



# Mechanism and process of methylene blue degradation by manganese oxides under microwave irradiation



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## ABSTRACT

Numerous studies have been conducted on the removal of dyes from wastewater, although fewer were focused on the reactions under the influence of microwave irradiation (MI). In this paper, degradation of methylene blue (MB) in simulated wastewater by manganese oxides (MOs) under MI was investigated. A significant increase in MB removal efficiency by akhtenskite or birnessite was observed in the presence of MI. After 30 min MI, the MB removal by birnessite was 230 mg/g, in comparison to only 27 mg/g in the absence of MI. The kinetics of MB removal by MOs under MI followed the pseudo-first-order kinetic model well with rate constants of 0.005 and 0.04 min<sup>-1</sup> for akhtenskite and birnessite, respectively. In contrast, the rate constants were only 0.0006 and 0.0007 min<sup>-1</sup> for MB removal by akhtenskite and birnessite in the absence of MI. Results of XPS and LC–MS showed cyclic redox processes responsible for the step-wise degradation from MB to C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>OS, C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>OS, C<sub>12</sub>H<sub>8</sub>NO<sub>2</sub>S, C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>OS, and eventually to smaller molecules. As akhtenskite and birnessite had no electric dipole moment in their crystal structure, it was deduced that stronger MI effect on MB removal by birnessite could be attributed to the larger spin dipole moment of the central manganese ion in octahedra.

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## 1. Introduction

Recently, microwave irradiation (MI) to increase the efficiency of contaminant degradation is becoming increasingly important in wastewater treatment [1–3]. For example: a ClO<sub>2</sub>–CuO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalytic oxidation system could significantly enhance the removal of phenol under MI and the reaction fitted to the pseudo-first-order kinetic well [4]. NiFe<sub>2</sub>O<sub>4</sub> could also gain a promising application in treatment of various dyestuff wastewaters under MI [5]. The removal of phenol by CoFe<sub>2</sub>O<sub>4</sub> was significantly enhanced under MI with CoFe<sub>2</sub>O<sub>4</sub> acting as a microwave catalyst [6]. NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> are ferrites which have excellent microwave adsorption to be used in magnetic and electronic products [7]. However, most of the previous studies on microwave adsorbents were focused on ferrites for the applications in electronic and magnetic fields [8–11]. In addition, previous studies of microwave catalytic oxidation were centered on the removal efficiency and physico-chemical conditions to achieve higher efficiency [12]. Few involved in discussion

on the reaction mechanism and the effect of structure details on catalytic properties.

Microwave catalysts are good microwave adsorbents. Their catalytic properties depend not only on chemical constituents, but also on grain size, lattice distortion, ion occupation, and electron configuration. Therefore, investigating the reaction mechanism, reaction process, and relationship between structural properties and degradation efficiency may present a great opportunity for the best selection of new microwave catalysts and microwave catalytic oxidation in environmental fields.

Manganese oxides (MOs) are excellent microwave adsorbents, which may play a potential role in organic pollutants removal. MOs are mainly constituted by [MnO<sub>6</sub>] octahedra with tunnel or layered structure and are classified as pyrolusite–ramsdellite family with (1 × n) tunnel structure, hollandite–romanechite family with (2 × n) tunnel structure, todorokite family with (3 × n) tunnel structure, and birnessite family with (1 × ∞) layered structure [13,14]. MOs can produce “hotspot” under MI [15,16] and present an excellent oxidation capacity for the removal of organic macromolecules [17,18].

In this study, we reported a new approach that combines the use of MOs with MI for wastewater treatment using methylene blue (MB) as the example of contaminants. The focus of the

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study was on elucidating structure characterization and oxidation mechanism, characterizing reaction products, and establishing relationship between degradation efficiency and intrinsic structural properties of the MOs.

## 2. Materials and methods

### 2.1. Experimental materials

KMnO<sub>4</sub>, NaOH, MnCl<sub>2</sub>·4H<sub>2</sub>O, MB, and distilled water were purchased from Beijing Chemical Works. MB, also called 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride, is a heterocyclic aromatic chemical compound with a molecular formula of C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl and molar mass of 319.85 g/mol (284.35 g/mol in solution due to dissociation of Cl<sup>-</sup>). At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. It is soluble in water (4 g/100 mL) and ethanol (1.5 g/100 mL) and insoluble in ether [19,20]. It is a typical dye in wastewater that leads to pollution of environment. Akhtenskite was obtained from Beijing Kang Puhui Technology Co., Ltd. while birnessite was synthesized according to the method by Feng et al. [21].

### 2.2. Methods of analyses

The crystal structures of MOs were characterized by X-ray diffraction (XRD) analysis under the following conditions: CuKα-radiation at 40 kV and 100 mA, scanning speed at 8°/min, and 0.02°/step. The elemental compositions of MOs were determined by X-ray fluorescence spectrometry (XRF, Beijing North Early Microstructure Analysis and Test Center Co., Ltd.). The visible spectra of products from 500 to 700 nm were collected using an ultraviolet–visible spectroscopy (UV–vis, Beijing North Temple Instrument Technology Co., Ltd.) with an optical bandwidth of 2.0 nm, a response time of 0.2 s, medium scanning speed at an interval of 1 nm. The surface valence of MOs before and after MI was determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Co., Ltd.) under a CuKα-radiation, a power of 150 W, and a background pressure of  $6.5 \times 10^{-10}$  mbar. The molecular weight of the products was identified using HPLC–mass spectrometer (LC–MS, Thermo Scientific) and their molecular formulae were calculated using high resolution search (Thermo Scientific).

