

## Research Article

# Degradation of Tetracycline by Birnessite under Microwave Irradiation

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The efficiency and factors affecting tetracycline (TC) degradation by birnessite under microwave irradiation (MI) were investigated under different initial TC concentrations, solution pH, MI time, and MI power. The crystal structure, degradation efficiency, and reaction mechanism were investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and ultraviolet-visible spectroscopy (UV-Vis). The results showed that birnessite was an excellent microwave catalyst. The maximum TC removal efficiency by birnessite was 99% under MI at 400 W for 30 min in strongly acidic media. Under MI, the surface activity of birnessite increased, resulting in the ability to accelerate TC removal in high temperature.

## 1. Introduction

In 1999, Daughton presented the idea of pharmaceuticals and personal care products (pharmaceuticals and personal care products, PPCPs) [1]. They are considered as the emerging environmental contaminants leading to contaminations in surface water, groundwater, and wastewater [2]. Antibiotic tetracycline (TC, Figure 1) is widely used in livestock for growth promotion and treatment of diseases [3]. Since the late 1990s, the use of TC on poultry farming reached up to  $3 \times 10^6$  Kg annually [4]. As TC was not able to be completely digested and absorbed by most organisms, more than 85% of TC was excreted in its original drug form [5]. Livestock, after ingestion of TC, will gradually accumulate TC. The use of animal wastes as well as biosolids from wastewater treatment facilities as fertilizers for field application would result in elevated TC concentrations in a variety of ecosystems [6].

Microwave technology was originated in the 1930s, but it was not widely applied to the environmental protection fields until the late 1990s. Microwave catalytic technology can be highly efficient when used in degrading macromolecular organic pollutants [7]. In essence, macromolecular organic pollutants are put into the microwave field; through the perturbation of popular molecules, the bonding of macromolecular organic pollutants will be broken, and then the purpose of the degradation of pollutants is reached [8].

Microwave irradiation (MI) has a fast response, high efficiency and selectivity, fewer side effects, and energy saving features; thus it has been widely used in macromolecular degradation prospects [9].  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$  were the most suitable microwave catalysts known as high-loss materials for microwave which presents a high activity by MI [10, 11].

Manganese oxides could act as an adsorbent, oxidant, and microwave catalyst; thus, they could be used in environmental remediation. Manganese oxides are mainly constituted by  $[\text{MnO}_6]$  octahedra with  $(1 \times n)$  pyrolusite pore structure in ramsdellite family, barium and manganese ore  $(2 \times n)$  pore structure in psilomelane family, barium, calcium, and manganese family  $(3 \times n)$  pore structure, and  $(1 \times \infty)$  layered structure manganese oxide minerals [12, 13]. Birnessite (Figure 2) has a layered structure and it is a typical  $\delta$ -type manganese dioxide material. The interlayer is made of a layer of water molecules containing different types of cations and  $[\text{MnO}_6]$  octahedral layers stacked together in the same direction [14–16]. Birnessite is one of the most widely distributed manganese oxides, and it is also an excellent material for microwave absorption [17]. This absorbing material has a long life, is nontoxic and efficient, and has no secondary pollution treatment. Microwave originated from the high energy sources could produce synergistic effect with a highly active center when exposed to air. The active center

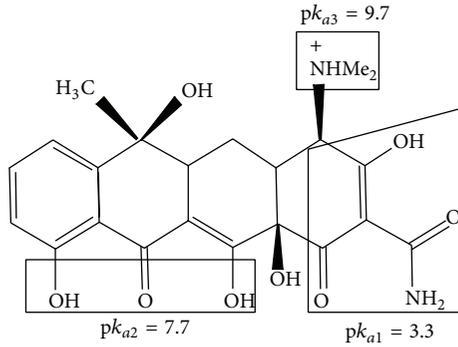


FIGURE 1: Molecular model of TC.

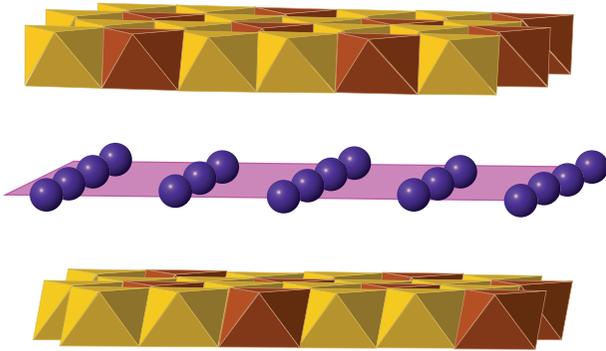


FIGURE 2: Layered structure of birnessite.

of birnessite will be oxidized under MI to produce an active substance, by which organic pollutants could be degraded into smaller, nontoxic molecules [18].

