Available online www.ejaet.com

European Journal of Advances in Engineering and Technology, 2022, 9(12):46-50

Research Article ISSN: 2394 - 658X

Study of the Degradation Efficiency of Glyphosate in Soils Using Microwave Heating Treatment

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ABSTRACT

Thermal treatment has long played a significant role in ex-situ soil remediation. Although it has a significant effect on eliminating semi-volatile and volatile organic compounds and is highly applicable to partial remediation of severely-contaminated soils, there are still limitations to such technology. On the other hand, not only can microwave heating treatment conserve time and energy, but it is also eco-friendly and can overcome difficulties encountered when applying traditional heating methods. Hence, microwave heating treatment will become a valuable technology for soil remediation in the future. Based on this observation, this study first applied microwave heating treatment to Taiwanese soil, a Taikang (Tk) series soil, and we observed factors that caused the temperature of the soil to rise. Then, we prepared a glyphosate-contaminated Tk series soil to simulate the degradation of high-concentration glyphosate in the soil.

The soil reached 1000°C in 5 min after being heated, indicating that microwave heating treatment largely outperformed traditional heating methods. Moreover, the results show that the rate of the rise in temperature is related to the amount of crystalline iron and quartz contained in the soil because the Tk series soil contains more than 15 g of crystalline iron oxide per kilogram. In terms of the relationship between heating time and the degradation of glyphosate, this study found that the degradation rate of glyphosate in the Tk series soil reached up to 99% after being heated with microwaves for 35 min. This outcome suggests that microwave heating treatment is an effective and efficient measure to degrade glyphosate in the soil. Microwave heating treatment has been widely adopted for the remediation of soil and underground water treatment sites. These findings can serve as references for the government in terms of soil restoration in the future.

Key words: thermal treatment, microwave heating, glyphosate, alluvial soil

1. INTRODUCTION

Microwaves are a part of the electromagnetic spectrum with frequencies ranging from 300 MHz to 300 GHz, lying between infrared and radio frequencies. Microwave technologies were developed rapidly during and after the Second World War for radar and communication uses [1,2]. These days, microwaves are extensively used for wireless communications, such as long term evolution; for major wireless local area network standard (Wi-Fi); space craft communication and radar applications like global positioning system; and air traffic control [3,4]. In addition to the radar and communication uses, microwaves are also widely used for heating. Foods are rapidly and conveniently heated by a microwave oven at home, and a variety of materials are heated at industries and laboratories using microwaves.

Electromagnetic waves deliver energy as radiation without being dissipated through heat transfer medium [5]. A representative example is the kitchen microwave oven, which can heat food products much faster than thermal heating. Microwave heating has been considered as a candidate for an energy-efficient graphitization method. Several reports have described the heating of carbon materials using microwaves, for example, to regenerate activated carbon, weld carbon nanotube/polymer composites, and exfoliate graphite [6,7]. Full graphitization by microwave heating, however, has yet to be achieved. In addition, the first chemists or alchemists as they may be called, transformed one body into another by means of, principally, fire. Fortunately, fire is now rarely used but it was not until Robert Wilhelm Eberhard Bunsen (1811-1899, discoverer of caesium in 1860 and rubidium in 1861) invented the burner that the energy from this heat source could be applied to the reaction vessel in a focused manner. The Bunsen burner was later superseded by the heating mantle, oil bath or hot plate. Recently, a new technique has come to the forefront of chemical research, microwave dielectric heating. In a similar way to the introduction of the heating mantle, this technology will no doubt require a change in the chemist's mindset. In 1986, Gedye and Giguere reported [8] for the first time that the organic reactions could be conducted very rapidly under microwave irradiation [8,9]. Since then, microwave has been widely used in synthetic chemistry to reduce reaction time and increase product yield [10,11]. Particularly over the past few years there has been a dramatic uptake in the use of microwaves as an energy source to promote synthetic transformations. The production of dedicated instrumentation by the leading manufacturers has propelled what was 20 years ago a fascinating idea into a day-to-day device for synthetic chemists. Microwave assisted organic synthesis (MAOS) is clearly a method by which a chemist can achieve target in a fraction of the time as compared to traditional conductive heating methods [12,13]. Reactions times in the best cases have been reduced from days or hours to minutes.

Based on the research findings mentioned above, this study concocted a glyphosate-contaminated soil, and the degradation of glyphosate in the soil after applying microwave heating treatment was observed.

