. The peaks at 1463 and 447 cm^{-1} can be indexed to the deformation vibrations [8]. These functional groups belong to the different kinds of polymers in MP-PCBs such as polyvinyl chloride, polycarbonates, acrylonitrile butadiene styrene, polystyrene, polyethylene, polypropylene, etc. [8].

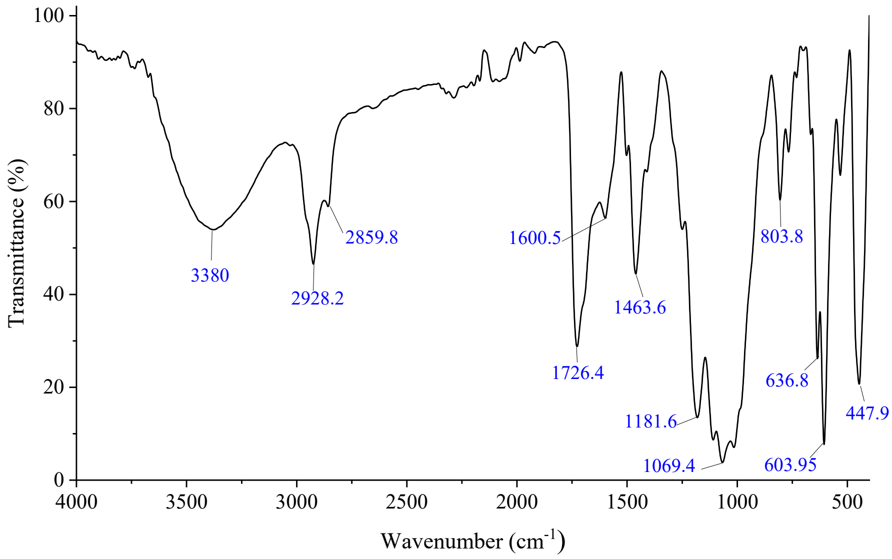

Figure 3. FT−IR spectrum of MP-PCBs.

The metallic contents of MP-PCBs were analyzed using the ICP-OES method and the results are given in Table 1. Copper, accounting for about 27%, is the primary metallic element in MP-PCBs. Iron is the second highest metal content, followed by aluminum, tin, and zinc. The contents of gold and silver are about 972 and 156 mg/kg, respectively. The analysis results in this work are similar to those reported in previous studies [3,8,13], and indicate that MP-PCBs are a valuable source for recycling metals.

Table 1. The metal contents of MP-PCBs.

Element	Concentration
Cu	27.56 ± 2.15%
Fe	3.24 ± 0.28%
Al	2.15 ± 0.16%
Sn	1.12 ± 0.07%
Zn	0.48 ± 0.03%
Ag (mg/kg)	972 ± 15.67
Au (mg/kg)	156 ± 6.34

3.2. Effect of Ultrasound

To investigate the effect of ultrasound on the copper leaching process, the experiments were conducted with and without the presence of ultrasound. As presented in Figure 4, ultrasound has a significant effect on copper leaching efficiency. In the presence of ultrasound conditions, the leaching efficiency reached about 21% after 30 min of reaction, which is around four times higher than its absence. As the reaction time further continued to 180 min, about 99% of copper was leached. The enhancement of the leaching efficiency under ultrasound conditions can be explained by the formation and collapse of cavitation bubbles [28]. When the bubbles collapse, they would rapidly increase the local temperature and pressure, then cracking of the surface and destroying the passive layer on the reacted surface area [26]. The presence of ultrasound during the leaching process can reduce the activation energy of the reactions of the leaching process [27]. In addition, with the crushing effect, ultrasound can promote the formation of ozone microbubbles, thereby promoting the mass transfer coefficient of ozone in the solution and the ozone concentration per unit of time. Consequently, the rate of the leaching reaction increased significantly in the presence of ultrasound [30].

