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Effect of Microwave Pretreatment on the Leaching and Enrichment Effect of Copper in Waste Printed Circuit Boards

Xiang Lv, Qinqin Wu, Xiaobing Huang, Ling ling Wu, Lin Hu, Peng Fei, Tian ming Liu, and Qing Yu*

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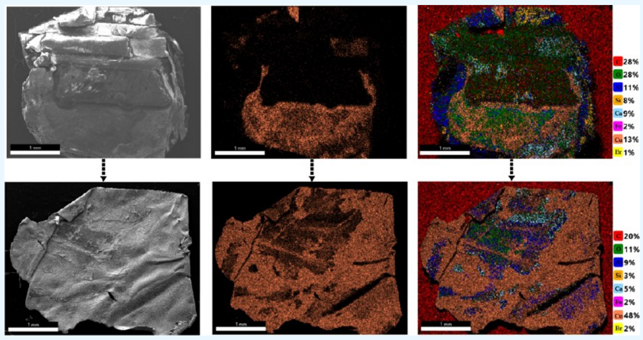
ABSTRACT: The use of efficient and clean methods for the recycling of waste circuit boards is an ongoing challenge. In this research, the effect of microwave pretreatment on the leaching and enrichment of copper from waste print circuit board (WPCB) was studied. The morphology and chemical structure of WPCB particles before and after microwave pretreatment were analyzed by SEM/EDS and Fourier infrared spectroscopy. Leaching experiments and copper enrichment tests were designed to investigate the effect of different microwave irradiation powers and microwave irradiation times on the copper leaching rate and copper enrichment rate in WPCB. The leaching experiment results showed that microwave pretreatment can effectively improve the leaching rate of WPCB. When the microwave irradiation power was 700 W, the irradiation time was 120 s, and the leaching time was 15 min, the copper leaching rate in WPCB was 57.01%, which was 24.34% higher than that in the untreated condition. The results of copper enrichment experiment show that microwave pretreatment can effectively improve the copper enrichment of WPCB. After microwave pretreatment, copper was effectively enriched in the 4−2 and 2−1 mm particle sizes. When the microwave irradiation time was 120 s, the copper enrichment rates in the 4−2 and 2−1 mm particle sizes were 1.74 and 1.66, which increased by 0.63 and 0.32, respectively, compared to the untreated condition. Microwave pretreatment enables the effective separation of metallic copper from non-metallic components in WPCB, increasing the exposure area of copper and promoting the monomer separation of copper, thus improving the leaching and enrichment of copper.



1. INTRODUCTION

With the rapid development of electronic information industry and the improvement of national living standard, the production of electronic products keeps a rapid growth trend.[1,2] The increasing frequency of electronic product replacement has led to a dramatic increase in e-waste generation, which has become one of the fastest growing solid waste streams in the world.[3,4] Waste print circuit boards account for a large proportion of electronic waste, and their recycling is an extremely complex process. It consists of metals and non-metals, and the metal components have a high value content, including copper, iron, lead, tin, nickel, antimony and aluminum, and so forth.[5,6] The abundance of these valuable elements is much higher than the natural abundance,[7] so it is important to promote the resource utilization of these "secondary resources" for environmental capacity and sustainable economic development.[8,9]

At present, the common WPCB resource treatment methods include mechanical method,[10,11] chemical method,[12,13] incineration method,[14,15] pyrolysis method,[16,17] biological method,[18,19] and so forth. Regardless of the method, efficient extraction of metals is the key to resourceful treatment of WPCB. In this regard, numerous studies have been conducted by scholars at home and abroad.[20] Cayumil[21] carried out a high temperature pyrolysis study of waste printed circuit boards in the temperature range of 800−1000 °C. The results of the study found that pyrolysis temperatures below the melting point of copper and short heating times were found to play an important role in limiting the diffusion/pickup of lead and tin in the copper rich fractions. Yan et al.[22] studied the fragmentation of WPCBs using heat treatment techniques and showed that thermal pretreatment improved the release of metals from non-metallic components, improved the fragmentation of WPCBs and promoted the enrichment of copper in WPCBs. Diao[23] used high-voltage pulses to pre-treat waste circuit boards. It was found that the high-voltage pulse technology can take advantage of the difference in electrical properties of metals and non-metals in WPCB to crush them,

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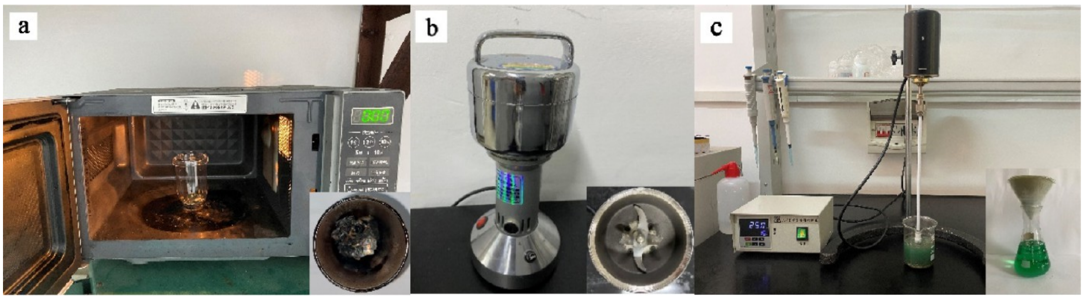

Figure 1. Microwave irradiation equipment is shown in (a), the crushing equipment is shown in (b), and the copper leaching process is shown in (c).

facilitating the subsequent sorting and recycling of metals in WPCB. Li[24] studied the sorting process of metals and non-metals in WPCB with different dispersion media in combination with a multi-stage comminution process, and the results showed that the use of an alcohol-based gravity sorting process can effectively promote the sorting and recovery of metals and non-metals in WPCB. Han et al.[25] used the organic solvent dimethylacetamide to treat the WPCB, and the results showed that this method could improve the crushing efficiency of the WPCB, achieve the release and enrichment of metals from the crude fraction, and reduce the generation of fine particles. Jadhao et al.[26] used ammonia-ammonium sulfate to leach copper and nickel from WPCBs, and the results showed that this method has a very high recovery rate of copper and nickel from WPCBs.