2. MATERIALS AND METHODS

2.1 Sources of test soils

This study selects Taiwanese soil- Taikang (Tk) series soil as the sampling soil sample. Tk series soil evolved from the sedimentary material from the recent time is wind-eroded sand shale deposit of alluvial soil. Tk series soil was collected and dried at room temperature for two days. It was then ground using glass bottles after impurities were removed. After running through 2 mm sieves, the ground soil was stored in boxes, pending an analysis on its basic properties.

2.2 X-ray Diffraction Analysis (XRD Analysis) of Tk series soil

The X-ray Diffraction Analysis utilizes the X-ray Diffractometer coded with Rigaku RINT 200 to conduct the analysis. The CuK_{α} is used as a photo source to separately analyze the crystalline forms of Tk series soil after modifications in order to explore spacing of layers for these materials. The wavelength of the X-ray produced is 1.5418 $\mathring{A}$ and 10 mA for testing operational current, 20 kV fr voltage, 5 deg/min for a scanning rate with a scanning angle of $2\theta=2\sim40^{o}$.

2.3 Field emission scanning electron microscope (FE-SEM) analysis of Tk series soil

With a scanning electron microscope (SEM), this study observes the size of Tk series soil and its distribution. The model in use is JEOL-6330, and its emitting energy comes from the field emission filament with high space and energy resolution.

2.4 Preparing glyphosate-contaminated soil

Place 10 g of the Tk series soil in a centrifuge bottle and add 25 mL of 3.1% glyphosate solution to the bottle. Shake the bottle for 30 minutes before centrifuging it at 3000 rpm for 10 min. Remove the supernatant and add another 25 mL of 1M NaOH to the bottle before shaking it for 30 min. Centrifuge the solution at 3000 rpm again and remove the supernatant. After drying the centrifuged Tk series soil by freezing it and leaving it for 2 d, soil contaminated by high-concentration glyphosate (10000 mg/kg) can be obtained.

2.5 Applying microwave heating treatment to glyphosate-contaminated soil

Put 10 g of glyphosate-contaminated Tk series soil into each of five 50 mL beakers and heat with microwaves for 0 min, 5 min, 15 min, 25 min, and 35 min, respectively. One sample was not microwaved so as to serve as a control group. The heated soil was then put into centrifuge bottles and mixed with 25 mL of 1 M NaOH each. After shaking the mixture for 30 min, we centrifuged it at 3000 rpm for 10 min and removed the supernatant. Finally, we analyzed the degradation rate of glyphosate in the centrifuged Tk series soil.

3. RESULTS AND DISCUSSION

3.1 An analysis of the basic properties of Tk series soil

Table 1 presents results from the analysis of the basic properties of Tk series soil, including its texture, organic matter content, and pH value. The particle size of the Tk series soil falls between that of silt and clay; its texture is categorized as silty clay. Although it also feels like silty loam, it is much stickier but not as sticky as clay. Table 1 also indicates that the Tk series soil has a high content of organic matter. The stronger the palletization on the surface, the easier it is to form soil. In other words, high organic matter content makes it easier to form clay-organic compounds, which in turn facilitates soil cementation [2,7]. Usually, structures of soils are destroyed during microwave digestion because microwaves cause the temperature in the soil surface to rise. However, under an environment that favors cementation, the Tk series soil can maintain its structure even after being microwaved. Therefore, the structure of the Tk series soil can remain stable even when glyphosate is removed during our experiments.

Table -1 Basic Properties of Tk Series Soil

Size distribution of soil particles			Texture	Soil organic matter (SOM)	pH
Sand	Silt	Clay			
--------------------%--------------------				---------g/kg---------	
7.2	47.5	45.3	SiC	20.1	8.66

Note: SiC refers to silty clay.