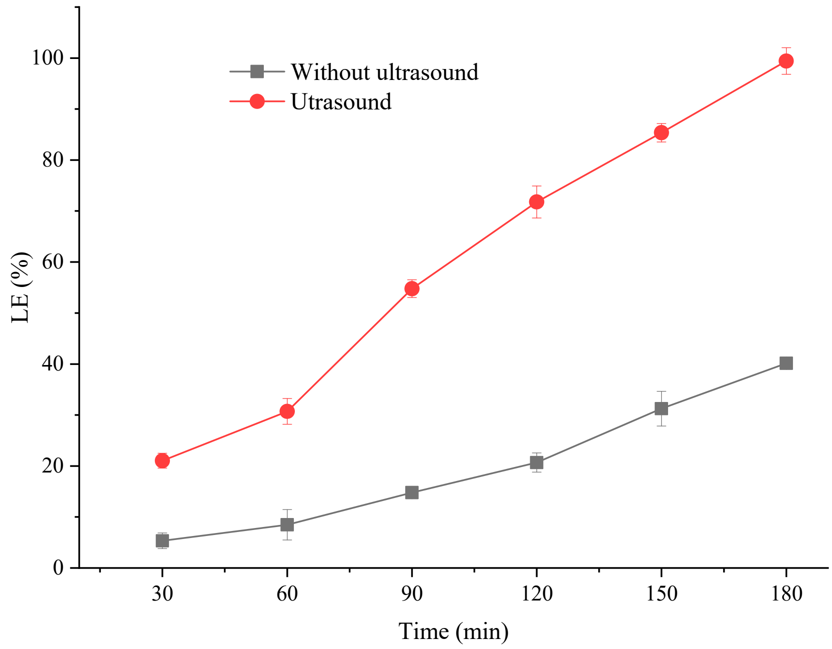

Figure 4. Copper leaching efficiency with and without the assistance of ultrasound: ozone dose of 900 mg/h, temperature of 323 K, and HCl concentration of 4 M.

3.3. Effect of Ozone Dose

The effect of the ozone dose, from 300 to 900 mg/h, on the copper leaching efficiency was investigated and the results are shown in Figure 5. The leaching efficiency significantly increases as the ozone dose increases from 300 to 700 mg/h, then remains constant as the ozone dose increases from 700 to 900 mg/h. The reaction between the copper and ozone in the solution can be presented as the following Equation (2):

$$Cu + O_3 + 2H^+ = Cu^{2+} + O_2 + H_2O \tag{2}$$

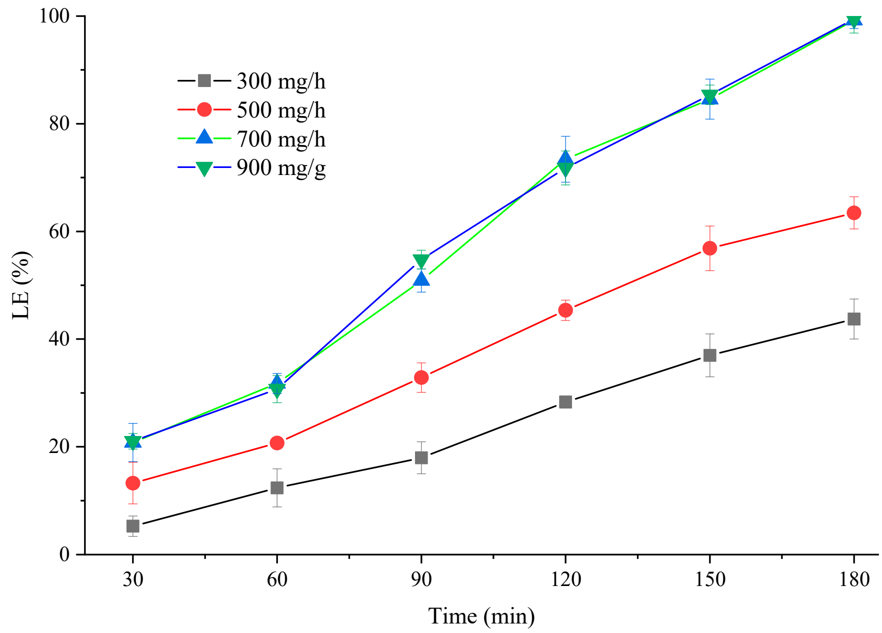

Figure 5. Effect of ozone dose on the copper leaching efficiency.