However, there are many problems in the recycling process of the above-mentioned study of WPCB. Such as the jamming of circuit board fragments during the crushing of WPCB, the difficulty of controlling the uniform distribution of forces in impact crushing and thus the phenomenon of over-crushing of materials, and the phenomenon of low dissociation of metals and non-metals. Moreover, the leaching process also suffers from low extraction rates of metals and long leaching cycles.[27] Therefore, it is very important to find a new method to systematically reveal the broken mechanism of the WPCB and realize the efficient dissociation of metal and non-metal and the efficient extraction of metal. Microwave technology is selective and internally heated compared to traditional heat-assisted fragmentation and some chemical methods.[28,29] Microwave irradiation produces an internal heating effect on microwave-sensitive materials,[30,31] creating thermal stresses and cracks between different components and achieving monomeric dissociation of useful minerals.[32] Theoretically, the separation of metals and non-metals in WPCB can be carried out according to their different wave absorption properties, thus improving the dissociation of metallic copper in WPCB and thus the subsequent metal leaching effect.[33]

This study intends to use different microwave irradiation parameters to pretreat WPCB. For the traditional treatment of WPCB with high separation difficulty, low metal and non-metal dissociation effect, low metal extraction rate, and other shortcomings, the use of microwave pretreatment has the characteristics of selective heating and internal heating according to the characteristics of different materials in the WPCB for the effective separation of metals and non-metals.[34] This improves the efficiency of subsequent crushing, sorting, and leaching, enables the effective recovery of metals from WPCB and reduces the occurrence of secondary pollution. In addition, microwave irradiation consumes less energy and can produce a larger crushing and lifting effect in a shorter irradiation time, which can greatly save energy compared to the traditional heat-assisted crushing method, and has certain economic benefits.[35] The study has important implications for microwave-assisted metal extraction from WPCB.

2. EXPERIMENTAL SECTION

2.1. Materials. The WPCBs used in this experiment are all scrapped mobile power supply motherboards, sourced from the second-hand market, whose main components and dimensions remain similar. First, the electronic components are removed from the surface of the WPCB to obtain a complete bare board. Then, the sample is cut into rectangular pieces with a side length of 20 mm × 15 mm to meet the basic requirements for microwave pre-treatment and crushing.

2.2. Experimental Procedure. *2.2.1. Microwave Pre-treatment and Crushing.* WPCB specimens with a mass of 10.00 g were placed in a quartz crucible with a volume of 150 mL and irradiated with different microwave parameters. After irradiation, the crucible lid was opened and the temperature of the pretreated WPCB specimens was measured using an infrared thermometer; the small amount of fumes generated during the experiment was drawn in by a fume hood and discharged through an exhaust gas treatment unit to ensure that it was environmentally sound. After the temperature was measured, the samples before and after pretreatment were crushed for 120 s by a high-speed functional crusher (with a speed of 25,000 r/min). Crushed specimens were used for copper leaching and copper enrichment experiments. All experiments were carried out three times. The experimental procedure and equipment are shown in Figure 1a,b.

2.2.2. Leaching of Copper from WPCB. The WPCB samples before and after pretreatment were loaded into a 200 mL beaker, then 100 mL of H_2SO_4 at a concentration of 2 mol/L and 10 mL of H_2O_2 at a mass fraction of 30% were added, an electric stirrer was started (set at 250 rpm), leached for 15 min, and then filtered and volumetized into a 250 mL volumetric flask. After fixing the volume, the leachate was diluted by a certain multiple and then the content of copper ions in the solution was measured; the leaching process is shown in Figure 1c. The formula for calculating the leaching rate of copper is as follows

$$\text{leaching rate of copper} = (\text{Cu content in filtrate} / \text{Cu content in WPCB}) \times 100\%$$

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mass of copper in sample = mass of copper in leachate + mass of copper in residue

2.2.3. Yield Distribution and Cu Yield Distribution Calculation. The WPCB crushed products before and after microwave pretreatment were sieved through experimental sieves with sieve holes of 4, 2, 1, and 0.5 mm, respectively. After sieving, the mass of each particle size was measured with an analytical balance (accurate to 2 decimal places). After measuring the mass, the Cu content in the different particle sizes was determined by nitric acid digestion using the following procedure: As the +4, 4−−2, and 1−2 mm samples were too large, they were loaded into 100 mL crucibles and calcined in a muffle furnace at 600 °C for 2 h in order to ensure sufficient leaching of copper from the samples. After cooling, the residue was transferred into a 100 mL beaker, and then, 50 mL of concentrated nitric acid was added. After the reaction was stable, the residue was placed on an electronic universal furnace at 120 °C for 2 h to intensify digestion;[38] the sample was cooled, 10% nitric acid was added, filtered into a 150 mL volumetric flask and diluted by a certain multiple to determine the amount of copper ions in the solution. The yield of WPCB crushed products, copper yield, and copper enrichment were calculated as follows.

The yield of different size fractions can be defined as follows

yield = mass at different particle sizes/total mass

The Cu yield of different size fractions can be defined as follows

Cu yield = mass of copper at different particle sizes/total mass of copper

The copper enrichment ratio can be defined as follows

enrichment ratio = Cu yield/yield

2.3. Experimental Analysis Equipment. Atomic absorption spectrophotometers (PerkinElmer, Pin AAcle 900F, USA) are used to determine the concentration of copper ions in solutions. Scanning electron microscopy (SEM, HITACHI, Regulus8100, Japan) and energy-dispersive spectroscopy were used to analyze the morphology and elemental distribution of WPCB particles before and after microwave pretreatment. A Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher, Thermo Nicolet iS5, USA) was used to measure changes in chemical bond types before and after WPCB pretreatment; X-ray fluorescence (XRF, PANalytical, Axios, Netherland) spectrometry is used to measure elements and content in WPCB; and analytical balances (METTLER TOLEDO, AL-104, China) are used to measure the mass of WPCB in different particle size intervals.

3. RESULTS AND DISCUSSION

3.1. WPCB Composition Analysis. In order to determine the composition and content of elements in WPCB, it was crushed and mixed evenly for X-ray fluorescence analysis. The basic elements and content of the WPCB used are shown in Table 1. Table 1 shows that the main metals in WPCB are Cu, Ca, Sn, Al, and Fe, and the non-metals are mainly Br, Si, and a small amount of precious metals Pb, Ba; the metallic components such as Al, Fe, Zn, and Cu have higher conductivity and faster heating rates in the microwave field,[36] while the non-metallic components Si and Br have weaker microwave absorption capabilities.[37]

Table 1. Elements and Content in WPCB

Cu	Br	Ca	Si	Sn	Al	Fe	Ce
39.70	24.33	9.43	8.49	5.84	3.20	1.61	1.48
Mg	Ti	Ni	Ba	Pb	Cl	S	Sr
1.15	0.90	0.84	0.62	0.58	0.38	0.34	0.28
Zn	Na	K	Cr	P			
0.24	0.22	0.13	0.12	0.02			

3.2. Metal Exposure Characteristics of WPCB before and after Microwave Pretreatment. Figure 2 shows the metal exposure characteristics of the WPCB surface at different microwave powers (irradiation time fixed at 90 s) and different irradiation times (microwave power fixed at 700 W). With the increase in microwave power and irradiation time, the copper foil layer in the WPCB was gradually revealed. The specific phenomenon was as follows: the solder mask resin layer attached to the top of the copper foil layer was gradually pyrolyzed, the epoxy glass cloth plate layer below the copper foil layer was gradually separated from the copper foil layer, and the WPCB was gradually carbonized and turns black. At the lower microwave power and microwave irradiation time, the WPCB surface metal exposure was not obvious and slight pyrolysis occurs. When the irradiation time was elevated to 90 s, the copper foil layer in the WPCB reaches obvious exposure, which was due to the metal and non-metal components of the WPCB having different dielectric constants, resulting in their different response characteristics to microwaves, and with the elevation of microwave power and time, the local temperature difference was gradually amplified and warmed unevenly thus generating thermal stress, resulting in the gradual separation of the metal copper foil layer from the non-metal epoxy glass cloth board layer.[39] The optimum microwave pretreatment conditions were 700 W microwave power and 120 s irradiation time.