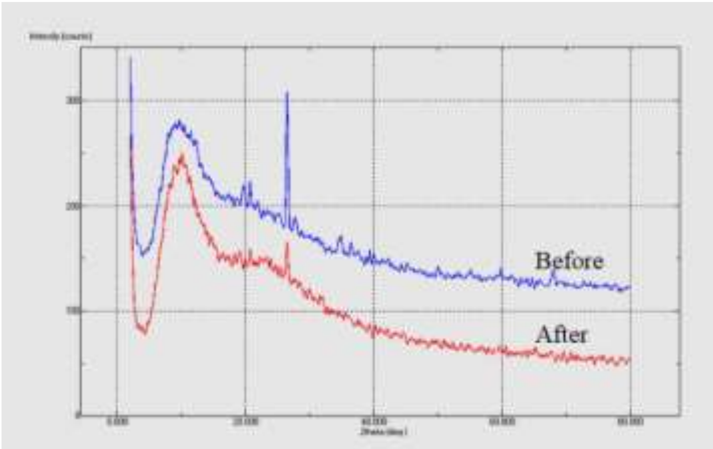
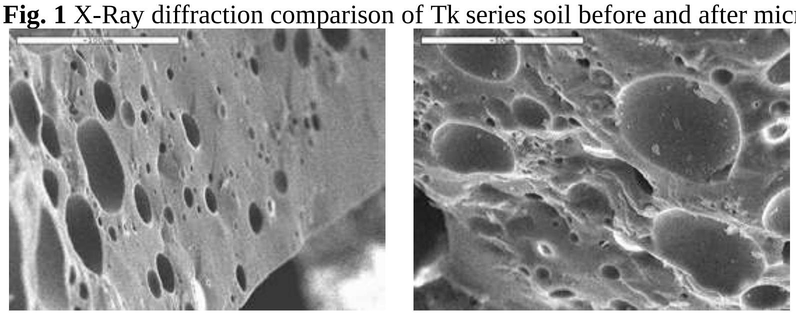
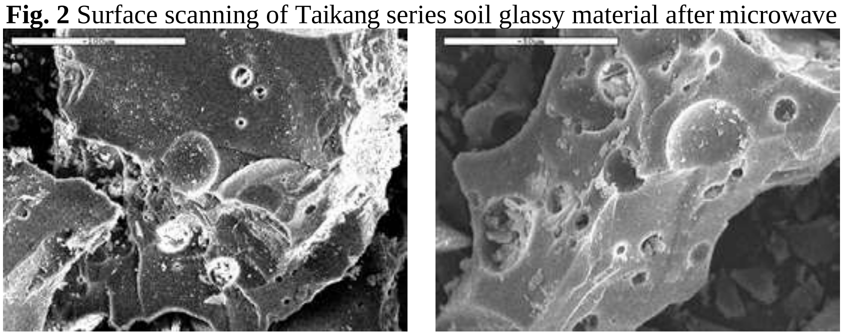


Fig. 1 X-Ray diffraction comparison of Tk series soil before and after microwave



X500 X1000

Fig. 2 Surface scanning of Taikang series soil glassy material after microwave



X500 X1000

Fig. 3 Surface scanning of grinding Taikang series soil glassy material

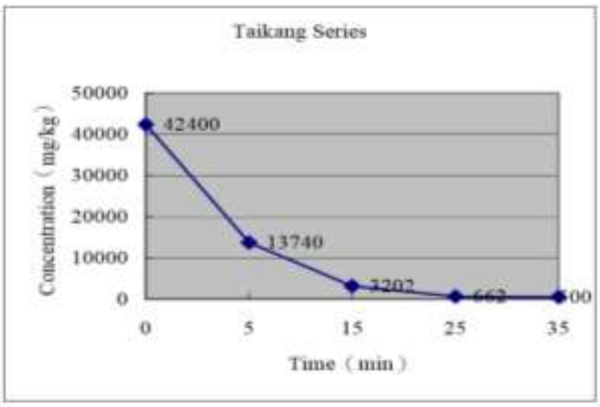


Fig. 4 The relationship between microwave heating time and degradation rate of glyphosate in Tk series soil

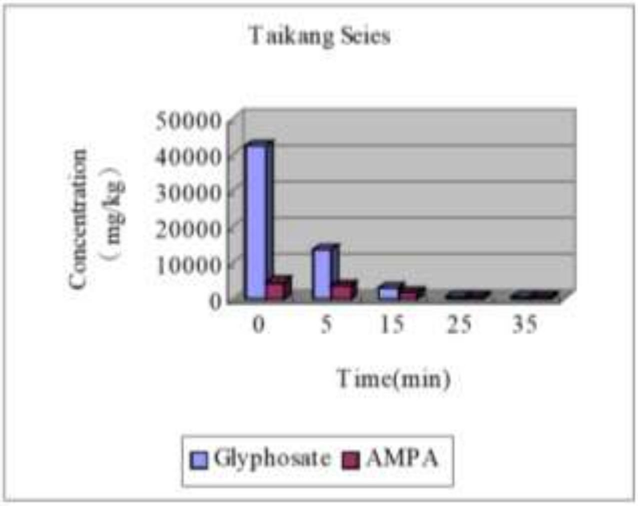


Fig. 5 The relationship among microwave heating time, concentration of remaining glyphosate, and concentration of AMPA formed