Therefore, increasing the ozone dose from 300 to 700 mg/h leads to a high concentration of ozone in the solution, thus accelerating the rate of the Reaction (2) [20,33]. As the ozone dose reaches 900 mg/h, the efficiency does not increase due to the excessive content of ozone in the system. Therefore, an ozone dose of 700 mg/h is selected for the leaching process.

3.4. Effect of HCl Concentration

The effect of HCl concentration on the leaching process was monitored in the range of HCl concentration from 0.5 to 4.0 M, and the results are illustrated in Figure 6. When the concentration increases from 0.5 to 1.0 M, there is a slight increase in the leaching efficiency. The value of LE rises significantly when the acid concentration increases from 1.0 to 2.0 M, and continues to go up when the concentration reaches 3 M. The leaching efficiency of the samples with an HCl concentration of 4.0 M is approximate to that of the 3 M samples. The effect of HCl concentration on the leaching efficiency can be explained according to Equation (2). When HCl concentration increases from 0.5 to 3 M, the H^+ concentration increases, accelerating Reaction (2) [21]. In addition, an increase in HCl concentration leads to an increase in chloride-free ions (Cl^-), which can react with Cu^{2+} to form several chloro-copper complexes with the number of Cl^- ligands (j) in the range of 1–4 [34] as presented in Reaction (3):

$$Cu^{2+} + jCl^- \rightleftarrows CuCl_j^{2-j} \tag{3}$$

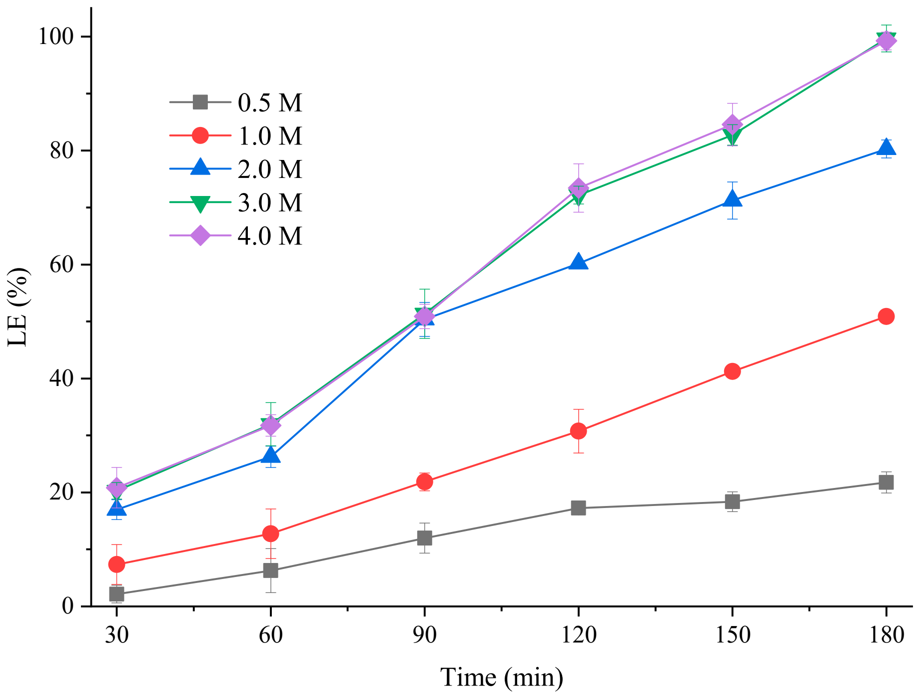

Figure 6. Effect of HCl concentration on the copper recovery efficiency.

Reaction (3) will deplete Cu^{2+} ions formed in Reaction (2), thereby promoting the leaching efficiency. When HCl concentration increases from 3 to 4 M, the leaching efficiency remains approximate, indicating that a HCl concentration of 3 M is sufficient for the leaching process. Therefore, the HCl concentration of 3.0 M was selected for the leaching process of copper with ozone and ultrasound assistance, due to its economic and environmental benefits.

Figure 7 presents the color of the samples obtained at different HCl concentrations, and the absorbance spectra of the solutions obtained at HCl concentrations of 0.5 and 3.0 M.

