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RESEARCH ARTICLE

Microwave enhanced stabilization of copper in artificially contaminated soil

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Abstract Microwave processing was used to stabilize copper ions in soil samples. Its effects on the stabilization efficiency were studied as a function of additive, microwave power, process time, and reaction atmosphere. The stabilization efficiency of the microwave process was evaluated based on the results of the toxicity characteristic leaching procedure (TCLP) test. The results showed that the optimal experimental condition contained a 700 W microwave power, 20 min process time and 3 iron wires as the additive, and that the highest stabilization efficiency level was more than 70%. In addition, the different reaction atmospheres showed no apparent effect on the stabilization efficiency of copper in the artificially contaminated soil. According to the result of the Tessier sequential extraction, the partial species of copper in the contaminated soil was deduced to transform from unstable species to stable states after the microwave process.

Keywords microwave, copper, stabilization

1 Introduction

Heavy metals such as Cadmium, Copper, Lead and Mercury are considered to be the most hazardous pollutants, and are included on the US Environmental Protection agency's (EPA) list of priority pollutants. Cu contaminated soils result in serious consequences for ecosystem productivity, food chain quality, and water supply. In the past decade, there has been a greater awareness with the studies on transportation, decontamination, and biologic enrichment of copper in the Cu-contaminated soils [1–3]. Immobilization and separation are two general methods that reduce the pollution of heavy metals in soils. In recent years, there have been more effective methods such as chemical extraction, bioleaching process, electro-kinetic process, supercritical extraction, and microwave assisted extraction that have been developed in order to eliminate the potential risks of environmental pollution of heavy metals [4]. Despite the many efforts, the sufficient removal of heavy metals from soil remains unsuccessful. Accordingly, the stabilization or immobilization technology of heavy metals in soil was developed, and various stabilization or immobilization reagents have been investigated, such as phosphorus and manganese oxide [5], bauxite residue [6], calcium sulfate [7], cement [8,9], fly ash [10], phosphate [11,12], zerovalent iron, [13,14] . As mentioned above concerning stabilizing agents, the suggested mechanisms of Cu retention were the precipitation of Cu carbonates and oxyhydroxides, ion exchange, and formation of ternary cation-anion complexes on the surface of Fe and Al oxyhydroxides [15].

The microwave radiation process, as an efficient technology for the stabilization or immobilization of heavy metals, can be used in the remediation of soils contaminated with heavy metals. Chih-Ju G. Jou found that more than 93% of the Pb(II)-contaminated soil was vitrified to a glass/ceramic formation after 30 min of microwave radiation [16]. The chromium-contaminated soil was vitrified after 60 min of microwave radiation, and the chromium (VI) concentration in the leaching test was less than the USEPA regulatory limit of $5.0\ \mathrm{mg \cdot L^{-1}}$ [17]. In Abramovitch's study, chromium in contaminated soil can also be stabilized by microwave radiation [18]. Moreover, microwave radiation can also be used in the detoxification of heavy matals in sewage sludge [19–23]. However, insufficient research has been conducted on the studies on the stabilization of Cu-contaminated soils in previous reports.

Microwave (MW) radiation systems often use three classes of media: conductors, insulators, and dielectrics. Metallic conductors such as copper, brass, and aluminum, reflect MW. Insulators such as teflon and polypropylene

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can reflect or transmit MW, and generally absorb only small amounts of MW energy. Dielectrics have reflective and absorptive properties between those of conductors and insulators. Dielectrics, such as iron and granulated activated carbon, have properties in between conductors and insulators. Therefore, iron and granulated activated carbon were often used as additives [16,17,19].

In this study, the microwave enhanced stabilization of copper in Cu-contaminated soil has been researched. The effects of microwave processing on the stabilization efficiency were investigated as a function of additive, microwave power, process time, reaction atmosphere, temperature, and spiking copper concentration. Moreover, the possible stabilization mechanism of copper by microwave radiation was also discussed concerning the speciation analysis of copper in soil before and after microwave radiation.

