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Synthesis of birnessite with adjustable electron spin magnetic moments for the degradation of tetracycline under microwave induction

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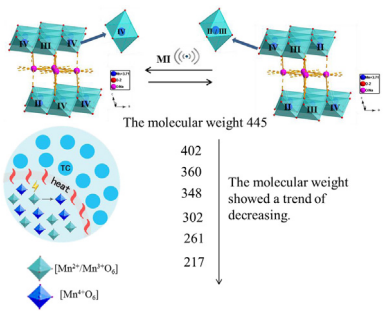
HIGHLIGHTS

- Birnessite, a manganese dioxide with varying Mn(II)/Mn(III)/Mn(IV) ratios were synthesized.
- The birnessite was used for tetracycline (TC) degradation under microwave induction.
- Higher Mn(II) and Mn(III) resulted in faster TC degradation due to better microwave response of Mn.
- LC–MS analyses revealed progressive removal of N, C, and H for the reaction intermediates.
- The catalyst could be regenerated under microwave induction.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese dioxides (MOs) are excellent microwave absorbing materials and have been used as substrates or catalysts for enhanced degradation of organic compounds. In this study, we extended our research on using birnessite (Birn), a type of MOs, for the degradation of tetracycline (TC) in aqueous solution under microwave induction (MI). The Birns were fabricated to achieve different ratios of Mn (II)/Mn(III)/Mn(IV) in the crystal structure. Their physical and chemical characteristics were determined by X-ray diffraction, field-emission environmental scanning electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray absorption fine structure spectra, and a microwave network analyzer. Their removal of TC under MI was evaluated under different physicochemical conditions. Lower solution pH, higher MI power, and higher Mn(II) and Mn(III) in the structure resulted in more TC removal. And the Birns are regenerable. LC–MS analyses confirmed the presence of degradation intermediates. The better performances of TC removal by Birns under MI was attributed to the high magnetic spin moment of Mn(II) and Mn(III) in the structure that has higher MI response.
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1. Introduction

Antibiotics are a large group of pharmaceutical compounds used in human and veterinary medicines. Among them tetracycline (TC) is the second mostly used in the world due to its high quality

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and low price [1]. As it is poorly absorbed by human and animals, the majority of administrated TC (about 80–90% of initial value or its metabolites) could be discharged into the environment [2]. As TCs are normally resistant to biodegradation [3], the residual antibiotics could stimulate selective genetic variations of microorganisms and lead to the emerging of antibiotic-resistant pathogens. Due to its low degradation efficiency in conventional wastewater treatment, different catalysts were tested to promote its catalytic degradation. TiO_2 could enhance TC degradation, but only the ultraviolet portion of the solar spectra could be absorbed by TiO_2 for such an enhancement [4]. Still, the removal efficiency of TC in the presence of P25 (TiO_2) under 60 min sunlight was about 39% [5]. Incorporating TiO_2 into MWCNT/TiO_2 nano-composite under UVC could achieve effective TC removal in 100 min [6].

In recent years, microwave induction (MI) technologies attracted great attention to increase the degradation efficiency of organic pollutants in water [7,8]. Compared with α-Bi_2O_3 alone, a poor photocatalyst, the removal efficiency of nitrophenol reached 98% under microwave catalytic oxidation [9]. In the presence of $MnFe_2O_4$-activated peroxymonosulfate, 97% of nitrophenol was degraded in 2 min [10]. For degrading organic pollutants of high concentrations under MI, the catalyst was the key factor to limit the removal efficiency of organic contaminants.

Birnessite (Birn) is a type of manganese oxides (MOs) and an excellent microwave absorbing material. Its removal efficiency of methylene blue (MB) doubled that of pyrolusite [7]. The frameworks of MOs were mostly in tunnel and layered structures with the [MnO_6] octahedra shared by common vertices or edges [11]. MOs also had an excellent ion exchange and molecular adsorption performance [12] and were widely used in the field of ion and molecular sieves, etc. For the past few years, separation and sensing technology were developed based on the ionic sieve effect of MOs [13]. MnO_2 with Co_3O_4 nanoparticles had a heterogeneous interface to enhance remarkably catalytic oxidation activity [14]. Magnetic porous Fe_3O_4-MnO_2 had a highly efficient removal of bivalent heavy metals [15]. The microwave absorption performance of core-shell Fe_3O_4@MnO_2 composite microspheres was tunable [16]. The catalytic property of MOs was attributed to different valances of Mn in the structure [17]. In addition, the spin state of Mn may also affect the performance of MOs as demonstrated in our previous study using MOs [7].