3.2 Results of Tk series soil XRD analysis

Figure 1 shows the results of an XRD analysis on vitrified sintered materials formed before and after the soil was heated with microwaves. Kingman and Rowson [14] assumed that the higher the quartz content (2θ=26.2) in the soil, the more difficult it will be to heat the soil with microwaves because parent salt rocks such as quartz, calcite, and feldspar are difficult to heat with microwaves. Figure 1 indicates that the diffraction intensity of the Tk series soil remains low (with a maximum of approximately 300) before and even after being heated with microwaves. This result suggests that the quartz content in the Tk series soil was low, so microwaves could efficiently raise the temperature of the soil. Moreover, since XDR can also be used to perform a semi-quantitative analysis, the relative diffraction value obtained from the experiment can also reflect the mineral content in the soil. As shown in the figure, the diffraction intensity of the vitrified materials decreases after the soil is microwaved, meaning that the temperature was high enough to destroy the crystal lattice of minerals in the soil. Also, minerals were not even able to crystallize and form vitrified materials due to the decline in temperature after microwave heating ended [15].

3.3 FE-SEM analysis of Tk series soil

Figures 2 and 3 show the SEM images of vitrified materials in the microwaved Tk series soil. A large number of pores, which were the result of a drastic rise in temperature, can be observed on the cross-section of the vitrified materials. These pores provide sufficient space for the degradation of glyphosate [7]. On the other hand, whether the soil was ground or not does not seem to affect the result [13].

3.4 Effects of microwave digestion on the degradation rate of glyphosate in Tk series soil

Figure 4 demonstrates the relationship between the microwave heating time and the degradation rate of glyphosate in the Tk series soil. After being microwaved for 35 min, the concentration of the remaining glyphosate in the Tk series soil dropped to 500 mg/kg and the degradation rate was 98.8% ((42400-500)/42400=0.988). This result suggests that microwave heating serves as an effective measure for removing glyphosate. Figure 5 shows the relationship among the microwave heating time, the concentration of the remaining glyphosate in the Tk series soil, and the concentration of aminomethyl phosphonic acid (AMPA), which is the metabolite of the glyphosate disintegration. As soon as glyphosate was added to the Tk series soil, 5-10% AMPA was formed, indicating that the degradation rate of glyphosate in the Tk series soil was high. Besides, Figure 5 indicates that the concentrations of AMPA and glyphosate decline proportionally, suggesting that glyphosate first disintegrated into AMPA and then, degraded to H_2O and CO_2 [12,16].

4. CONCLUSION

In this research, we first heat the Taiwanese soil – Taikang series soil (Tk series soil) – with a microwave to study the factors affecting the temperature rise of the Tk series soil. Next, we concocted glyphosate-contaminated Tk series soil and simulated the degradation of high-concentration glyphosate in the soil.

In terms of the basic properties of the Tk series soil, the analytic results indicate that it is a kind of soil with high organic matter. The stronger the palletization on its surface, the easier to form a soil structure; i.e., the higher the organic content in the soil, the easier to produce clay-organic compounds, which facilitates cementation. On the other hand, the SEM analysis shows that a significant number of pores, which were formed due to a drastic temperature rise, appeared on the cross-sections of the vitrified materials in the Tk series soil. These pores provide enough space for glyphosate degradation.

This study proves that microwave heating treatment serves as an efficient measure for eliminating glyphosate in the Tk series soil. We heated the glyphosate-contaminated Tk series soil (42400 mg/kg) with microwaves during the experiment; and the concentration of the remaining glyphosate decreased to 500 mg/kg after being heated with microwaves for 35 min, while the degradation rate reached 98.8%. Lastly, in terms of the relationship among the microwave heating time, the concentration of the remaining glyphosate, and the concentration of AMPA formed after glyphosate disintegrated, we found that the concentrations of AMPA and glyphosate decreased proportionally, which suggests that glyphosate first disintegrated into AMPA after being microwaved and then, degraded into H_2O and CO_2. Microwave heating treatment has now been adopted for various environmental remediation schemes. It is especially effective in terms of the remediation and restoration of soil and underground water treatment sites.

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