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Oxidative degradation of sulfamethoxazole by different MnO_2 nanocrystals in aqueous solution

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ABSTRACT

Several MnO_2 nanomaterials synthesized at autoclave temperatures ranging from 130 to 210 °C were characterized and investigated for sulfamethoxazole (SMX) oxidative degradation in aqueous solution. The pure single-crystal α-MnO_2 nanorods prepared at 150 °C showed the highest SMX degradation efficiency. We concluded that the crystallographic structure and the surface species of MnO_2 were more important than BET surface area and crystallinity in influencing the activity in SMX oxidative degradation. The high degradation efficiency of α-MnO_2 nanorods resulted from a (2×2) tunnel structure, rich surface adsorbed oxygen and high oxygen mobility. The degradation efficiency of α-MnO_2 nanorods was also greatly influenced by the initial SMX concentration, MnO_2 dosage and pH value. The particular reaction orders with respect to these three factors were 0.70, 0.54 and −0.15, respectively. Under lower pH conditions (e.g., pH < 2.4), a rapid oxidative degradation of SMX by α-MnO_2 was achieved as well as generation of intermediate products and Mn^{2+}. Moreover, α-MnO_2 exhibited high stability in recycling tests, which demonstrated itself to be a good oxidant for oxidative degradation of SMX. These results may be useful in understanding the interaction of SMX and MnO_2 in soil and water environments.

1. Introduction

Sulfamethoxazole (SMX) is a common sulfonamide antibiotic, which has been found in trace concentrations (μg/L or ng/L) in wastewater treatment plant effluents and surface waters [1] as well as sewage sludge or soils [2,3]. Subtherapeutic concentrations of SMX may alter the composition of the enriched nitrate-reducing microcosms and inhibit their nitrate reduction capabilities [4]. This may also lead to the transfer of antibiotic resistance genes to pathogenic organisms [5,6]. To assess the potential risks of SMX in the soil/water environments, the role of natural attenuation processes such as the sorption/transformation onto sediments must be understood. In the natural environment, sulfonamide antimicrobials may be degraded by several transformation processes such as chemical degradation [7], biodegradation [8], and photodegradation [9]. Recently, many attentions have been focused on abiotic degradation of sulfonamides in the presence of manganese dioxide (MnO_2) [9–12]. As oxidants in organic chemistry, Mn oxides are also used as efficient catalysts for oxidation of organic compounds [13]. Manganese hydroxides/oxides have the most abundant reactive surfaces typically presenting in aquatic and terrestrial environments under suboxic and anoxic conditions. Synthetic manganese hydroxides/oxides efficiently degrade antibiotics in aqueous solution [9,10,14–17]. Unlike the well-characterized interaction of sulfonamides with manganese oxides in amorphous form, the oxidative activity of MnO_2 in crystallographic forms has not yet been investigated in detail.

As an important transition metal oxide, MnO_2 exists either in an amorphous form or in different crystalline forms including α, β, γ, and δ [18–21]. Although manganese dioxides in different crystalline forms have the same basic octahedron units [MnO_6], they exhibit various oxidation activities and catalytic properties because of differences in their crystal lattice structures and crystal cell parameters. For example, Liu et al. [11] prepared eight MnO_2 to conduct sulfadiazine (SD) oxidative degradation and observed that SD degradation strongly depended on the physicochemical properties of different manganese dioxides including the average oxidation state, reductive potential, pH at the point of zero charge (pH_{PZC}), and apparent activation energy. Liang et al. [22] synthesized α-, β-, γ-, and δ-MnO_2 nanorods to evaluate their catalytic properties for carbon monoxide (CO) oxidation and showed that CO oxidation

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was predominated by the crystal phase and channel structure of the MnO_2 nanorods. Santos et al. [23] reported that the reactivity and mobility of lattice oxygen played an important role in the catalytic activity of manganese oxides towards the oxidation of volatile organic compounds. Wang et al. [24] prepared nanosized rod-like, wire-like, and tubular α-MnO_2 using a hydrothermal method. This group concluded that the excellent catalytic performance of α-MnO_2 nanorods might be associated with the high oxygen adspecies concentration and good low-temperature reducibility. The catalytic oxidation properties of reactants over MnO_2 are widely reported in the literature, but the corresponding mechanism remains controversial. It is generally accepted that the catalytic oxidation activity of MnO_2 is due to its phase structure, high mobility of lattice oxygen, and mixed valence character of manganese [22,23,25–27]. Therefore, our goal is a better understanding of the factors dominating the reaction mechanism of MnO_2. We report a simple hydrothermal method for direct growth of single crystalline α- and β-MnO_2 nanorods by adjusting hydrothermal temperature, and investigate the mechanism of SMX oxidative degradation by these MnO_2 nanorods.

2. Materials and methods

2.1. Chemicals

SMX (purity>99%) was purchased from Sigma–Aldrich Co. LLC. All other chemicals used in this investigation were of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The chemicals were used without further purification and all the solutions were prepared with deionized water obtained from a Milli-Q system (Millipore, Bedford, MA) to the required concentrations.