3.3. Effect of Microwave Pretreatment on Copper Leaching from WPCB. Different microwave irradiation powers (210, 350, 560, 700 W, microwave time fixed at 90 s) and microwave irradiation time (30, 60, 90, 120 s, microwave power fixed at 700 W) were used to pretreat WPCB. The crushing time was 120 s, and the leaching temperature was room temperature. The leaching time was 15 min, and the results are shown in Figure 3.

As shown in Figure 3a, the microwave irradiation power has a significant effect on the increase of leaching rate of WPCB crushing products. With the increase of microwave power, the leaching rate of WPCB crushed products increases gradually, and the temperature of WPCB samples also increases gradually. The leaching rate of copper from the WPCB increases slowly when the microwave power was low. When the microwave power was 210 W, the copper leaching rate increased from 32.67 to 34.19% under untreated conditions, which was only a 1.52% increase. When the microwave power was 700 W, the leaching rate of WPCB increased from 32.67% in the untreated condition to 49.35%, a 16.68% increase in leaching rate. This was due to the fact that in a low-power microwave field, the microwave energy was converted into lower heat energy. Such as microwave powers of 210 and 350 W when the temperatures of the WPCB specimens were 173 and 260 °C, the lower temperature so that the WPCB metal

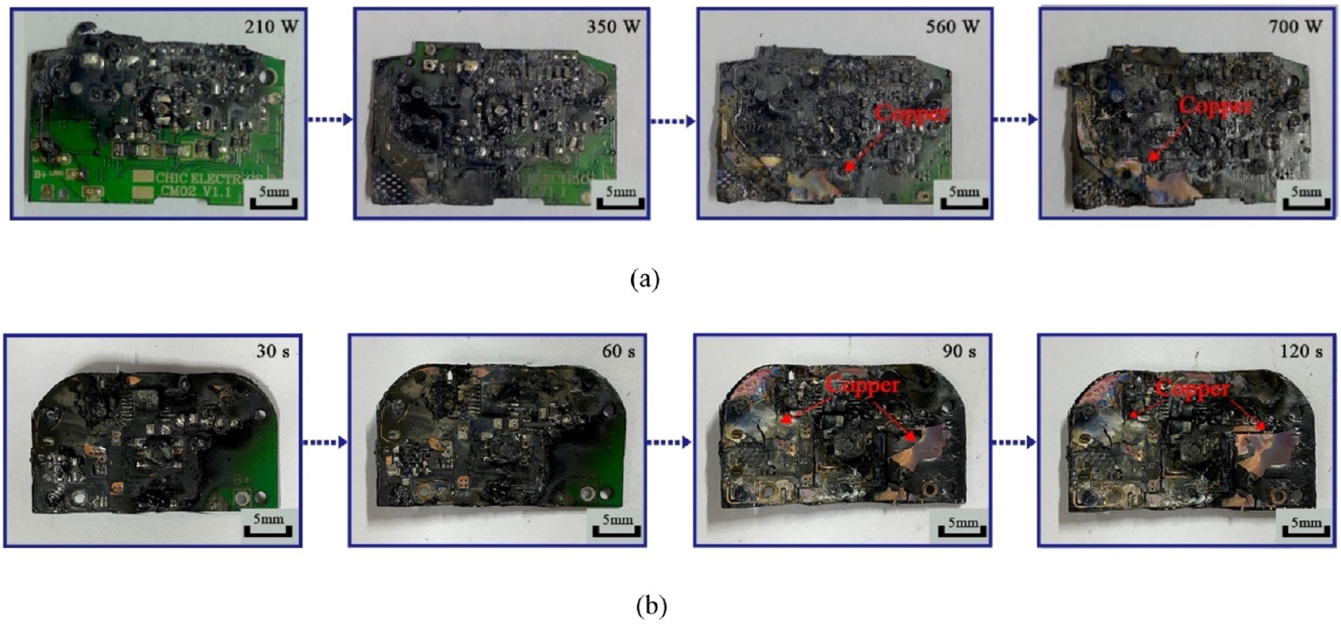

Figure 2. Metal exposure characteristics of WPCB under different microwave pretreatment conditions. (a) Different microwave powers, and (b) different microwave times.

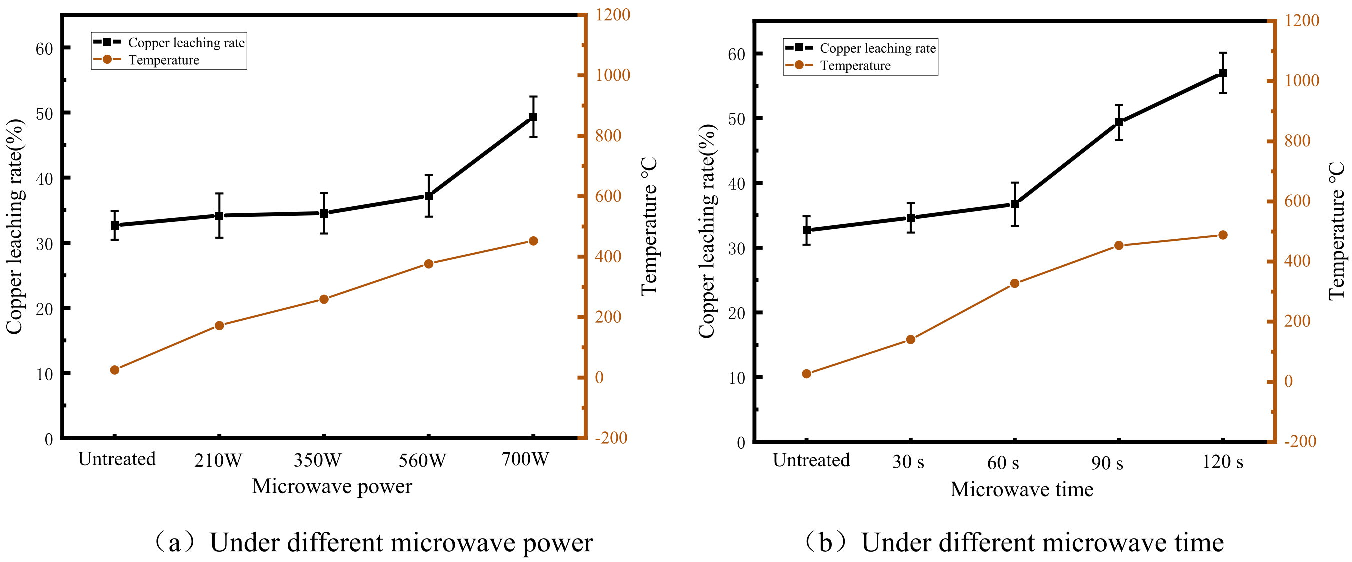

Figure 3. Effect of microwave pretreatment on the leaching rate of copper.

and non-metallic components of the thermal stress was low, metal, and non-metallic was not enough to be generated between the cracks, which was not conducive to the copper foil layer was separated and exposed, on the other hand, at lower temperatures the resin component in the WPCB does not reach its melting point and there was only slight pyrolysis of the WPCB specimen, which makes it difficult to fully expose the copper foil layer and thus has less effect on the leaching rate.