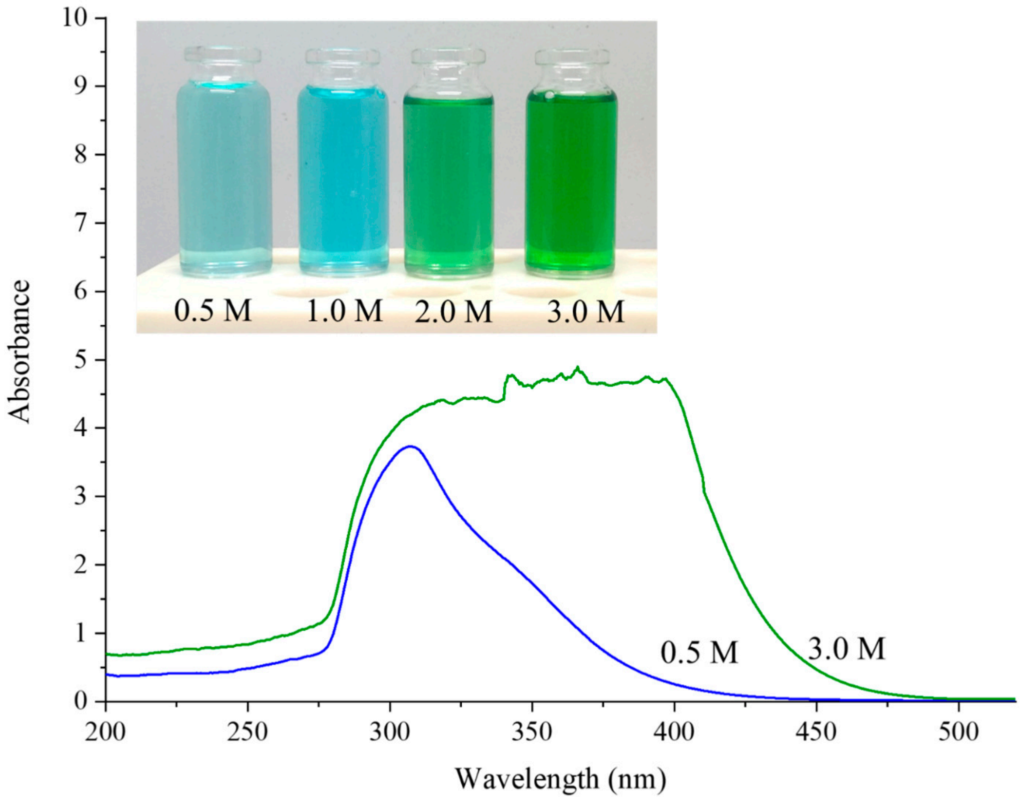

Figure 7. Color and absorbance spectra of the solutions obtained with different concentrations of HCl.

The samples with HCl concentrations of 0.5 and 1.0 M show a blue color, while the samples with HCl concentrations of 2.0 and 3.0 M have a green color. The dependence of the colors of the leachates on the acid concentration originate from the complexation between Cu^{2+} and Cl^{-} ions. In the solution of Cu^{2+} and Cl^{-}, there are at least five species, including Cu^{2+}, $CuCl^{+}$, $CuCl_2$, $CuCl^{3-}$, and $CuCl_4{}^{2-}$. These species have different colors, depending strongly on the free chloride concentration [35]. The spectrum of the solution obtained at a HCl concentration of 0.5 M shows a strong band in the range of 275–400 nm, with a maximum absorbance at about 308 nm. In contrast, the solution obtained in the presence of the HCl concentration of 3.0 M has a green color. The spectrum of this solution shows a complicated pattern with various peaks at different wavelengths, suggesting that various copper-containing complexes can exist in the solution [35].

3.5. Effect of Solid/Liquid Ratio

The effect of the liquid/solid ratio (from 2 to 10) on the Cu leaching efficiency was investigated. As shown in Figure 8, the leaching efficiency increases remarkably as the ratio rises from 2 to 8, then remains unchanged as the ratio increases to 10. The effect of the liquid/solid ratio can be due to the ratio between ozone and the reaction surface of MP-PCBs. As the liquid/solid ratio increases, a sufficient amount of the oxidizing agent would promote the reaction rate of the leaching process [25]. From the results, the liquid/solid ratio of 8 is the optimum value for the copper leaching from MP-PCBs under ozone–ultrasound conditions.

