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Article

Ordered mesoporous manganese oxide as catalyst for hydrogen peroxide oxidation of norfloxacin in water

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ABSTRACT

Ordered mesoporous manganese oxide (om-MnO_x) was prepared and used in oxidation by hydrogen peroxide of norfloxacin (NFX). The om-MnO_x was prepared using a hard template method. The catalytic activity of om-MnO_x was investigated by evaluating the changes in degradation efficiency and antibacterial activity of NFX. om-MnO_x exhibited significant catalytic activity for the degradation of NFX in water by hydrogen peroxide. Lower pH conditions favored the catalytic activity of om-MnO_x/hydrogen peroxide. The presence of om-MnO_x achieved a greater reduction in the antibacterial ability of NFX than that was obtained with hydrogen peroxide alone. The inhibiting effect of *t*-butanol indicated that om-MnO_x enhanced the generation of hydroxyl radicals. Byproducts from NFX were detected during the om-MnO_x-catalyzed hydrogen peroxide process, and possible reaction pathways were proposed.

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1. Introduction

Awareness of antibiotics in the environment has increased in the last decade. Most antibiotics are incompletely metabolized during therapy [1]. Norfloxacin (NFX) is one of the quinolones that are among the most important classes of synthetic antibacterial agents, and it is widely used in human and veterinary medicine [2]. It is difficult to biodegrade NFX in aqueous solutions, and chemical oxidation has been considered [3].

Hydrogen peroxide is a very attractive oxidant for the remediation of wastewater containing organic substances. It is cheap, environmentally clean, and easy to handle. However, hydrogen peroxide is a moderately strong oxidant, and poorly active without a catalyst. In recent years, heterogeneous catalytic hydrogen peroxide has been developed, which can partly overcome the drawbacks of the homogenous Fenton system (Fe²⁺/H₂O₂), such as disposing of the Fe-containing waste

sludge and the irreversible loss of activity of the reagent. Manganese oxides (MnO_x) have been found to be active for the decomposition of hydrogen peroxide in aqueous solutions by enhancing the generation of hydroxyl radicals (HO·) [4–6]. Manganese oxide catalysts are often loaded on porous materials (e.g., GAC, SBA-15, and mesoporous Al₂O₃ [5,7,8]) because a higher specific surface area and porous structure favor catalytic activity. However, the unavoidable leaching of Mn from the surface of the support may cause a deterioration in its catalytic activity.

In the present study, manganese oxide with an ordered mesoporous structure (om-MnO_x) was prepared and introduced into a hydrogen peroxide oxidation process. Ordered mesoporous materials have attracted growing attention in the last two decades, and they have great potential for applications in environmental remediation as catalyst supports and adsorbents [9]. However, few studies have focused on the catalytic

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performances of ordered mesoporous transition-metal oxides. To the best of the authors' knowledge, the catalytic activity of manganese oxide with an ordered mesoporous structure and hydrogen peroxide for the degradation of organic pollutants in water has not been investigated. It is expected that an ordered mesoporous structure and a specific surface area of up to 85.67 m²/g would provide favorable manganese oxide catalytic performances in the degradation of NFX by hydrogen peroxide.

2. Experimental

2.1. Catalyst preparation

The ordered mesoporous MnO_x was prepared by a hard template method using SBA-15 as the hard template and Mn(NO₃)₂ as the Mn source [10]. The calcination conditions were varied and were found to be an important factor in the ordered structure of MnO_x. SBA-15 was prepared using a non-ionic triblock copolymer (P123) as a surfactant and tetraethoxysilane as the silica source [11]. SBA-15 powder was impregnated with Mn(NO₃)₂ solution under stirring. The composite was dried in air at 100 °C for 12 h. The resulting solid was heated at a rate of 1 °C/min and calcined at 150, 200, 250, and 300 °C for 2 h and 350 °C for 5 h. The silica template was removed using a 2 mol/L NaOH solution. As a reference, manganese oxide without an ordered mesoporous structure, designated no-MnO_x, was prepared by Mn(NO₃)₂ decomposition and the same calcination conditions as those used in the preparation of om-MnO_x.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) images of the samples were obtained using a JEM2011 instrument (JEOL, Japan). The sample purities were determined by X-ray fluorescence (XRF) using a Bruker-AXS S4 Explorer instrument. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-RB diffractometer with Cu K_α radiation. Nitrogen absorption-desorption isotherms were obtained using a Micromeritics ASAP 2010 apparatus. The multipoint Brunauer-Emmett-Teller method was used to measure the specific surface area, and the pore size distribution was calculated using the Barrett-Joyner-Halenda method. The average oxidation state of Mn in the samples was measured by potentiometric titration [12].