As shown in Figure 3b, microwave irradiation time has a significant effect on the leaching effect of crushed products, with the increase of microwave irradiation time, the leaching rate of copper gradually increased, and the temperature of WPCB specimen also gradually increased. When the irradiation time was increased to 90 s and the temperature of the WPCB specimen reached 453 °C, there was a significant increase in the copper leaching rate. The maximum copper leaching rate of 57.01% was achieved when the irradiation time was 120 s, an increase of 24.34% compared to the untreated condition.

Hong[37] placed crushed WPCB powder in a leaching solution of sulfuric acid and hydrogen peroxide and subjected it to microwave irradiation during the leaching process to investigate the effect of microwave-assisted heating on the leaching rate. The results showed that microwave irradiation promoted the leaching of copper from WPCB. The study concluded that the effect of microwaves on the reactants intensified the molecular activity, greatly increased the frequency of collisions between the reactants, and increased the rate of chemical reaction, thus increasing the leaching rate. Compared with the study carried out by Hong, this study applied the microwave irradiation process directly to the WPCB itself, rather than microwave-assisted heating during the leaching process, which made the microwave effect more

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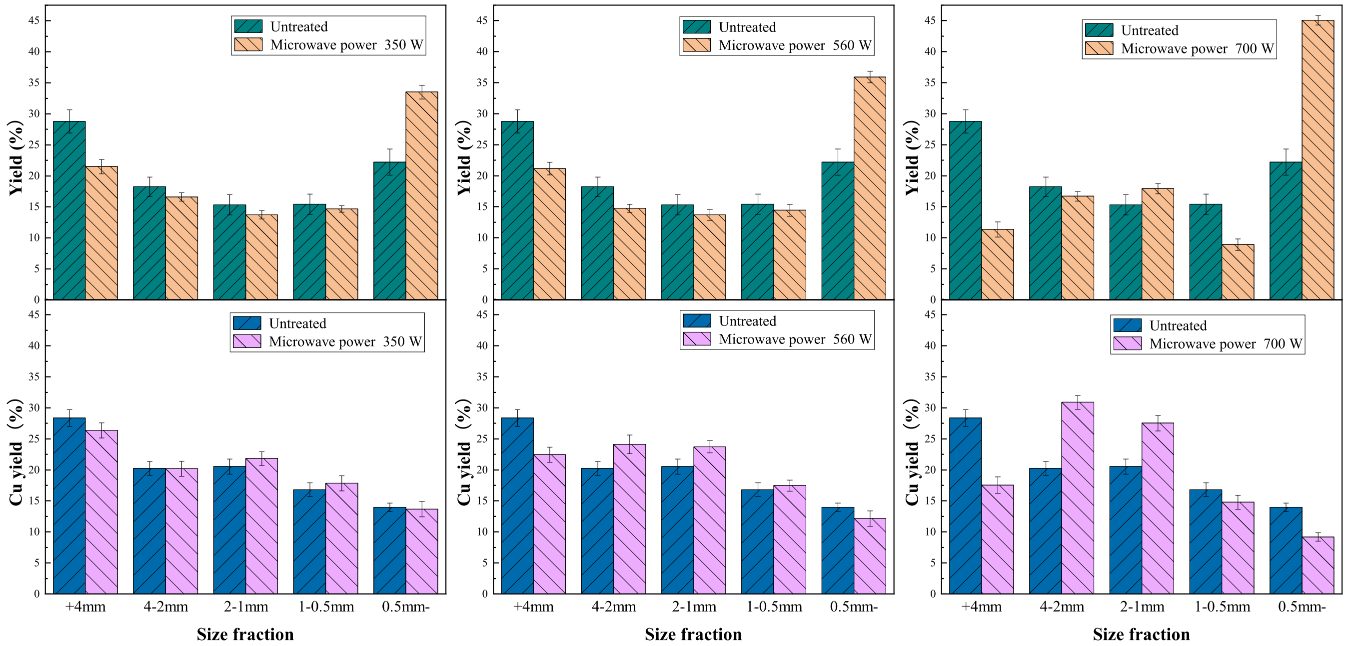
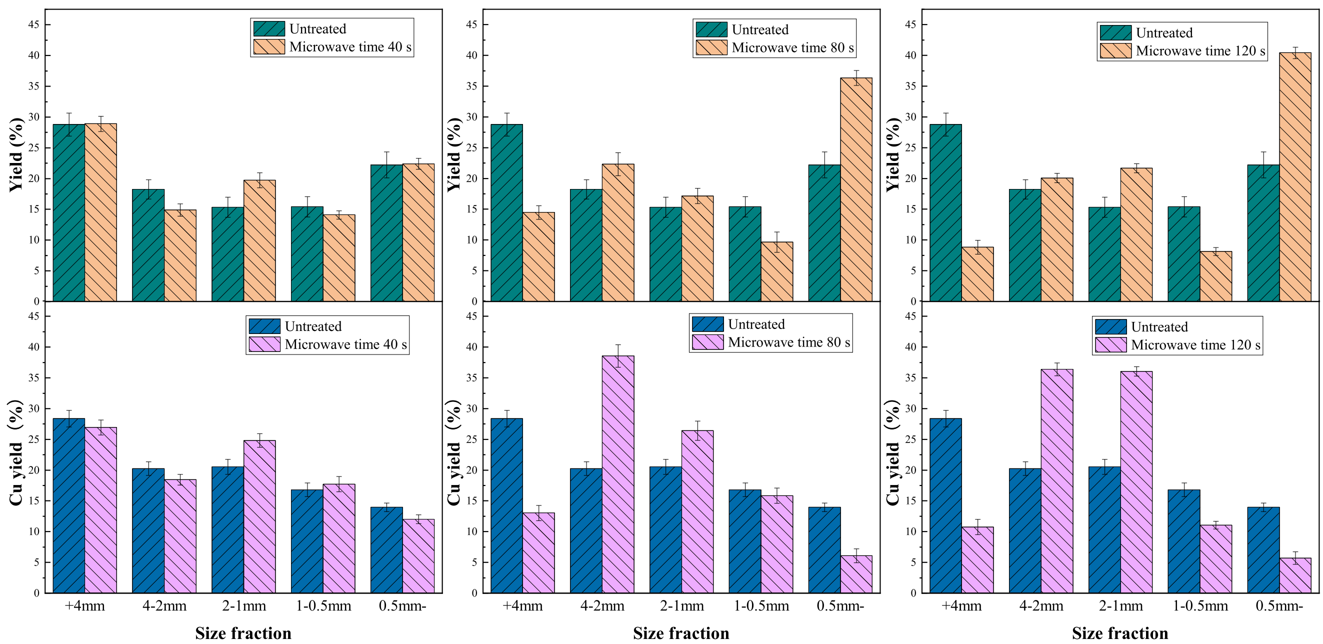


（a）Under different microwave power



（b）Under different microwave time

Figure 4. Crushed product and copper yield distribution under different microwave pretreatment conditions.

direct. Because microwave irradiation during the pretreatment phase greatly facilitates the separation of metals from non-metals in the WPCB, thereby increasing the contact area between the subsequent metals and the leaching agent, on the other hand, the WPCB absorbed more significant thermal energy and generated higher temperatures under direct microwave irradiation, which caused the organic matter attached to the copper surface to undergo pyrolysis, thus enhancing the exposed area of metallic copper and boosting the leaching rate.