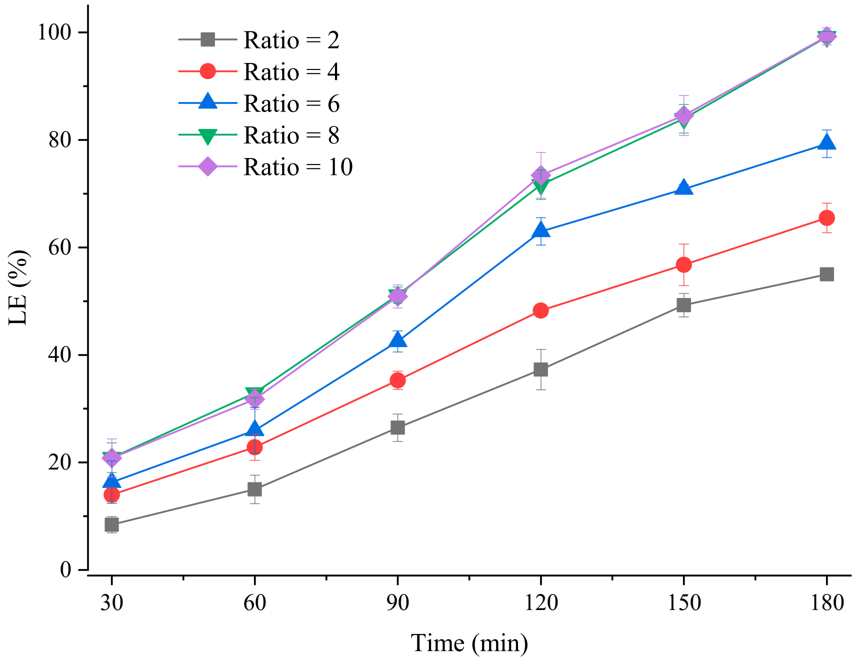

Figure 8. Effect of liquid/solid ratio on the copper leaching efficiency.

3.6. Effect of Temperature

The effect of temperature on copper leaching efficiency was investigated at different temperatures, from 323 K to 353 K. As shown in Figure 9, the leaching efficiency increases when the temperature rises from 323 to 333 K. However, the leaching efficiency decreases when the temperature continues to increase to 353 K. The increasing efficiency in the temperature range of 323–333 K can be explained by the release of hydroxyl radicals. When the temperature exceeds 333 K, the solubility of the ozone reduces, thereby lowering the leaching efficiency [11,15,21].

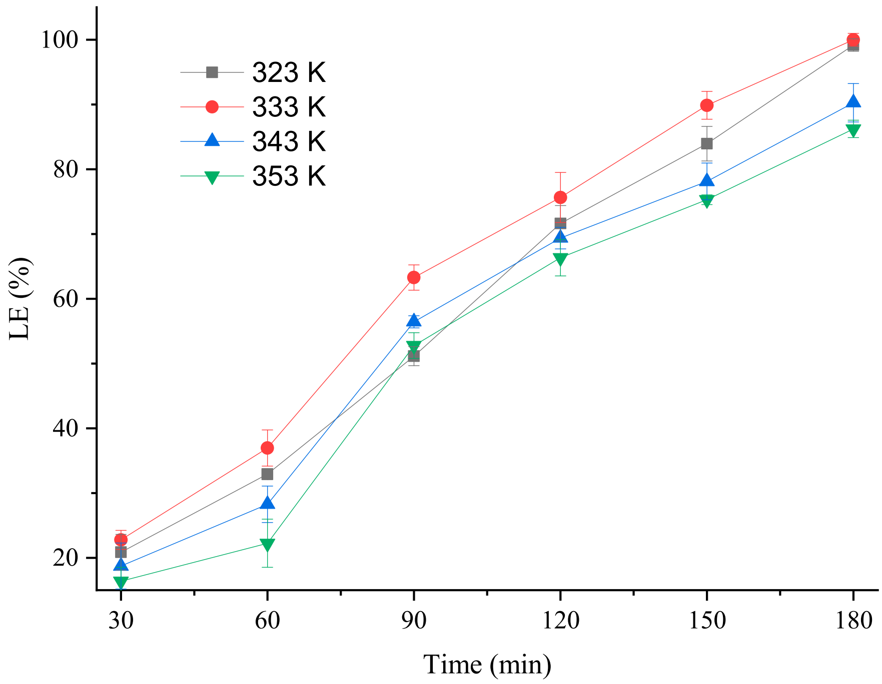

Figure 9. Effect of temperature on the Cu recovery efficiency.