A preliminary study showed that Birn could degrade TC effectively under MI and the accelerated TC degradation was attributed to a drastic increase in surface temperature due to strong absorption of microwave by Birn [18]. However, the valence states of Mn and their effects on MI response and TC degradation were not discussed. Moreover, TC degradation in the presence of Birn under MI under different physicochemical conditions was not fully evaluated. Due to a strong relationship between structure and performance, detailed mechanistic studies are needed, particularly, for a type of microwave absorbing materials with controllable responses to MI and variable degrading efficiencies. For this reason, we selected Birn as the microwave absorbing material and characterized its TC degradation under controllable Mn valance states and other physicochemical conditions.

2. Materials and methods

2.1. Materials

The materials used for the syntheses of Birn were $KMnO_4$ and $MnCl_2{\cdot}4H_2O$, purchased from Beijing Chemical Industry Co. The TC was purchased from Hefei Bomei Biological limited company with a purity of 98%. It has a few functional groups that could contribute to its dissociation (Fig. S1) with the ammonia acyl-1,3-enol ketone as center A, $pKa_1 = 3.3$; 10-phenolic groups-11, 12-enol ketone is center B, $pKa_2 = 7.6$; and 4-dimethylamino is center C, $pKa_3 = 9.7$ [19].

2.2. Syntheses of Birn

The Birns were synthesized based on a previous method [20]. The process of involved two steps. Firstly, 25 mL of 0.4 M $MnCl_2{\cdot}4H_2O$ solution was mixed with 25 mL of 8 M NaOH solution to form precipitates of $Mn(OH)_2$. Then, 50 mL $KMnO_4$ solution was added dropwise to oxidize the precipitates and to form buserite as an intermediate, whose layer spacing was about 1 nm. After dehydration, the layer spacing collapsed to 0.7 nm and Birns were produced. The initial concentrations of $KMnO_4$ solutions were 0.25, 0.23, 0.22, 0.21, 0.20, and 0.19 M to achieve different ratios of Mn (II)/Mn(III)/Mn(IV). They were named as 1-, 2-, 3-, 4-, 5-, and 6-Birn. The overall reaction involves in $MnO_4^- + Mn(OH)_2 \rightarrow$ Mn(II)/Mn(III)/Mn(IV). The charge deficit of Birn was balanced by metal cations (Na and K, due to the addition of NaOH and $KMnO_4$) and H_2O in the interlamination of Birn [21].

2.3. Microwave degradation

For all batch experiments, 0.1 g of Birn and 50 mL of TC solution at an initial concentration of 50 mg/L were mixed in a conical flask (100 mL) and placed into a microwave reactor (Galanz, P70D20TP-C6) under varying microwave powers for 30 min. The mixtures were then centrifuged for 5 min at 6000 rpm. The equilibrium TC concentrations in the supernatants were analyzed using a UV–Vis spectrophotometer. The differences between the initial and final TC concentrations were used to calculate TC removal. For the pH effect, time series, and regeneration study, the same procedures were followed except that the variables were equilibrium solution pH adjusted by adding minute amount of concentrated HCl or NaOH, time for MI, and cycles of regeneration.

2.4. Methods of analyses

The crystal structure of synthesized Birn was characterized by powder X-ray diffraction (XRD) analysis (Rigaku D/max-RC) using a CuKα radiation at 40 kV and 100 mA, a scanning speed of 8°2θ/min, and a step size of 0.02° 2θ from 3° to 70°. Micro-textures of the Birn were observed on an FEI Quanta 250 field-emission environmental scanning electron microscope (Thermo Fisher Scientific) at 15 kV. Parts of the sample powders were dispersed in ethanol and the suspensions were placed on copper grid-supported carbon films to be dried for high-resolution transmission electron microscopy (HRTEM) imaging. The fast Fourier transform (FFT) of the HRTEM of the six synthesized Birn was analyzed by Digital Micrograph software. The valence state of Mn in the synthesized Birn was characterized by X-ray photoelectron spectroscopy (XPS) with a monochromatic AlKα radiation at 150 W and a base pressure at 6.5×10^{-10} mbar. The binding energy was calibrated using the C1s binding energy of alkyl carbon at 284.8 eV. An atomic emission spectrometer (ICP-AES, Thermo Scientific, iCAP 7000 SERIES, Ltd) was used to analyze the concentration of Mn in solution using environmental standard sample of Mn for calibration. The X-ray absorption fine structure (XAFS) spectra of Birn were obtained at room temperature with 1W1B beamline, in Beijing Synchrotron Radiation Facility [22]. The K-edge XAFS data of Mn were collected in the transmission mode in the energy range of 6392–7316 eV. An Mn metal foil was used as a reference (absorption edge jump at 6539 eV) to calibrate the monochromator. The XAFS spectra were analyzed by Ifeffit [23]. The backgrounds of K-edge spectra were subtracted with the following parameters: $E_0 = 6555$ eV, k-weight = 2, and Rbkg = 1 Å. Fitting of XAFS spectra was performed

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