3.4. Effect of Microwave Pretreatment on Copper Enrichment in WPCB. The effect of different microwave power and irradiation time on the WPCB fragmentation effect and copper enrichment effect was investigated. The microwave powers were 350, 560, and 700 W (microwave time fixed at 90 s) and the irradiation times were 40, 80, and 120 s (microwave power fixed at 700 W), respectively. The crushing time was 120 s. The yields of the crushing products and the copper yield are shown in Figure 4 and Table 2. With the increase of microwave power and irradiation time, the content of WPCB

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Table 2. Enrichment Rate of Copper under Different Microwave Pretreatment Conditions

particle size distribution (mm)	untreated			treated (350 W)		
	yield (%)	Cu yield (%)	enrichment rate	yield (%)	Cu yield (%)	enrichment rate
+4	28.78	28.39	0.99	21.49	26.40	1.23
4−2	18.23	20.26	1.11	16.60	20.21	1.22
2−1	15.35	20.54	1.34	13.72	21.84	1.59
1−0.5	15.41	16.82	1.09	14.68	17.86	1.22
0.5-	22.22	13.98	0.63	33.51	13.69	0.41
total	100	100		100	100	

article size distribution (mm)	treated (560 W)			treated (700 W)		
	yield (%)	Cu yield (%)	enrichment rate	yield (%)	Cu yield (%)	enrichment rate
+4	21.18	22.45	1.06	11.37	17.56	1.54
4−2	14.75	24.14	1.64	16.71	30.89	1.85
2−1	13.70	23.74	1.73	17.95	27.54	1.53
1−0.5	14.44	17.49	1.21	8.90	14.80	1.66
0.5-	35.93	12.17	0.34	45.07	9.20	0.20
total	100	100		100	100	

particle size distribution (mm)	treated (40 s)			treated (80 s)			treated (120 s)		
	yield (%)	Cu yield (%)	enrichment rate	yield (%)	Cu yield (%)	enrichment rate	yield (%)	Cu yield (%)	enrichment rate
+4	28.90	26.95	0.93	14.49	13.04	0.90	8.84	10.77	1.22
4−2	14.89	18.45	1.24	22.32	38.57	1.73	20.90	36.39	1.74
2−1	19.72	24.84	1.26	17.17	26.42	1.54	21.69	36.06	1.66
1−0.5	14.09	17.72	1.26	9.67	15.87	1.64	8.14	11.06	1.36
0.5-	22.40	12.03	0.54	36.35	6.10	0.17	40.44	5.72	0.14
total	100	100		100	100		100	100	

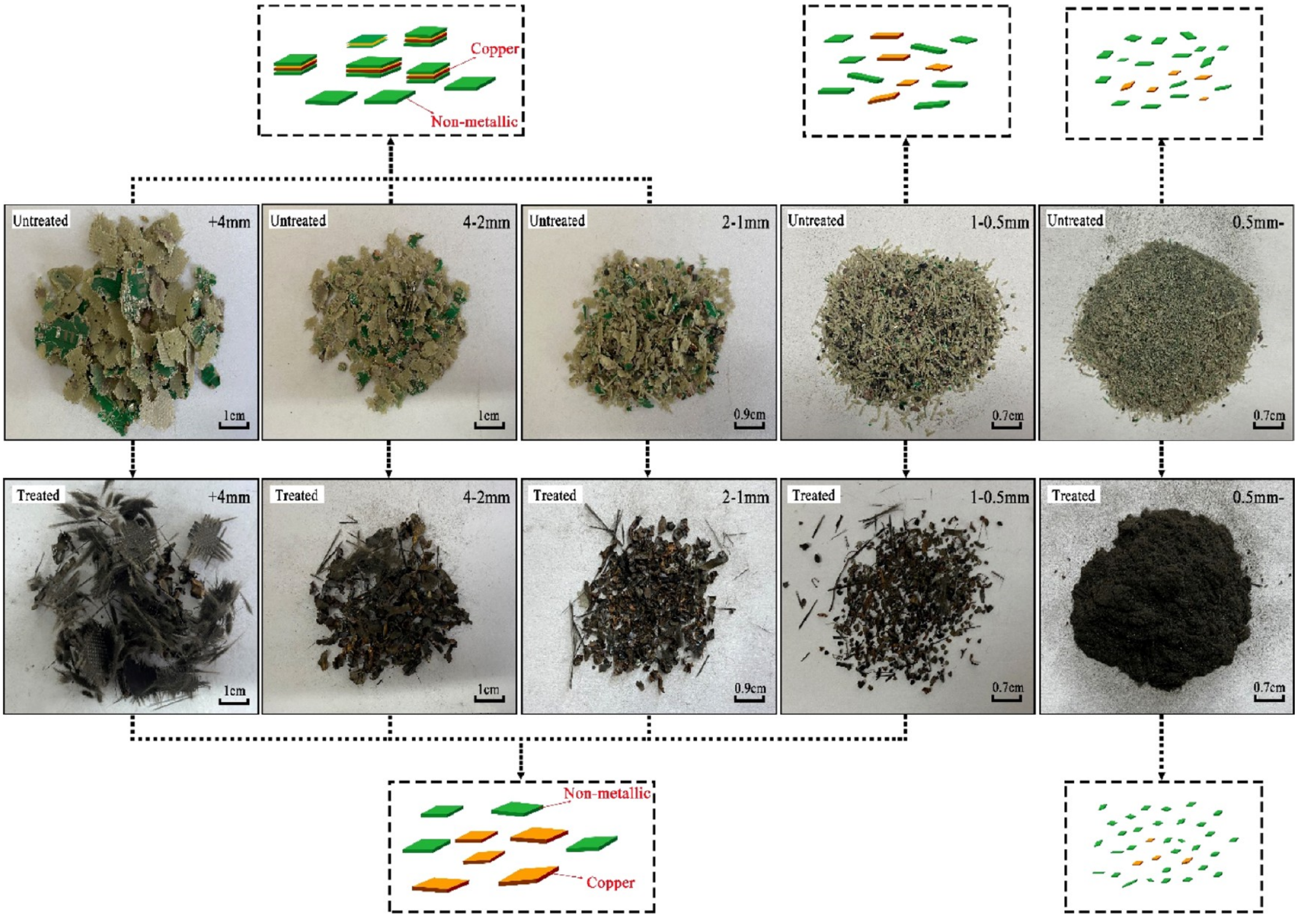

Figure 5. Morphological characteristics of WPCB at different particle sizes before and after microwave pretreatment.