2 Materials and methods

2.1 Soil sample

The soil sample used in this study, ZAO humic soil, was bought from an ordinary flower shop in Japan. The initial content of copper in soil was 4.7 $\mathrm{mg \cdot kg^{-1}}$. The original soil was dried at 105°C for 24h after drying at room temperature. An aqueous solution of 0.1 $\mathrm{mol \cdot L^{-1}}$ copper sulfate ($CuSO_4$) was poured over the soil to prepare the artificially contaminated soil sample. A 500 $\mathrm{mg \cdot kg^{-1}}$ copper contaminated soil was prepared. The contaminated soil was stirred in a container, heated to dry at 105°C for 24h in an oven, and then stored in a plastic bag before microwave radiation treatment.

2.2 Experimental methods

When each experiment was initialized, a certain amount of artificially contaminated soil sample was placed in a columned quartz container, whose weight was recorded by a scale connected to the microwave apparatus. A quartz tube with a closed bottom for installing thermal couples was inserted into the center of the columned quartz container. The maximum power of the microwave oven employed in this study was 770W. When the aforementioned soil sample was prepared, the quartz container with sediment samples was moved into the microwave oven. Then, the microwave power and reaction time were set. After the microwave process completed, the soil sample was cooled at room temperature.

Iron wires were used as an additive and applied to enhance the stability of copper in contaminated soil for the microwave radiation process. The toxicity characteristic leaching procedure (TCLP) was used to evaluate the effect of heavy metals stabilization in soil following the microwave process. The TCLP test was modified from the Toxicity Characteristic Leaching Procedure Standard (method 1311) published by USEPA in this study. The main difference in the modification was that the sample weight was reduced from 100 g to 1 g. A 1.0000±0.0002 g mass of soil sample after the microwave process was recorded and used. The extractant, extraction fluid #2 in the method 1311, 0.1 $\mathrm{mol \cdot L^{-1}}$ acetic acid solution with pH value of 2.88±0.05 were used to provide a critical circumstance. Every solution sample obtained in the experiment was filtrated before testing.

2.3 Analytical methods

The stabilization efficiency of copper in the contaminated soil was calculated as follows:

$$E = (C_0 - C_t)/C_0 \times 100\%, \tag{1}$$

where E is the stabilization efficiency of copper in the artificially contaminated soil; C_0 ($\mathrm{mg \cdot L^{-1}}$) is the total concentration of copper in the artificially contaminated soil; and C_t ($\mathrm{mg \cdot L^{-1}}$) is the TCLP leachate concentration before or after the microwave process.

The concentration of copper ion was determined using inductively coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer, ELAN DRC II, USA) and Argon was used as a carrier gas. Table 1 presents the ICP-MS operational conditions. In the experiment with speciation analysis, samples were tested via Tessier’s sequent extraction method [24].

Table 1 ICP-MS instrumental parameters

parameter	setting
radio frequency power	1100W
cones sampler and interface	Pt
signal	area peak
resolution	0.7 amu
sweeps/reading	1
reading/replicates	55
replicates	3
dwell time	25 ms
gas flow rate	1.2 $\mathrm{L \cdot min^{-1}}$

3 Results and discussion

3.1 Stabilization of copper in soil at the different spiking time before microwave radiation

Figure 1 shows the stabilization trend of copper spiked in soil samples at different times before microwave radiation. Copper is known to contain some chemical behaviors in soil, such as forming sulfide, oxide, carbonate, complex

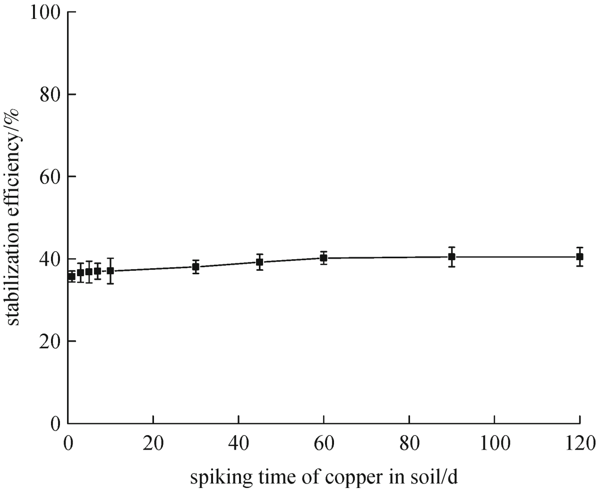

Fig. 1 stabilization of copper in soil at the different times (without microwave radiation)