### 2.3. Microwave irradiation

A stock MB solution (500 mg/L) in distilled water was prepared and allowed to stand overnight. In batch experiments, 0.1 g of solid and 50 mL of MB stock solution were added into a glass beaker (100 mL). While, in the research of identifying the reaction pathway, 50 mL of MB (100 mg/L) and 0.1 g of birnessite were mixed in a glass beaker. Then the mixture was placed into a microwave reactor under a microwave power of 400 W. After MI, the slurry was cooled and centrifuged for 5 min at 6000 rpm. At the end of the process, a 10 mL aliquot of the supernatant was transferred and filtered with syringe-type filter to a 50-mL colorimetric tube for UV–vis analyses. All experiments were run in duplicates.

## 3. Results and discussion

### 3.1. Characterization of MOs structure

Akhtenskite had a space group of P6<sub>3</sub>/mmc with  $a=2.8 \text{ \AA}$ ,  $b=2.8 \text{ \AA}$ ,  $c=4.45 \text{ \AA}$ ,  $Z=1$ . It shows a NiAs type structure with the [MnO<sub>6</sub>] octahedra in hexagonal close-packing [22]. The diffraction peaks of akhtenskite matched with those in the PDF card well. The

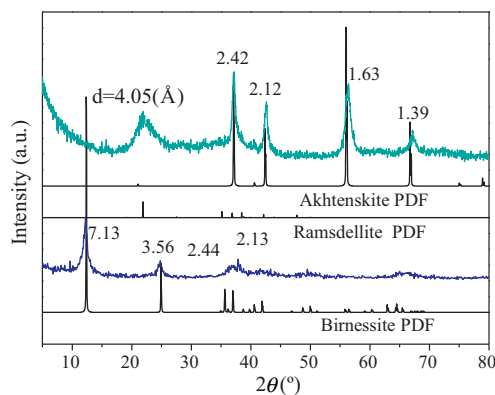


Fig. 1. XRD patterns of manganese oxides.

4.05 Å peak for akhtenskite should be very weak. Thus, the substantial higher peak at 4.05 Å was attributed to the (1 1 0) peak of ramsdellite [23]. Therefore, this MO was characterized as an akhtenskite with minor ramsdellite (Fig. 1). The birnessite-type MO, synthesized using the method of Feng et al. [21] had a space group of C2/m and unit cell parameters of  $a=5.175 \text{ \AA}$ ,  $b=2.849 \text{ \AA}$ ,  $c=7.338 \text{ \AA}$ ,  $Z=1$ . Natural birnessite has good adsorption and cation-exchange properties [24] with a fine laminated texture. The ideal structure of birnessite consisted of [Mn(III)O<sub>6</sub>] octahedra and [Mn(IV)O<sub>6</sub>] octahedra, with one [Mn(III)O<sub>6</sub>] octahedral chain inserted in two [Mn(IV)O<sub>6</sub>] octahedral chains, and the negative charge was balanced by the interlayer ions [25,26]. Besides, the actually structure of birnessite usually contains little Mn(II) as the residue after synthesis based on the mechanism of adsorption of Mn(II) [27].

The chemical formulae determined by XRF were (Na, Al, K)<sub>0.03</sub>Mn<sub>2</sub>O<sub>4</sub> and (Na, K, Al)<sub>0.49</sub>Mn<sub>2</sub>O<sub>4</sub>·0.62(H<sub>2</sub>O) for akhtenskite and birnessite, respectively. Due to the higher large-cation content, it is anticipated that birnessite had a much higher fraction of Mn(III) in the lattice than akhtenskite.

### 3.2. Efficiencies and kinetics

In the absence of MO, the removal efficiency of MB by MI was almost 0% (Fig. 2a). In the presence of MO and absence of MI, the MB removal efficiency was approximately 10% after 30 min of reaction. A higher removal efficiency was achieved using birnessite compared to akhtenskite. This could be attributed to the surface charge of birnessite. Because of the replacement of Mn(III) for Mn(IV), the surface of birnessite was more negatively charged than that of akhtenskite. Therefore, the positively charged MB could be more easily adsorbed on the surface of birnessite. Similarly, an enhanced adsorption of ciprofloxacin on birnessite was noticed when ciprofloxacin was in a cationic form [24].

The MB removal efficiency increased to approximately 40% (removal amount of 98 mg/g) and 98% (removal amount of 230 mg/g) by akhtenskite and birnessite after 30 min MI, respectively (Fig. 2a), compared to the removal efficiency of approximately 9.8 and 10.9% by akhtenskite and birnessite in the absence of MI. These corresponded to an increase by a factor of 4 and 9, respectively. Similarly, the amounts of MB removal by akhtenskite and birnessite after 30 min MI increased from 25 to 98 and from 27 to 230 mg/g, respectively. As the removal efficiency was approximately 0% by MI in the absence of MO, it demonstrated that the residual oxygen in air was nonreactive with MB under MI. The significant increase of MB removal by MOs under MI suggested that MOs acted as oxidants and both akhtenskite and birnessite had an excellent response to MI. This approach was also obviously better than the methods of physical adsorption (maximum of 27 mg/g) or photochemical catalytic oxidation (maximum of 172.4 mg/g) [28].

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