In this study, the degradation of TC by birnessite under MI was systematically investigated in order to explore the catalytic effects and optimize reaction conditions.

## 2. Experiments

**2.1. Materials.** NaOH,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{KMnO}_4$  were used for the preparation of birnessite. They were purchased from Beijing Chemical Works. TC was obtained from Calbiochem (Darmstadt, Germany). They were used as received without further purifications.

Aqueous  $\text{MnCl}_2$  solution (40 mL, 0.50 mol/L) was slowly added to NaOH solution (50 mL, 5.0 mol/L) under vigorous stir for 5 minutes, allowing formation of  $\text{Mn}(\text{OH})_2$ .  $\text{KMnO}_4$  solution (0.20 mol/L) was then gradually added dropwise, and stir was continued for 30 minutes to complete the reaction. The product was centrifuged for 3 min at 10000 rpm, washed 10 times with distilled water, and dried at  $40^\circ\text{C}$  for 48 h.

**2.2. TC Degradation under MI.** TC removal efficiency ( $f$ ) was determined by the following equation [19]:

$$f = \frac{C_o - C_e}{C_o} \times 100\%, \quad (1)$$

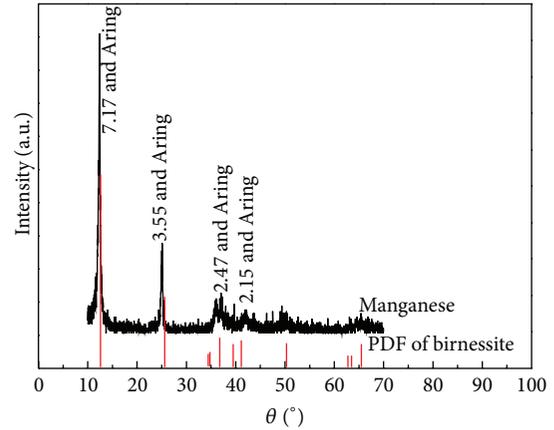


FIGURE 3: The XRD of synthesized birnessite.

where  $C_o$  and  $C_e$  are the initial and equilibrium TC concentrations. The amount of TC degraded ( $q_e$ ) was calculated by the following equation:

$$q_e = \frac{C_o - C_e}{M} \cdot V, \quad (2)$$

where  $V$  is the solution volume and  $M$  is the mass of the solid.

**2.3. TC Concentration Measurement.** Calibration was made with the following concentrations: 1, 2, 5, 10, 15, and 20 mg/L under pH 3, 7, and 11. The UV absorbance was determined at the wavelength of 360 nm [20]. The coefficients of linear regression were all greater than 0.999.

## 3. Results and Discussion Mechanism

**3.1. Birnessite Characterization.** The synthesized birnessite matched with the PDF file of birnessite well as revealed by XRD diffraction analyses (Figure 3).

**3.2. Effect of Microwave Irradiation Time on Removal Efficiency of TC Solution.** With 0.2 g of birnessite and 50 mL of 50 mg/L TC solution, a significant increase in  $f$  was found in the presence of MI (Figure 4). Also noticed was a fast increase in TC degradation rate within the first 5 to 10 min, suggesting a very significant role of MI. Meanwhile, equilibrium was reached at 30 min with an  $f$  of 43%.

**3.3. Influence of Initial TC Solution Concentration on Removal Efficiency.** With 0.2 g of birnessite and 50 mL of TC solution, the TC removal efficiency by birnessite under MI decreased as the TC solution concentrations increased (Figure 5). On the other hand, with an increase in initial TC concentration, the amount of TC degraded increases gradually to 6.5 mg/g, when the initial TC concentration reached 70 mg/L. Further increase in initial TC concentration resulted in no further change in amount of degradation.