compounds. Therefore, the spiking copper in soil samples will to some extent stabilize through the soil component of the above process. The results showed that, with the increment of spiking time of copper in the artificially contaminated soil, the stabilization efficiency initially increased only slightly and then leveled off. The different spiking times of copper in soil showed effect on the stabilization efficiency. During a 60 d period, the artificially contaminated soil spiked copper was adopted in the followed experiments.

3.2 Effect of iron wire as additive on stabilization efficiency of copper

Figure 2 shows the effect of iron wire as the additive on the stabilization efficiency of copper in the process of microwave radiation. Compared to the stabilization of copper spiked in soil before microwave radiation (Fig. 1), the microwave radiation process noticeably improved the stabilization efficiency of copper. After adding the iron wire as the additive, the stabilization efficiency of copper had further improved. Thus, the stabilization efficiency gradually increased with each increment of iron wire number. When the iron wire number was more than eight, hot spot would occur, which could lead to excessively high temperatures, and potentially cease the process in order to protect the device apparatus. However, it was unclear why the six iron wire as the additive led to lower stabilization efficiency. Unaccountably, the triangle array of iron wires in the soil could easily generate a discharge phenomenon and rapid temperature increase compared to the circle array of iron wires. However, the triangle array of iron wires in the soil did not improve the stabilization efficiency compared to the circle array.

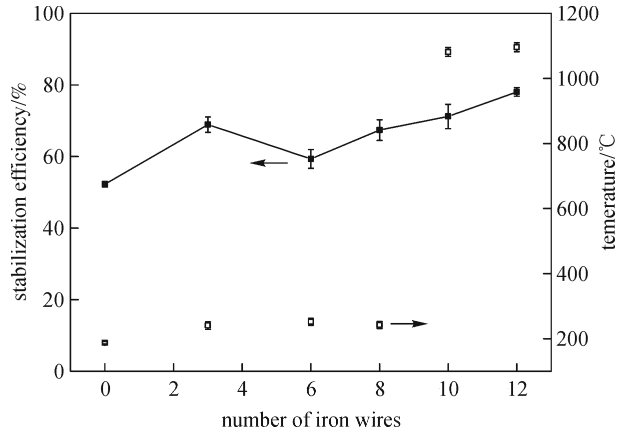

Fig. 2 Effect of iron wire on stabilization efficiency (microwave power: 700 W; reaction time: 20 min)

When the temperature reached above 1000°C and the samples contained 10 or 12 iron wires, the soil in the container presented two parts, the vitrified product and the non-vitrified product, which displayed a different color after microwave treatment. If the contaminated soil after the microwave process was to be recycled, the vitrification of soil would not typically be a good choice.

Figure 3 shows the effect of the different diametric iron wires as additives on the stabilization efficiency of copper. In the situation where the samples contained three iron wires, the incremental increase of diameter of iron wire showed no improvement on the stabilization efficiency of copper in soils. When the iron wire with 0.28mm diameter was used, the stabilization efficiency showed a gentle digressive trend with each increment of iron wire number. The top stabilization efficiency was 69.6% with three iron wires. As for the iron wire with 0.45mm diameter, the stabilization efficiency did not present an apparent corollary trend with the increment of iron wire number. Therefore, the increase of iron wire number did not accelerate the stabilization efficiency of copper under the