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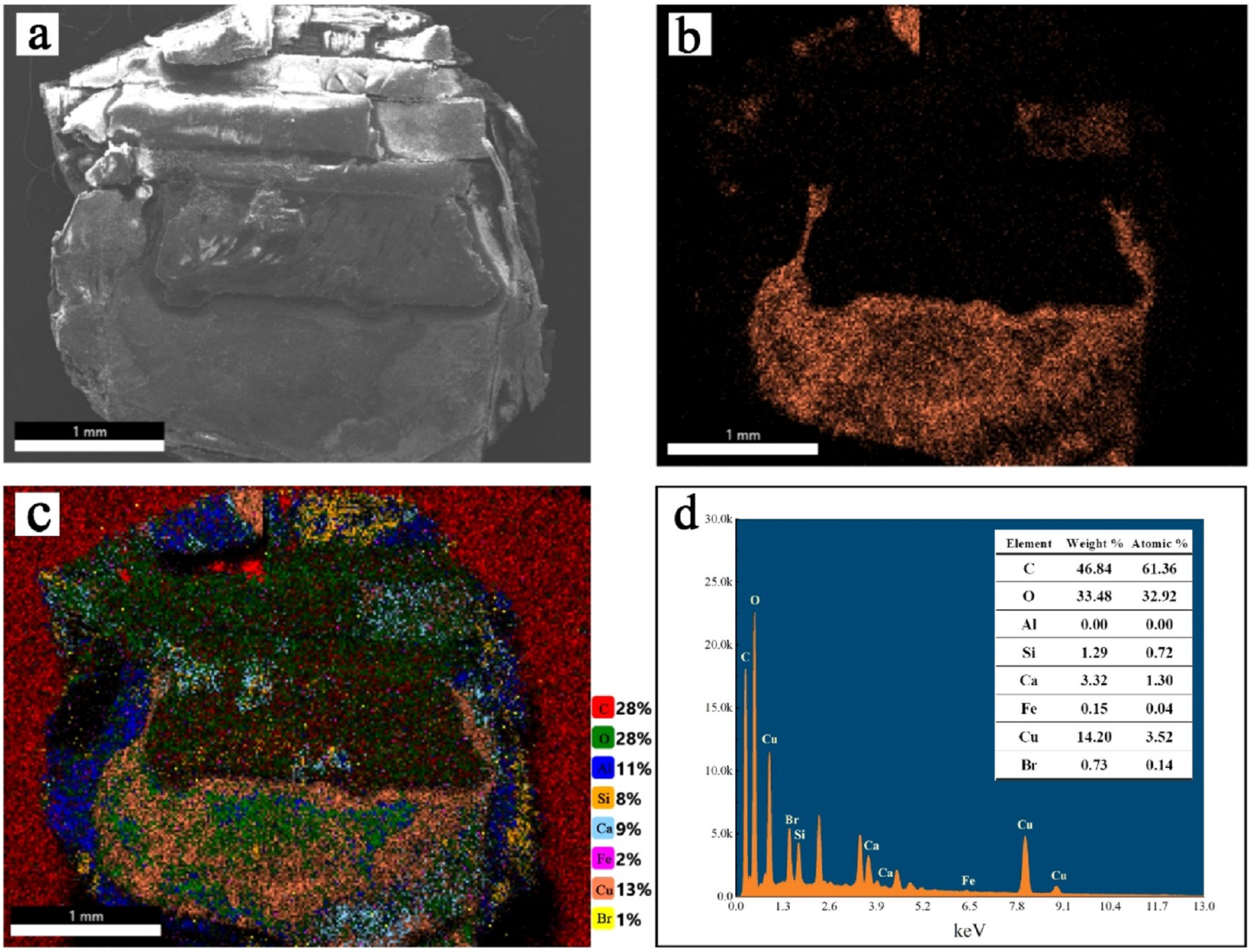

Figure 6. SEM image of WPCB particles before pretreatment is shown in (a). The distribution of copper elements and multi-elements are shown in (b,c), respectively, and the EDS mapping analysis is shown in (d).

fines gradually increased and the content of coarse particles gradually decreased, and the distribution of copper content was concentrated in the range of 4−2 and 2−1 mm, and the enrichment rate of copper was significantly increased in this range.

It can be seen from the yield of crushed products in Figure 4, under the untreated condition, the size fraction of crushed products in WPCB shows that the content of coarse fraction (+4 mm) and fine fraction (0.5 mm-) was relatively large, and the proportion of intermediate fraction was relatively uniform. With the increase in microwave power and microwave time, the coarse fraction of WPCB increases and the fine fraction decreases, when the microwave power increased to 700 W, the 0.5 mm-fraction was 45.07%, and the +4 mm fraction was 11.37%. Compared with the untreated condition, the fine fraction (0.5 mm-) increased by 22.85%, and the coarse fraction (+4 mm) decreased by 17.41%; when the microwave time increased to 120 s, the size fraction of 0.5mm-was 40.44%, and that of +4 mm was 8.84%. Compared with the untreated condition, the fine fraction increased by 18.22%, and the coarse fraction decreased by 19.94%. This indicated that microwave pretreatment can effectively improve the crushing effect of WPCB.

It can be seen from the copper yield in Figure 4, under untreated conditions, the distribution of copper content in WPCB shows a decrease with the decrease in particle size. This was due to the fact that metallic copper was more ductile than non-metallic components such as epoxy glass cloth sheets and resins, so it was difficult to reduce the size after being crushed to a certain size during the crushing process.[40] With the increase of microwave power and microwave irradiation time, copper content decreased in coarse (+4 mm) and fine (0.5 mm-), and enriched in 4−2 and 2−1 mm fraction. Under untreated conditions, the copper contents of 4−2 and 2−1 mm were 20.26 and 20.54%, respectively, and the enrichment rates were 1.11 and 1.34, when the microwave time was 120 s, the copper content of 4−2 and 2−1 mm fraction reached 36.39 and 36.01%, respectively, increased by 16.13 and 15.52% compared with the untreated condition; and the enrichment rates were 1.74 and 1.66, respectively, increased by 0.63 and 0.32 compared with the untreated condition. This indicates that microwave pretreatment effectively improves the enrichment of copper in WPCB, and copper was effectively enriched within 4−2 and 2−1 mm fraction, while the content of copper in +4 mm fraction and 1 mm fraction were reduced. Yan et al.[22] investigated the effect of crushing time on copper enrichment in WPCB under crushing conditions only, showing that as crushing time increased, more copper in WPCB was enriched with finer particle sizes. Compared with the results of Yan et al., it was found that the copper in WPCB under