2.3. Oxidation experiments

Experiments were carried out in a glass batch-reactor with continuous stirring. The reaction was initiated by adding catalyst to a solution containing NFX and hydrogen peroxide. Samples were withdrawn at intervals and then filtered through a 0.22 μm one-off poly(ether sulphone) syringe filter. Methanol was used to quench any additional oxidation reactions involving residual H₂O₂. The pH of the reaction solution was adjusted using 0.1 mol/L NaOH and HCl, but was not buffered, to avoid the effects of the buffer salt on the catalyst's properties [13,14].

NFX was analyzed at 275 nm using an ultra-high-performance liquid-chromatography system (ACQUITY UPLC H-Class) and a 100 mm × 2.1 mm C₁₈ 1.7-μm reversed-phase column (ACQUITY UPLC BEH) with 0.1% formic acid and acetonitrile (85:15, v/v) as the mobile phase. Mass spectrometric (MS) analysis (*m/z*: 100–450) was performed using a TSQ Quantum (Thermo Fisher Scientific) spectrometer equipped with an electrospray ionization source [15]. The titanium sulfate method was used to analyze the concentration of H₂O₂ [16]. The antibacterial activity of NFX was evaluated using the method proposed by Dodd et al. [17,18], and a phosphate buffer of pH 7.0 was used for serial dilution. Mn ions were determined using an Optima 2100 DV ICP spectrometer (PerkinElmer, USA).

3. Results and discussion

3.1. Catalyst characterization results

The XRD patterns are shown in Fig. 1. Three well-resolved reflections, indexed to (100), (110), and (200), were observed for SBA-15, which suggested that the SBA-15 synthesized in this study possesses a highly ordered hexagonal mesostructure [19]. The positions of the (100) and (110) peaks of om-MnO_x shifted to a lower *d* spacing. The peak intensities decreased and the (200) peak almost disappeared, which is a result of the incomplete ordered framework of the om-MnO_x sample [20]. The no-MnO_x sample did not show any peaks in the 2θ range 0°–6° (data not shown here).

The TEM image of SBA-15 suggested a highly ordered porous structure (Fig. 2(a)). From Fig. 2(b), it was clear that om-MnO_x copied the template tunnels. However, the pore diameter of om-MnO_x was smaller than the wall thickness of SBA-15. This may be caused by excessive grain growth of transition-metal oxides in the calcination process. No ordered pore structure was observed for no-MnO_x.

Some of the important physicochemical properties of om-MnO_x are listed in Table 1. The specific surface area of om-MnO_x (85.67 m²/g) was higher than that of no-MnO_x. The TEM image in Fig. 2(d) shows that no-MnO_x has almost no pores. The average pore size of om-MnO_x (13.2 nm) is in the

Fig. 1. XRD patterns of SBA-15 and om-MnO_x.

Fig. 2. TEM images of SBA-15 (a), om-MnO_x (b, c), and no-MnO_x (d).

Table 1

Physicochemical properties of different samples.

Sample	MnO _x content (wt%)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Average oxidation state
om-MnO _x	99.2	85.67	0.28	13.2	3.67
no-MnO _x	97.4	0.90	0.0076	–	3.83

mesoporous range. The average oxidation state of manganese oxide showed that there were more Mn⁴⁺ species in no-MnO_x than in om-MnO_x.

3.2. Performance of om-MnO_x as catalysts in hydrogen peroxide oxidation of NFX

As shown in Fig. 3, under the pH conditions investigated in these experiments (pH 3.0, 7.1, and 8.7), H₂O₂ alone cannot effectively degrade NFX. However, a higher efficiency of NFX degradation was observed in the presence of MnO_x. It is obvious that the catalytic activity of om-MnO_x in NFX degradation with H₂O₂ is greater than that of no-MnO_x. Although om-MnO_x and no-MnO_x both improved the oxidizing ability of H₂O₂, a higher NFX degradation efficiency was observed in the catalytic hydrogen peroxide process using om-MnO_x. Lower pH condi-

tions were also found to favor the catalytic activity of om-MnO_x/H₂O₂. At pH 3.0, 58.7% of NFX was degraded in the presence of 1.0 g/L of om-MnO_x. This was 53.5% higher than the degradation percentage obtained using H₂O₂ alone (5.2%). Although the degradation efficiency of NFX decreased with increasing pH, 31.3% of NFX was still degraded at pH 8.7. It is worth noting that the adsorption of NFX on om-MnO_x accounted for 44%–68% of the total removal efficiency for NFX at the three pH values, indicating that adsorption of NFX on om-MnO_x plays an important role in NFX removal. The catalytic activity of om-MnO_x/H₂O₂ is evident from a comparison of the NFX catalytic degradation efficiency in om-MnO_x/H₂O₂ with the cumulative degradation efficiency of NFX by H₂O₂ alone, and adsorption of NFX on om-MnO_x.