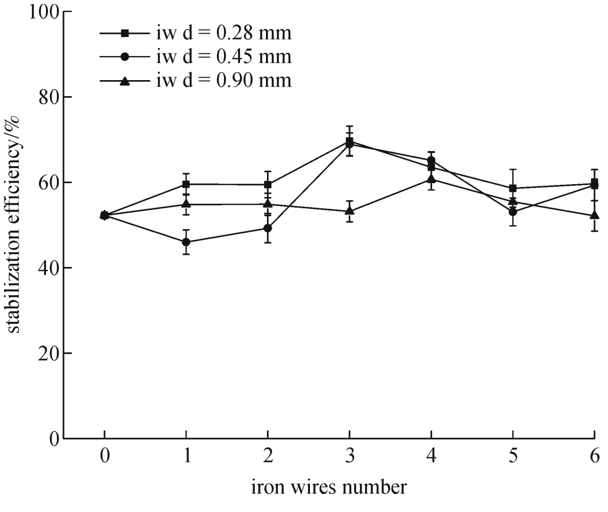

Fig. 3 Effect of iron wire diameter on the stabilization efficiency of copper (microwave power: 700 W; reaction time: 20 min)

experimental conditions. As a whole, the three iron wires with 0.28mm diameter had a greater effect among all experimental conditions.

As seen in Table 2, the results showed a complicated relationship of diameter (ID), numbers of iron wires (IN), and highest temperatures during the microwave process. For example, in the experimental condition with three 0.45mm diameter iron wires, the stabilization efficiency and the highest temperature were 68.9% and 240.5°C respectively, but the values were 53.2% and 1083.6°C, respectively, when three 0.90 mm diameter iron wires were used. The high temperature resulted from a hot spot, which reached more than 1000°C. Moreover, the hot spot appeared to occur accidentally in the experiments. Therefore, the possible reason for the temperature effect shown in Table 2 might have been attributed to the formation of hot spots resulted from iron wires.

Table 2 Relationship of the different diameter (ID), numbers of iron wires (IN) and the highest temperatures during the microwave process (microwave power: 700W; reaction time: 20 min)

IN	ID = 0.28 mm	ID = 0.45 mm	ID = 0.90 mm
1	242.2	899.0	271.5
2	240.0	288.7	413.4
3	346.7	240.5	1083.6
4	483.6	815.7	493.6
5	320.0	899.0	538.8
6	414.3	252.0	235.1

As described in the above experiments, the use of more than seven iron wires would cause the vitrification of contaminated soils. A small quantity of iron wires could limit the vitrification of soil in the microwave treatment. Therefore, three iron wires were used as the additive in the following experiments to avoid the vitrification of soil.

3.3 Effect of microwave power on stabilization efficiency of copper

Various microwave power levels were set to stabilize copper in contaminated soil. Three iron wires were used as additives and had a reaction time set for 20 min in the experiment. As shown in Fig. 4, the result showed that the stabilization efficiency increased gradually with the increase of microwave power. The stabilization efficiency at low power was less than 60%, and the peak temperature was less than 200°C. When high power was set, the stabilization efficiency increased to about 70%. However, the higher power associated with the higher temperature, such as when the power was 770W with a peak temperature of 1022.4°C, at which hot spots occurred. Therefore, the 560W power had the preferred stabilization efficiency with 66.1%, and a peak temperature of a moderate 752.2°C. Thus, the experimental condition using 700W microwave power and had a 20 min reaction time was a reliable choice when three iron wires were used as the additive. As shown in Fig. 5, the temperature increased gradually with the increase of time in the various microwave power levels. In low power, such as 420W and 490W, the temperature increased slowly. However, the temperature increased quickly with 770W, and reached more than 1000°C. Therefore, a high power level may form hot spots, and thermal run away could occur.

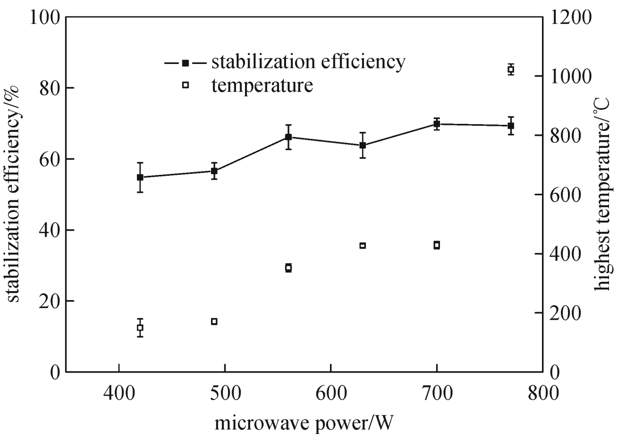

Fig. 4 Effect of microwave power on the stabilization efficiency (reaction time: 20 min; iron wire number: 3)