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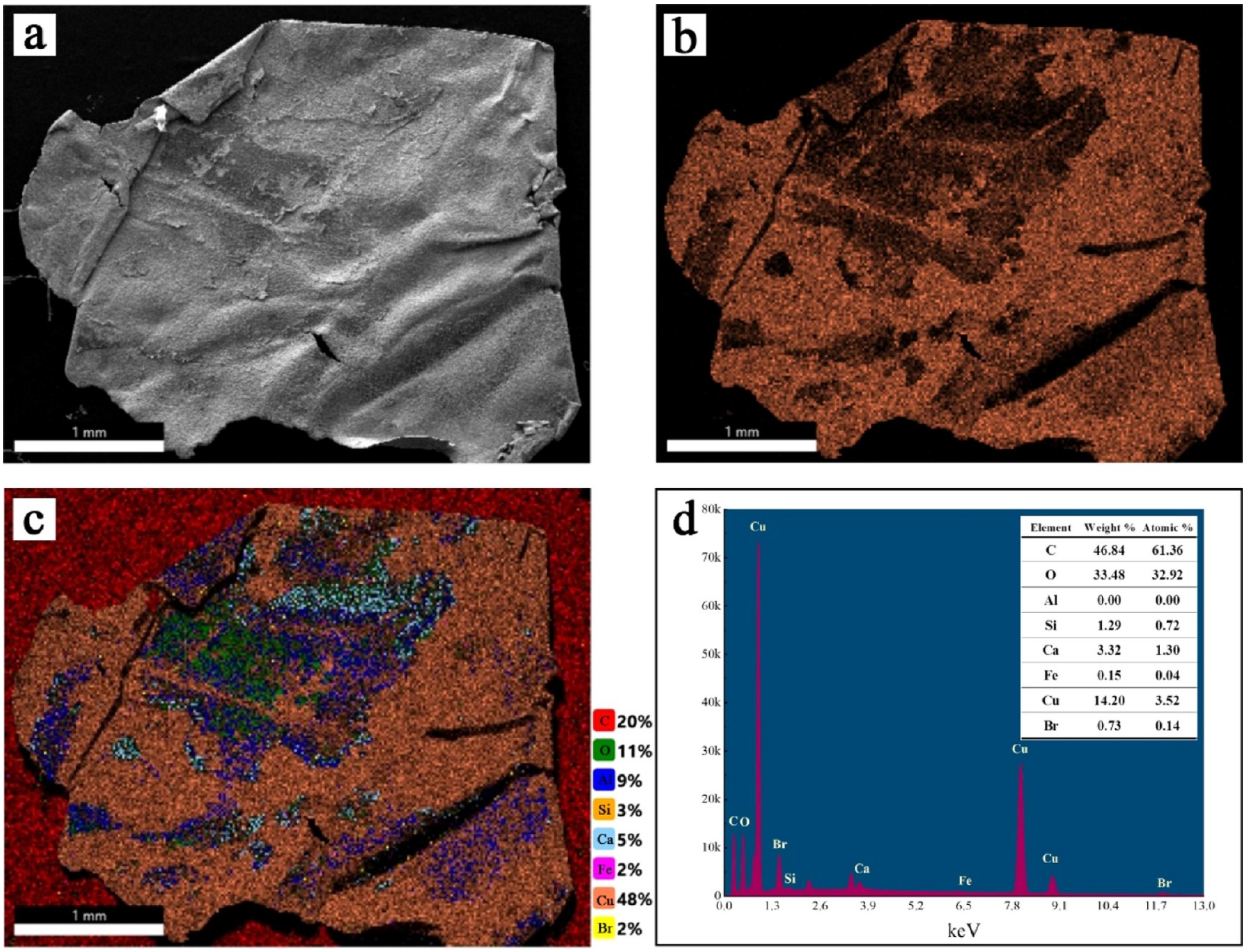

Figure 7. SEM image of WPCB particles after pretreatment is shown in (a). The distribution of copper elements and multi-elements are shown in (b,c), respectively, and the EDS mapping analysis is shown in (d).

microwave pretreatment was more enriched in the coarser particle size. This was due to the fact that the microwave pretreatment enhances the crushing effect of the coarse particles (+4 mm) in the WPCB, resulting in a reduction in the content of coarse particles and a consequent reduction in the copper metal content of the coarse particles; in addition, the microwave pretreatment enhances the separation of metals from non-metals, and in the subsequent crushing process, metallic copper was crushed as a monomer rather than as a composite (encapsulated with non-metals), highlighting the ductile nature of copper, which made it difficult to reduce metallic copper particle size and leaded to a reduction in copper content in smaller particle sizes. Under untreated conditions, metallic copper was more tightly bonded to non-metallic components, which were less stable and more easily crushed, and copper attached to non-metallic components was more easily crushed.

3.5. Morphological Characteristics of WPCB under Different Particle Sizes before and after Microwave Pretreatment. The morphological characteristics of WPCB crushing products at different particle sizes before and after microwave pretreatment were shown in Figure 5. As can be seen from the Figure 5, there was a significant difference in the WPCB before and after pretreatment. In the untreated condition, the copper metal in WPCB was wrapped with the non-metal material, and they exist in the composite form; after pretreatment the metallic copper and non-metal of the WPCB are almost completely separated and the copper foil layer was present as a monomer. The distribution of copper in the crushed products without pretreatment was relatively uniform, and the degree of dissociation between copper and nonmetal increases with the decrease of particle size. Within the particle size range of 1 mm-, the degree of dissociation between copper and nonmetal reached the maximum, and more monomer copper particles can be observed. The copper metal in the crushed product after pretreatment was concentrated in the range of 4−1 mm, and the crushed product in the +4 mm range was mainly non-metallic. The copper content was minimal in the 0.5 mm range under both conditions, and the crushed product was predominantly non-metallic in this range, but the after pretreated product was finer compared to the untreated condition.

3.6. SEM and EDS-Mapping Analysis of WPCB Particles before and after Microwave Pretreatment. WPCB particles (>1 mm) before and after microwave pretreatment were subjected to SEM and EDS-mapping spectroscopy to analyze the distribution characteristics of copper elements on the surface of WPCB before and after