**3.4. Influence of MI Time and Power on TC Degradation.** With 0.2 g of birnessite and 50 mL of 50 mg/L TC solution,

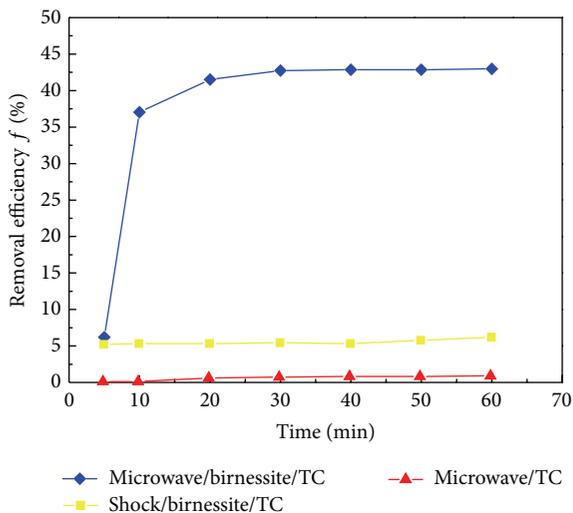


FIGURE 4: TC removal efficiency of different processes change over time.

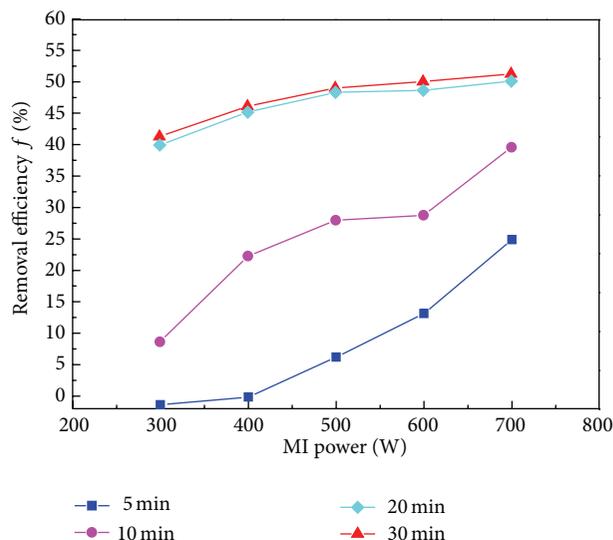


FIGURE 6: Removal efficiency varies with the microwave power.

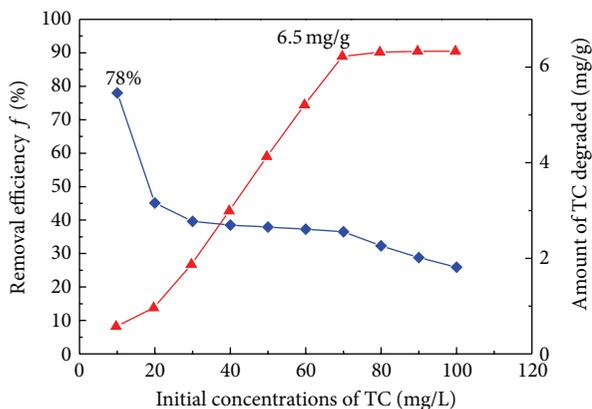


FIGURE 5: Changes in removal efficiency and the amount of degradation with different initial concentrations of TC solution.

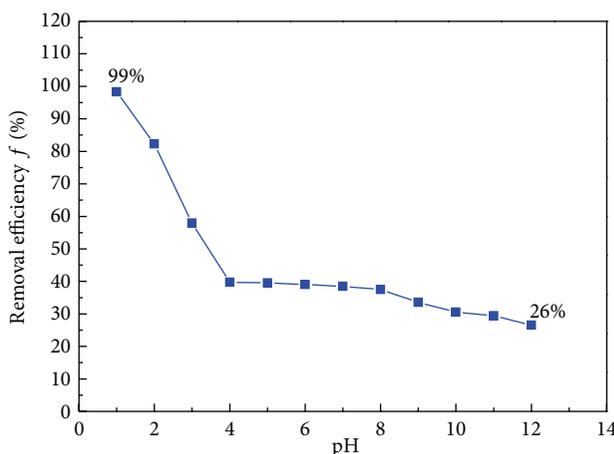


FIGURE 7: Influence of solution pH on TC removal efficiency.

an increase in MI time from 5 to 20 min significantly increased  $f$  when the MI power was 300 W (Figure 6). On the other hand at 20 or 30 min of MI, the change in  $f$  was from 40 to 50% as the MI power increased from 300 to 700 W. XRD results showed no change in material phases under MI up to 700 W (data not shown); see Supporting Figure S1, available online at <http://dx.doi.org/10.1155/2014/409086>.