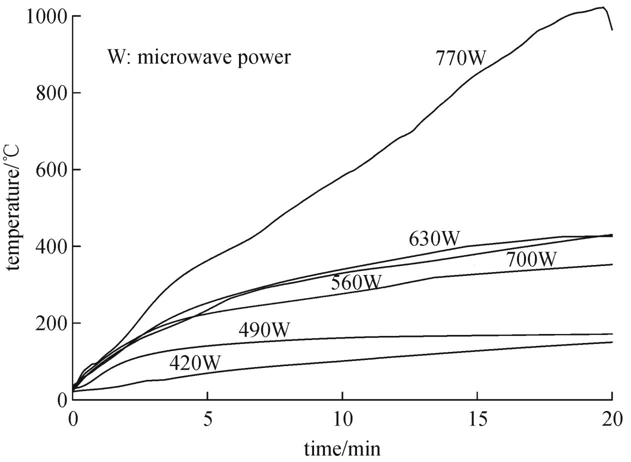

Fig. 5 Function of reaction time and temperature in the different microwave power (reaction time: 20 min; iron wire number: 3)

3.4 Effect of microwave processing time on stabilization efficiency of copper

Figure 6 shows the effect of the microwave processing time on the stabilization efficiency of copper. The stabilization efficiency of copper was found to increase with the increase of radiation time under the conditions of a 700W microwave power and three iron wires as an

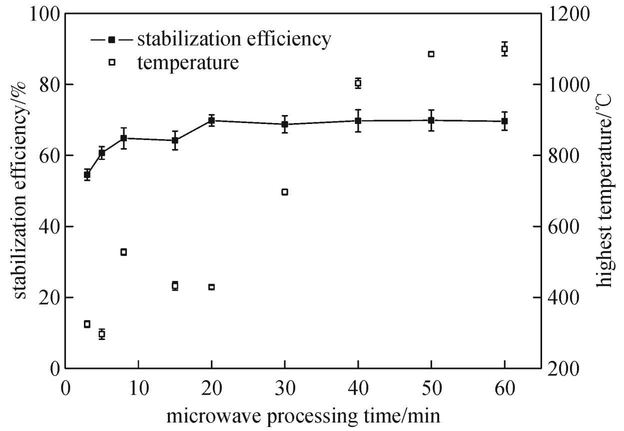

Fig. 6 Function of reaction time and stabilization efficiency (microwave power: 700W; iron wire number: 3)

additive. From the period of 3 to 20 min, the stabilization efficiency increased rapidly and reached its maximum at 20 min. From the period of 20 to 40 min, the stabilization efficiency first decreased very slightly and then eventually flattened out. The stabilization efficiency was steady from 40 min to 60 min. During the whole process period, the corresponding highest temperature did not show a regular trend. As a whole, 20 min was the appropriate reaction time at the experimental condition, reaching the considerable stabilization efficiency of almost 70%. The stabilization efficiency did not present the proportional relationship with the peak temperatures.

3.5 Effect of the reaction atmosphere on the stabilization efficiency of copper

The test was conducted on the effect that the reaction atmosphere, i.e., air or nitrogen, has on the stabilization efficiency. The experiments occurred at 700W microwave power, 20 min reaction time, and three iron wires as the additive. The stabilization efficiency with 50 $mL \cdot min^{-1}$ nitrogen flow was slightly better than that of 100 $mL \cdot min^{-1}$ nitrogen flow and air. There was no noticeable difference of stabilization efficiency when 100 $mL \cdot min^{-1}$ nitrogen and air were used as the reaction atmosphere. Considering the reuse of soil after the microwave process, a nitrogen atmosphere was considered to be better than air because organic substances in soil can avoid the overexposure of oxidation in the nitrogen atmosphere, so that soil fertility can be maintained partially.