The deactivation potency with respect to the biological activity must be considered in assessing the oxidation ability when treating antibacterial agents. Deactivation is sufficient for antibacterial agents. Complete removal of the agent from the water is unnecessary and uneconomical. Changes in the antibacterial activities of NFX in H₂O₂ oxidation with and without om-MnO_x were investigated. Figure 4 shows the growth inhibition curves. The percentage growth inhibition *I* of a reference bacterium (Eq. (1)) was plotted against the log of the corresponding sample dilution. Hydrogen peroxide alone and in the

Fig. 3. Catalytic activity of om-MnO_x on hydrogen peroxide for degradation of NFX at pH 3.0 (a), 7.1 (b), and 8.7 (c). Initial concentration of H₂O₂ 20 mmol/L, dose of om-MnO_x and no-MnO_x 1.0 g/L, initial concentration of NFX 78 μmol/L, temperature 20 °C.

Fig. 4. Dose-response relationship for deactivation of NFX in om-MnO_x catalytic hydrogen peroxide. Initial concentration of H₂O₂ 20 mmol/L, oxidation/adsorption time 60 min, dose of om-MnO_x 1.0 g/L, initial concentration of NFX 78 μmol/L, initial pH of 3.0, temperature 20 °C.

presence of om-MnO_x both caused a shift to the right relative to the curve corresponding to the untreated NFX sample in the corresponding dose-response curves, indicating that the antibacterial activity of NFX was reduced. However, it is obvious that the presence of om-MnO_x reduced the antibacterial ability of NFX to a greater extent than H₂O₂ alone did. The adsorption of NFX on om-MnO_x caused some of the reduction in the antibacterial activity of NFX.

$$I(\%) = \frac{(A_{\max} - A)}{(A_{\max} - A_{\min})} \times 100 \quad (1)$$

where $A_{\min}$ and $A_{\max}$ are 100% and 0% growth inhibitions, which correspond to negative and positive growth controls, respectively, and A is the adsorption of each sample at 625 nm.

3.3. Preliminary considerations of reaction mechanism

3.3.1. Effect of *t*-butanol on om-MnO_x/hydrogen peroxide catalytic process

It has been suggested that the catalytic ability of Mn/hydrogen peroxide in aqueous solutions is the result of promotion of the generation of hydroxyl radicals in homogeneous or heterogeneous catalytic systems [5]. Hydroxyl radicals react non-selectively with organic matter in aqueous solutions at a rate of 10^3 – 10^{11} mol/(L·s) [21]. *t*-Butanol (TBA), a hydroxyl radical scavenger, was used to investigate whether hydroxyl radical generation was promoted in the presence of om-MnO_x. TBA has a relatively fast reaction rate with hydroxyl radicals [6×10^8 mol/(L·s)] [22], and the presence of TBA quenches the hydroxyl radical chain reaction by producing inert intermediates, resulting in a decrease in the oxidation of target compounds. The effect of TBA on the degradation efficiency of NFX is shown in Fig. 5. In oxidation with H₂O₂ alone, 1.5% and 2.6% reductions in the degradation efficiency of NFX were observed in the presence of 50 and 100 mg/L, respectively, of TBA. It was found that the presence of 50 and 100

Fig. 5. Effect of *tert*-butanol on om-MnO_x catalytic hydrogen peroxide. Initial concentration of H₂O₂ 20 mmol/L, dose of om-MnO_x 1.0 g/L, initial concentration of NFX 78 μmol/L, initial pH of 3.0, and temperature 20 °C.

mg/L of TBA had a significant impact on NFX degradation, and the degradation efficiencies decreased by 11.7% and 19.6%, respectively, indicating that om-MnO_x enhanced the generation of hydroxyl radicals. The generated hydroxyl radicals then reacted with NFX adsorbed on the om-MnO_x surface and/or diffused into the aqueous solution to oxidize NFX.