3.7. Effect of Reaction Time and Kinetics of the Leaching Process

To study the effect of reaction time on the leaching process of the residues of MP-PCBs were analyzed by the XRD method at different reaction times. As presented in Figure 10, the diffraction peaks of Cu decline as the reaction time is prolonged. The peaks of Cu were observed in the samples from 30 to 120 min, then became undetected from 150 min to 180 min, indicating that the Cu content in the residues after 150 min is very low.

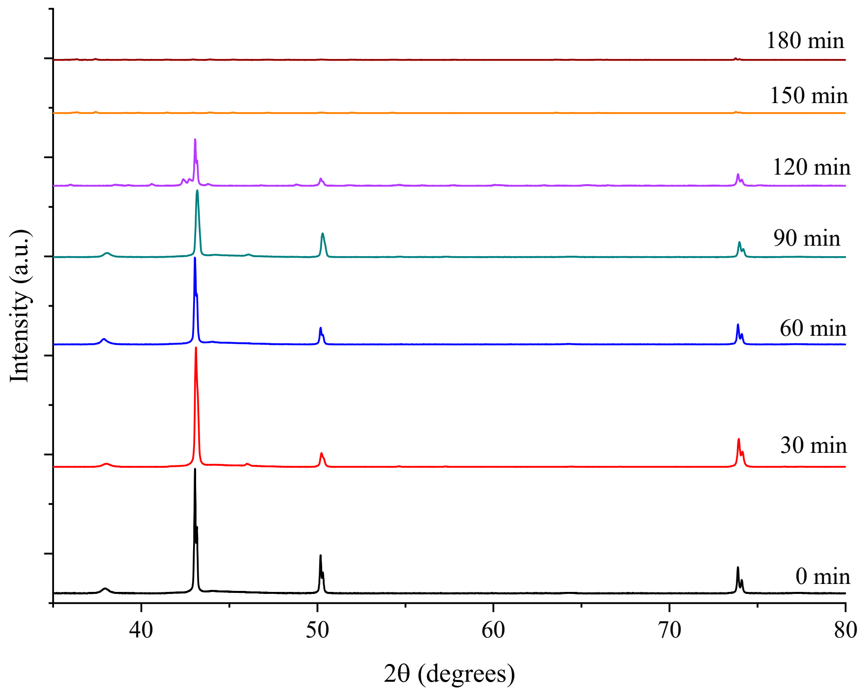

Figure 10. XRD patterns of MP-PCBs at different reaction times.

To further understand the kinetics of the leaching process, the experimental data in the time range of 0–150 min and at different temperatures were analyzed using the shrinking core model that is frequently used to study the kinetics of the leaching process of metals and oxides from ores [26,36]. According to the shrinking core model, the dissolution of particles can be controlled by a liquid-film diffusion or surface−chemical reaction [37].

The liquid−film diffusion can be expressed as:

$$1 - 3(1 - a)^{2/3} + 2(1 - a) = k_d t \tag{4}$$

The surface-chemical reaction can be ascribed as:

$$1 - (1 - a)^{1/3} = k_r t \tag{5}$$

where a is the fraction of metal dissolved into the solution, k_d and k_r are the rate constants, and t (min) is the reaction time.

The fitting of the results of the experimental data to Equations (4) and (5) of the shrinking core model are presented in Figure 11. Regarding the correlation coefficient (R^2), the order of fitness of the experimental data to the equation is (5) > (4). Moreover, the data also show a linear pattern with Equation (5). Therefore, the kinetics of Cu leaching can be well predicted by the shrinking model and controlled by the surface-chemical reaction step. The calculated rate constants from Equation (5) show that the reaction rate reached the highest value at 333 K. This result is in good agreement with the experimental data. In a study by Ding et al. (2022) [26], the reaction rates of Zn and Ga were accelerated proportionally with increasing reaction temperature. A similar result was also reported in the leaching of the rear earth element [37]. In this study, the rate of reaction was affected by both the mass transfer and solubility of the ozone, which responded to the increasing temperature in an opposite manner. The activation energy (E_a) of the Cu leaching process was calculated using the Two-Point form of the Arrhenius equation as follows [38,39]:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6)$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2, respectively; R is the universal gas constant (8.314 J mol^{-1} K^{-1}). In this work, the calculation was carried out using rate constants at 323 and 333 K. The calculated E_a was 10.852 kJ mol^{-1}.