3.6 Speciation analysis of copper in contaminated soil after the microwave process

Among various sequential extraction techniques, the Tessier sequential extraction method [24] was widely used for speciation analysis of heavy metals in soils, sediments, and sewage sludge due to its enhanced reproducibility, precision, and comparable performance. In the Tessier sequential extraction method, the metal elements were divided into exchangeables — bounding to carbonates, bounding to iron and manganese oxides, and bounding to organic matter and residual fractions. In this paper, a sequential extraction scheme according to Tessier's guidelines was applied to analyze the species distribution of copper in contaminated soil before and after microwave radiation. The results are shown in Fig. 7.

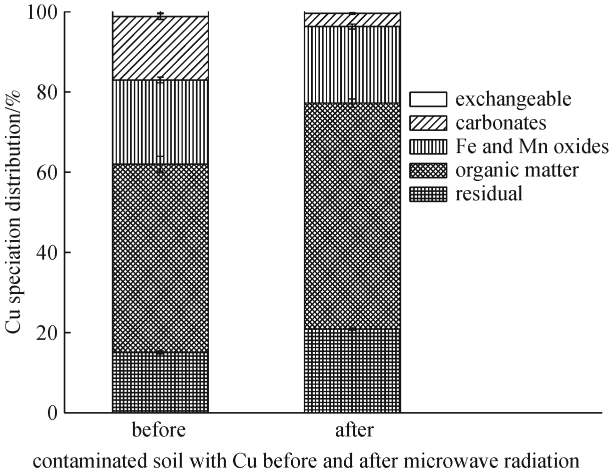

Fig. 7 Speciation analysis of copper in contaminated soil before and after microwave process

It was found that before microwave radiation, Copper in contaminated soil existed mainly in four species, namely carbonates, iron and manganese oxides, organic matter, and residual fractions, with 15.04%, 21.01%, 46.9% and 15.09% of total copper content, respectively. After microwave radiation treatment, the copper fractions of organic and residual states increased to 56.38% and 20.88% of total copper contents, respectively. The fraction of exchangeables and carbonates decreased accordingly, and the fraction of iron and manganese oxides decreased very slightly. Some copper species in contaminated soil were believed to have transformed from exchangeables and carbonates into organic matter and residual fraction after the microwave process. However, the fraction of iron and manganese oxides did not transform distinctly. Since the microwave process accelerated the stabilization of copper in Cu-contaminated soil, it was reasonable for copper species to transform into more stable states, such as organic matter and residual fractions.

Compared with other reports, this study achieved a moderate (about 70%) Cu stabilization efficiency though the microwave radiation method. According to previous reports, some stabilization or immobilization agents could offer good stabilization efficiencies for heavy metals in soil or sewage sludge. As an example of phosphate, $CaHPO_4$ and $Ca(H_2PO_4)_2$ could achieve more than 87% and 97% stabilization efficiency for Cu in soil, respectively [11].

However, the disadvantage is that it could add other chemicals in soils or sewage sludge, which may change the structure and property of soil. Microwave radiation, as a new technology for heavy metal stabilization in soil or sewage sludge, could offer an efficient and environmentally safe method for the stabilization of heavy metals.

4 Conclusions

The microwave process could accelerate the stabilization of copper in artificially Cu-contaminated soil. Iron wires used as an additive can enhance the stabilization of copper in the microwave process. Three iron wires as the additive was suitable for the stabilization of copper and would not generate the vitrified product, which was useful for the reuse of soil after the microwave process. The stabilization efficiency of copper was affected by several factors, including microwave power, reaction time, and the reaction atmosphere. The reaction atmosphere did not noticeably affect the stabilization efficiency. However, nitrogen atmosphere was proposed in view of the reuse of soil after the microwave process. Based on the speciation analysis of heavy metals, copper in contaminated soil was found to transform into a more stable species after the microwave radiation treatment. Moreover, Hot spots were occasional and difficult to control, which would lead to excessively high temperatures. The influence factors required further research on Hot spots in future studies, so that the microwave treatment technology can be controlled more effectively and be more practical.

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