2.2. MnO_2 preparation and characterization

Preparation of MnO_2 nanorods used a one-step co-precipitation reaction. Briefly, 45 mL of 0.60 mol/L $MnSO_4$ solution was added dropwise to 28.2 mL of 0.25 mol/L $KMnO_4$ solution under constant stirring. The mixture was then treated with a Teflon-lined stainless steel autoclave (100 mL) at temperatures ranging from 130 to 210 °C for 12 h. The precipitates were washed with deionized water several times until the pH reached to 7.0 and dried under vacuum at 60 °C to a constant mass. Eventually, a dark-brown powder was obtained. The products were denoted as MnO_2-130, MnO_2-150, MnO_2-170, MnO_2-190, and MnO_2-210, respectively, according to their autoclave temperatures.

The morphologies were characterized by a Philips SEM515. Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advanced diffractometer with Cu Kα radiation and the scanning angle from 10 to 80° of 2θ. Infrared (IR) spectra were recorded on a Thermo FTIR spectrometer using the KBr pellet technique. The specific surface areas were determined by multipoint N_2-BET analysis using a Micromeritics ASAP 2020 surface area analyzer. The zero point of charge (pH_{pzc}) was measured with a Malvern Zetasizer Nano ZS 90 zeta potential analyzer. The X-ray photoelectron spectroscopy (XPS) experiments were performed on a PHI-5000C ESCA spectrometer using Mg Kα radiation (1253.6 eV of photons). Temperature-programmed reduction (TPR) experiments were performed on a Micromeritics 2720 chemisorption analyzer under a 10% H_2 gas flow (50 mL/min).

2.3. Experimental setup and analytical methods

Batch experiments tested the variables affecting oxidative degradation of SMX by MnO_2 nanorods as well as the reaction kinetics. Each conical beaker (150 mL) was filled with 100 mL of SMX solution (1–10 mg/L) and kept in a temperature controlled shaker at 200 rpm and 25 °C for 24 h under dark and ambient O_2 conditions. For the oxidation reaction kinetic experiments, the initial SMX concentrations were 5 mg/L (0.02 mmol/L). While this is a higher value than the environmentally relevant concentrations, it approximates a contamination source and facilitates laboratory study. The experiments were conducted in 0.01 mol/L NaCl background electrolyte to maintain a constant ionic strength. The MnO_2 loading was 1.0 g/L. The pH was adjusted between 1.7 and 7.0 with 0.01–0.1 mol/L HNO_3 or 0.01–0.1 mol/L NaOH. Immediately after sampling, the reaction liquids were filtered with 0.45 μm filters. The samples were kept in amber vials at 4 °C and analyzed by liquid chromatography and ICP-MS within 1 d. The adsorbed fraction of SMX and its oxidation products were extracted by sonication (10 min) of MnO_2 nanorods, in the presence of 10 mL mobile phase containing 70% water (+0.1% formic acid) and 30% acetonitrile. After filtration through 0.22 μm filters, the extracts were analyzed by high performance liquid chromatography (HPLC). An Agilent 1200 liquid chromatograph system with UV detector was used to determine SMX concentration at 265 nm. The concentration of released Mn^{2+} ion was determined on an Agilent 7700*x* ICP-MS. For the recycle tests of the MnO_2-150 sample, the used MnO_2 nanorods were obtained by vacuum filtration, washed with deionized water, and then dried in a vacuum oven at 60 °C. The cycle was repeated three times and the obtained MnO_2 nanorods after recycling were characterized by XRD, FTIR, and SEM techniques.

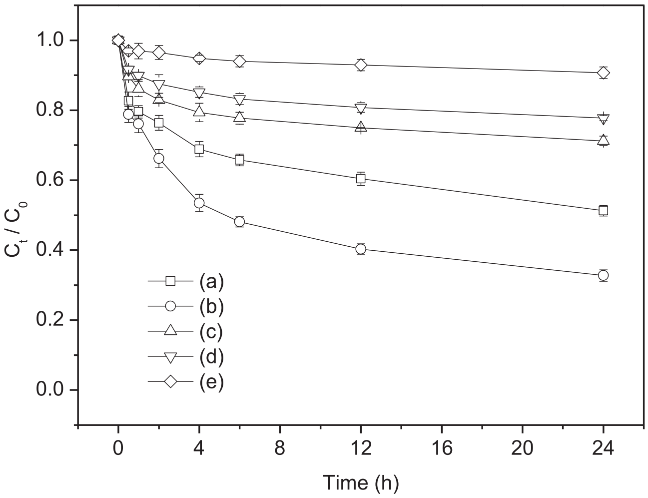

Fig. 1. XRD patterns of MnO_2 prepared at (a) 130 °C, (b) 150 °C, (c) 170 °C, (d) 190 °C, and (e) 210 °C.

3. Results and discussion

3.1. Materials characterization

XRD indicated the purity and crystallinity of the MnO_2 samples. Crystal forms of the produced MnO_2 nanocrystals are usually sensitive to hydrothermal temperature. Fig. 1 shows the XRD patterns of the samples resulting from the hydrothermal process at different temperatures. As shown in Fig. 1a and b, all the diffraction peaks can be exclusively indexed to a pure tetragonal phase of α-MnO_2 (JCPDS 44-0141) [28,29]. The intensities and widths of the diffraction peaks of the MnO_2-130 samples are lower and wider than those from MnO_2-150 indicating that MnO_2-130 samples have worse crystallinity. In Fig. 1c and d, in addition to the peaks of the α-MnO_2, several small peaks assigned to the β-MnO_2 (JCPDS 24-0735) [29,30] are also observed. This indicates a mixed phase of α-MnO_2 and β-MnO_2 in MnO_2-170 and MnO_2-190. All