3.3.2. Degradation intermediates and destruction pathways for NFX

The byproducts of NFX oxidation in the system with om-MnO_x/H₂O₂ at pH 3.0 were identified. MS analysis of NFX showed several fragmentation products, and an MS fragmentation pattern was proposed. The MS data are summarized in Table 2. The detailed degradation pathways are illustrated in Scheme 1. Based on the fragmentation products, the oxidation processes primarily occurred in the piperazine ring and nalidixic ring of NFX, indicating that hydroxyl radicals were involved in the catalytic reaction [15,23]. Three possible pathways for reactions between NFX and hydroxyl radicals are proposed. (1) Pathway I: oxidation at the nalidixic ring. First, hydroxyl radicals oxidize the carboxyl group in the nalidixic ring. Hydroxyl radicals then attack the double bond in the na-

Table 2
Summary of fragmentation products from NFX catalytic oxidation.

No.	[M + H] ⁺ measured	Nominal mass	Molecular formula	Chemical structure
NFX	320	319	C ₁₆ H ₁₈ FN ₃ O ₃	NFX
1	276	275	C ₁₅ H ₁₈ FN ₃ O	Da(1)
2	236	235	C ₁₃ H ₁₈ FN ₃	Da(2)
3	352	351	C ₁₆ H ₁₈ FN ₃ O ₅	Da(3)
4	320	319	C ₁₆ H ₁₈ FN ₃ O ₃	Da(4)
5	196	195	C ₁₀ H ₁₄ FN ₃	Da(5)
6	212	211	C ₁₀ H ₁₅ FN ₃ O	Da(6)
7	184	183	C ₈ H ₁₀ FN ₃ O	Da(7)
8	168	167	C ₈ H ₁₀ FN ₃	Da(8)
9	251	250	C ₁₂ H ₁₁ FN ₂ O ₃	Da(9)
10	318	317	C ₁₆ H ₁₉ N ₃ O ₄	Da(10)

Scheme 1. The proposed catalytic degradation pathways for NFX.

lidixic ring, resulting in ring-opening, and the opened ring is then oxidized. (2) Pathway II: oxidation at the piperazine ring. Hydroxyl radicals attack and substitute the piperazine ring. Ring-opening of the piperazine ring occurs as a result of oxidation by hydroxyl radicals, and then the opened piperazine ring is further oxidized, leading to cleavage of C_4H_7N (No. 9, Table 2). (3) Pathway III: oxidation at the benzene ring. As a result of strong oxidation by hydroxyl radicals, the F atom connected to the benzene ring is substituted by a hydroxyl, generating intermediates of mass 318 units. The structures of some of the products (No. 5, Table 2) showed that both the piperazine ring and the nalidixic ring were oxidized.

3.4. Stability of catalytic activity of om-MnO_x

The stability of the catalytic activity of om-MnO_x was tested by performing five runs at pH 3.0, 7.1, and 8.7, respectively. Withdrawn samples were filtered using a 0.22- μ m syringe filter, and the NFX degradation efficiency and the concentration of Mn ions in aqueous solutions were monitored. No detectable leaching of Mn ions was found under the pH conditions used (3.0, 7.1, and 8.7), and the catalytic activity of om-MnO_x was unchanged after the fifth run.

4. Conclusions

Ordered mesoporous manganese oxide was shown to have significant catalytic activity in degradation of NFX using hydrogen peroxide. Promotion of hydroxyl radical generation was proposed as the reaction mechanism. Fenton's reagent, a well-known homogeneous catalytic hydrogen peroxide system,

is effective at pH 2.0–5.0. However, catalysis by ordered mesoporous MnO_x proceeds in the pH range 3.0–8.7, and thus is promising for practical applications.

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Graphical Abstract

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Ordered mesoporous manganese oxide as catalyst for hydrogen peroxide oxidation of norfloxacin in water

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Compared with MnO_x without pores, ordered mesoporous MnO_x exhibited marked catalytic activity towards H_2O_2 for degradation of norfloxacin in aqueous solutions.

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有序介孔锰氧化物催化过氧化氢降解水中诺氟沙星

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摘要: 采用硬模板法制备了有序介孔氧化锰, 并用过氧化氢氧化诺氟沙星的降解率及其抗菌活性变化评价了其催化活性. 研究发现, 有序介孔锰氧化物表现出较高的催化活性; 低 pH 有利于提高其催化活性. 与单独过氧化氢氧化过程相比, 有序介孔锰氧化物的存在明显减弱了诺氟沙星的抗菌活性. 叔丁醇对催化体系的抑制作用表明有序介孔锰氧化物促进了过氧化氢分解生成羟基自由基. 通过对诺氟沙星在催化过程中的分解产物鉴定, 提出了可能的分解途径.

关键词: 有序介孔; 锰氧化物; 过氧化氢; 氧化; 诺氟沙星

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