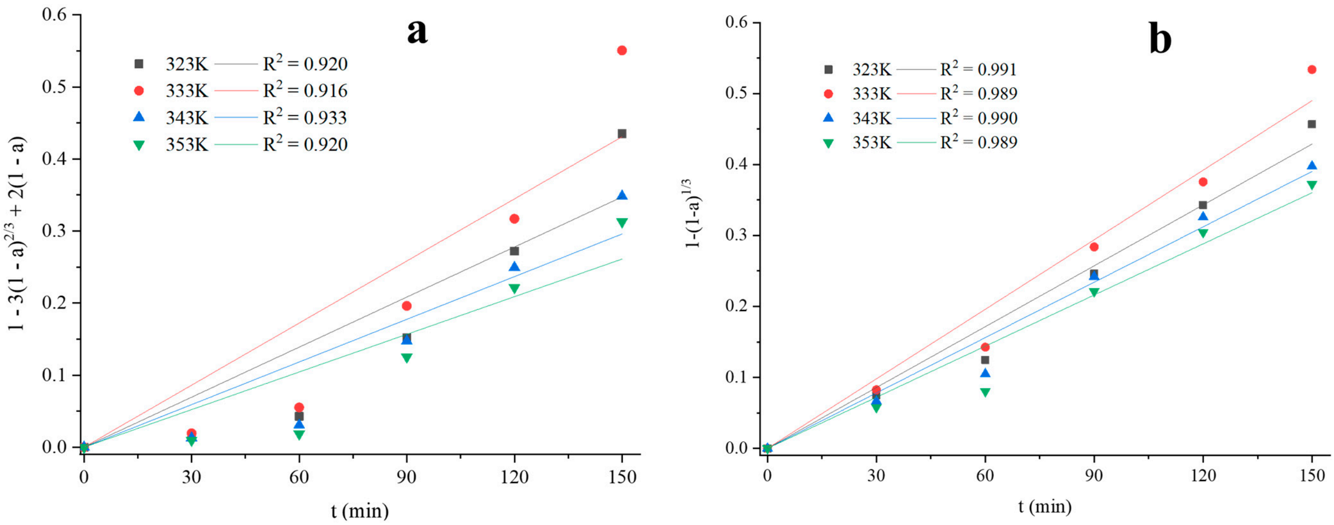

Figure 11. Plots of the shrinking core models at different temperatures: (**a**) liquid−film diffusion and (**b**) surface−chemical reaction.

4. Conclusions

The leaching of copper from MP-PCBs can be effectively enhanced by the combination of ozone and ultrasound. The leaching process is significantly dependent on the presence of ultrasound, ozone dose, HCl concentration, liquid/solid ratio, temperature, and reaction time. Ultrasound could remarkably increase the recovery efficiency, which is nearly four times higher than with ozone alone. HCl concentration is an important parameter in the leaching process. When HCl concentration increased from 0.5 to 3 M, the leaching efficiency increased from about 21% to about 99% after three hours. The effect of ozone dose on the leaching of Cu is also noticeable. The leaching efficiency significantly increased as the ozone dose increased from 300 to 700 mg/h. The liquid/solid ratio is also a crucial parameter. The leaching efficiency increased with the increase in the liquid/solid ratio from 2 to 8. The temperature was also a major factor affecting the leaching process and the optimum temperature for this process is 333 K. The leaching efficiency noticeably increases when reaction time increase from 0.5 to 3.0 h. Under optimum conditions, more than 99% of Cu was leached. The kinetics of the copper leaching process, which was analyzed by the shrinking core model, were governed by the surface-chemical reaction. The findings from this study showed that the combination of ozone and ultrasound is a simple, effective, and eco-friendly method that can be utilized for recovering metals from MP-PCBs.

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