**3.5. Effect of Solution pH on TC Removal Efficiency.** With 0.2 g of birnessite and 50 mL of 50 mg/L TC solution, TC removal efficiency was up to 99% under strong acidic conditions after MI for 30 min (Figure 7). Removal efficiency of about 60% was achieved under neutral pH conditions. The efficiency decreased to 29% under alkaline conditions.

Different functional groups of TC will be ionized under different pH conditions, resulting in different numbers of electric charges. When pH is less than 3.3, the main form is a monovalent cation. When the pH is between 3.3 and 7.7, a neutral molecule was dominating. As the pH is greater than

7.7, a monovalent anion prevailed. A dianion is formed when the pH is greater than 9.3 [21–23]. Figure 7 showed that when TC was in its cationic form, degradation of TC was enhanced. On the contrary, when TC was in monoanionic or dianionic form, its degradation efficiency was greatly reduced. The XRD results showed no change in solid phases under different pH conditions, ruling out that the change in the TC degradation efficiency was due to different types of  $MnO_2$  (data not shown); see Figure S2.

**3.6. Mechanism of Action of the Reaction System.** The enhanced TC degradation by birnessite resulted directly from MI and the oxidability of birnessite [23]. MI could increase the surface reactivity of birnessite and create a high temperature environment, resulting in an accelerated TC removal. Mn(IV), Mn(III), and little Mn(II) were found on the surface of birnessite and a cyclic trend was found with

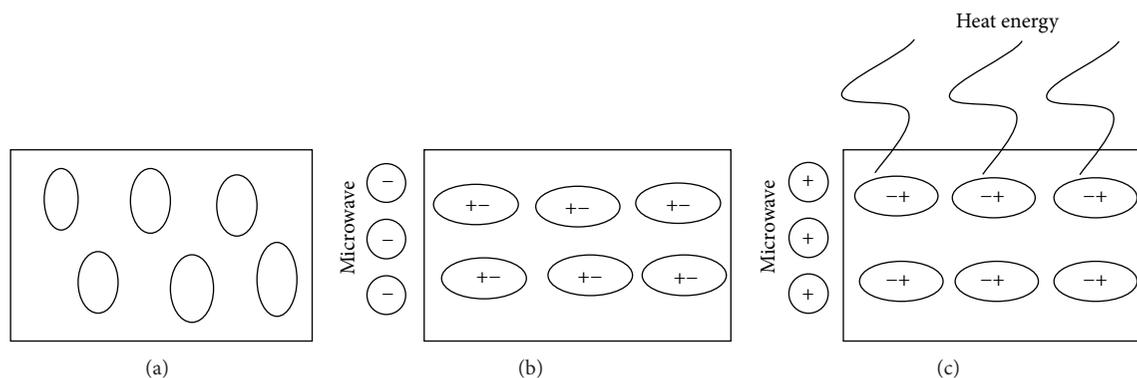


FIGURE 8: Schematic diagram of microwave heating. (a) Material distribution of molecules before microwave heating. (b) Distribution of materials during microwave heating. (c) Change in polarity under microwave field to generate heat.

the valence of Mn increased under MI and decreased after reaction with methylene blue [24]. The oxidation reaction of Mn(II) was slow under normal conditions, but dissolved Mn(II) could be quickly oxidized by  $O_2$  under MI [24]. Moreover, MI could provide a high temperature environment and accelerate the sustainable cyclic redox reaction processes until complete removal of MB [24].

Birnessite could greatly enhance reactivity through reduction in activation reaction, variation, and a high frequency alternation of electromagnetic field. It could also lead to changes in dipole moment directions in birnessite, which, in conjunction with hysteresis, would also cause the dielectric loss of the reaction system (Figure 8), so that part of the microwave energy could be converted into heat energy to result in a sharp rise in temperature of the system [25]. Studies have shown that the surface temperature of birnessite after 1 min microwave heating could reach thousands of degrees Celsius [26]. Thus, when the reaction system was exposed to air or oxygen, the surface activity of birnessite increased and the temperature could rise to approximately 1378 K [27], resulting in an accelerated degradation of TC.

#### 4. Conclusion

- (1) Birnessite is an excellent microwave catalytic oxidation material. TC removal efficiency of up to 99% could be achieved under MI power of 400 W for 30 min at a system of 0.2 g birnessite and 50 mL of 50 mg/L TC solution at pH = 1.
- (2) Comprehensive analysis showed that the mechanism of TC degradation by birnessite under MI was due to increased surface reactivity of birnessite and creation of a high temperature environment, resulting in an accelerated TC removal.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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