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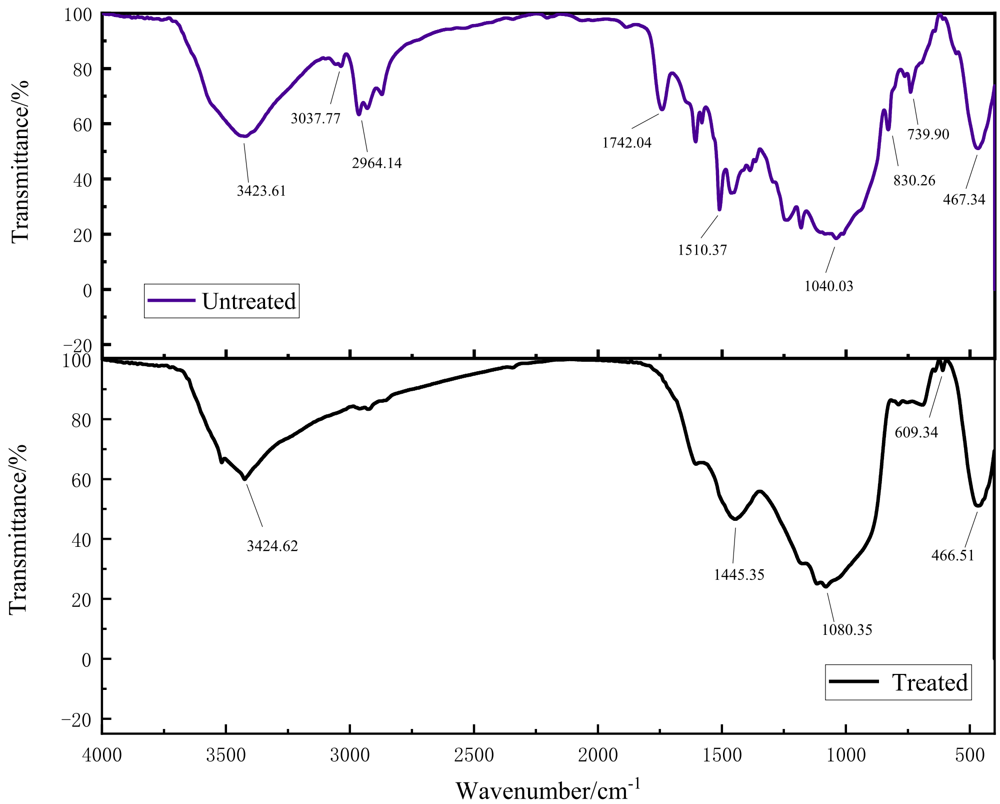

Figure 8. Infrared spectrum analysis for WPCB before and after microwave pretreatment.

pretreatment, Figure 6a shows the SEM image before pretreatment, and 6b−d shows the mapping and EDS of 6a, Figure 7a shows the SEM image after pretreatment, and 7b−d shows the mapping and EDS of 7a.

As shown in Figure 6a, the WPCB bedding before pretreatment was relatively complete and thick. Combined with the mapping analysis Figure 6b,c, it can be seen that the copper foil layer in the crushed particles was not fully exposed, the middle part was covered by non-metallic material and only the edge part was exposed. From the EDS analysis of Figure 6d, it can be seen that the crushed particles have a high relative content of C and O elements and a low relative content of Cu elements. This collectively indicates a low separation of metallic copper from non-metallic materials under untreated conditions and a large exposure area of non-metallic materials in the WPCB. This structure directly hindered the contact between the leaching solution and copper, which was the direct reason for the subsequent low leaching rate. As can be seen from Figure 7a, the copper foil layer in the after pretreated WPCB particles had a single bedding structure and had been completely separated from the non-metallic layer. Combined with the mapping analysis, Figure 7b,c can be seen that the area of copper elements in the particles was large to 48%, and only a small part of non-metallic substances were attached to the surface of the particles. EDS Figure 7d also shows that the relative content of C and O elements was relatively low, while the relative content of Cu elements was relatively high. This indicates that after the microwave pretreatment of the WPCB, the copper foil layer was efficiently dissociated from the epoxy glass cloth layer and the metallic copper was fully exposed, which increased the contact between the copper and the leaching agent and improved the leaching rate; in addition, the ductility of copper crushed in the form of monomer was more fully reflected, which leaded copper to be harder to crush and easier to be enriched in coarse particle sizes.

3.7. Microwave Pretreatment Mechanism Analysis. WPCB powder (<1 mm) before and after microwave pretreatment was analyzed by infrared spectrum, and the results are shown in Figure 8. It can be seen from Figure 8 that there was a significant difference in the intensity of the infrared spectral peaks of WPCB under untreated and pretreated conditions. The intensity of the infrared spectrum peaks was weakened after pretreatment. This indicated that the internal bond was changed, the strength of the bonding bond weakened, and the particles easily crushed.[41] The functional group at 2964.14 cm^{-1} was the asymmetric stretching vibration absorption peak of the C−H bond in the $-CH_3$ group. After pretreatment, the functional group disappeared, which indicated that the high temperature reaction occurring during the microwave pretreatment process caused the pyrolysis of the non-metallic organic epoxy resin in WPCB. Organic functional groups in the feedstock have disappeared after the pyrolysis process because of the organic matter decomposition.[42] The weak absorption peak at 1742.04 cm^{-1} may be the absorption peak of the carbonyl C═O in the WPCB. The peak at 1510.37 cm^{-1} was the characteristic absorption peak of the benzene ring skeleton, The peak at 1040.03 cm^{-1} was the result of C−O stretching vibrations. The peak between 700 and 900 cm^{-1} was the characteristic peak of substituted benzene. The peak at 467 cm^{-1} indicates a stretching vibration of C−Br, which indicated a brominated epoxy resin with a flame retardant effect in WPCB.

4. CONCLUSIONS

Microwave technology was used to improve copper leaching and enrichment in WPCB. These are summarized below:

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1. With the increase in microwave power and irradiation time, the copper foil layer in the WPCB was gradually exposed, the resin attached to the top of the copper foil layer is gradually pyrolyzed, the epoxy glass cloth layer below the copper foil layer was gradually separated from the copper foil layer, and the WPCB was gradually carbonized and blackened; under untreated conditions, the copper foil layer in the WPCB was wrapped with non-metallic material and exists in a composite form. After pretreatment the metallic copper and non-metal of the WPCB have been almost completely separated and the copper foil layer exists as a monomer, this structure promotes the subsequent leaching and enrichment of copper.
2. The increase in microwave power and irradiation time significantly improved the leaching of copper from WPCB. When the microwave time was 120 s, the copper leaching rate reached 57.01%, an increase of 24.34% compared to the untreated condition. The higher the microwave power and microwave time, the stronger the thermal energy received by the WPCB. The increased local temperature difference leads to an increase in the crack between the different components, which in turn increases the contact area between the copper metal and the leaching solution in the subsequent leaching, thus enhancing the leaching rate.
3. Microwave pretreatment enhances WPCB fragmentation and copper enrichment. With the increase in microwave power and microwave time, the coarse fraction of WPCB increases and the fine fraction decreases, and the distribution of copper content was concentrated in the range of 4−2 and 2−1 mm. When the microwave time increased to 120 s, the fine fraction increased by 18.22%, and the coarse fraction decreased by 19.94%, and the copper content of the range 4−2 and 2−1 mm increased by 16.13 and 15.52%, respectively, and the enrichment rate increased by 0.63 and 0.32, respectively.

AUTHOR INFORMATION

Corresponding Author

Qing Yu − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*; Email: ckyuqingk@126.com

Authors

Xiang Lv − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*; orcid.org/0000-0002-3864-2709

Qinqin Wu − *Hunan Technical College of Railway High-speed, Hengyang 421200, China*

Xiaobing Huang − *Hunan Technical College of Railway High-speed, Hengyang 421200, China*

Ling ling Wu − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*

Lin Hu − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*

Peng Fei − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*

Tian ming Liu − *School of Resources, Environment and Safety Engineering, University of South China, Hengyang 421001, China; Key Discipline Laboratory of Defense Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c07102

Notes

The authors declare no competing financial interest.

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