



Catalytic degradation of Acid Orange 7 by manganese oxide octahedral molecular sieves with peroxymonosulfate under visible light irradiation



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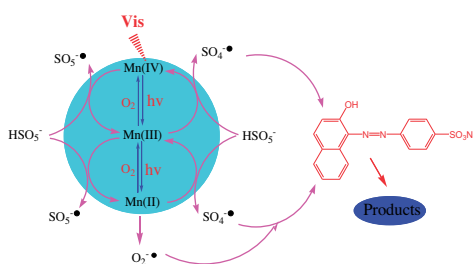
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HIGHLIGHTS

- OMS-2/PMS/Vis system could efficiently catalyze the degradation of organic dyes.
- The system showed much higher activity than that of OMS-2/PMS and OMS-2/Vis.
- The OMS-2 catalyst exhibited stable performance for multiple runs.
- Sulfate radicals were suggested to be the major reactive species in the system.
- The radicals production might involve the redox cycle of Mn(IV)/Mn(III) and Mn(III)/Mn(II).

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the photodegradation of Acid Orange 7 (AO7) in aqueous solutions with peroxymonosulfate (PMS) was studied with manganese oxide octahedral molecular sieves (OMS-2) as the catalyst. The activities of different systems including OMS-2 under visible light irradiation (OMS-2/Vis), OMS-2/PMS and OMS-2/PMS/Vis were evaluated. It was found that the efficiency of OMS-2/PMS was much higher than that of OMS-2/Vis and could be further enhanced by visible light irradiation. The catalyst also exhibited stable performance for multiple runs. Results from ESR and XPS analyses suggested that the highly catalytic activity of the OMS-2/PMS/Vis system possible involved the activation of PMS to sulfate radicals mediated by the redox pair of Mn(IV)/Mn(III) and Mn(III)/Mn(II), while in the OMS-2/PMS system, only the redox reaction between Mn(IV)/Mn(III) occurred. Several operational parameters, such as dye concentration, catalyst load, PMS concentration and solution pH, affected the degradation of AO7.

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1. Introduction

Process industries generate huge amount of water pollution containing many hazardous organic compounds, which are highly recalcitrant and difficult to degradation in biological treatment [1]. In recent decades, advanced oxidation processes (AOPs) such as photocatalytic oxidation [2], catalytic wet air oxidation [3], catalytic wet peroxide oxidation [4], catalytic ozonation [5] and sonocatal-

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ysis [6] are becoming more important technologies. Among the various AOPs, considerable attention has been focused on the use of heterogeneous photocatalysis as a means to oxidize pollutants [7]. However, the development of cheap catalysts that can efficiently harness solar energy still remains a huge challenge in this area [8], and various strategies such as design of new photocatalysts and modification of TiO_2 with metal or nonmetal compounds have been developed in an attempt to modify the process and improve the catalytic performance under visible light irradiation. Ye and coworkers reported an efficient photocatalyst, silver orthophosphate (Ag_3PO_4), which can efficiently oxidize water to release oxygen as well as degrade organic contaminants under visible light irradiation [9–11]. Although TiO_2 cannot be activated by visible light directly, the degradation of dyes on TiO_2 under visible light is enabled through a dye-sensitization process in which dyes are excited by absorbing visible-light photons [12]. The wrapped carbon-doped TiO_2 nanoparticles (NPs) with nano-sized graphene can be also used as high performance photocatalysts for phenol degradation under visible light irradiation [13].

Another approach to increase of the photodegradation efficiency is the addition of oxidants such as hydrogen peroxide (H_2O_2), persulfate (PS) and peroxymonosulfate (PMS) as electron acceptors, due to the immediate trapping of photogenerated electrons by the oxidants which in turn decreases the recombination of electron-hole pairs and thus enhances the quantum yield [14]. Chen et al. investigated the application of Vis/ TiO_2 /PMS treatment process to the aqueous degradation of Acid Orange 7 (AO7), and confirmed that PMS can be used as an efficient oxidant to accelerate the Vis/ TiO_2 process [15]. Kuriechen et al. found that the addition of PMS in the TiO_2 -Reactive Red 180 system increased the degradation rate by about 10 fold, which was more promising for the degradation of the dye when compared with other electron acceptors such as H_2O_2 and PS [16].

Cryptomelane-type manganese oxide, OMS-2, is an important functional oxide with salient features like mixed-valency of Mn, a hydrophobic nature, porous structure, easy release of lattice oxygen, and acidic sites [17–19]. The material has been widely used as catalysts in oxidation of thiols [20], styrene [21], *p*-chlorotoluene [22] and cyclohexane [23], CO [24] and VOC abatement [25], and degradation of organic pollutants in aqueous solution [26–29]. The material can also be used as photocatalyst. Liu et al. studied the solid-phase photocatalytic degradation of polyethylene film with OMS-2 as photocatalyst in the ambient air under ultraviolet and visible light irradiation [30]. Iyer et al. evaluated the activities of various K-OMS-2 and metal doped OMS-2 catalysts prepared by different synthesis procedures, and found that K-OMS-2 prepared by solvent free method showed the highest activity for selective oxidation of 2-propanol to acetone under visible light irradiation [31]. However, its performance for photodegradation of organic dyes in wastewater has not been studied intensely, although the removal of the pollutants from waste effluents has become environmentally important [29].

The current study reports the photo decomposition of AO7 under visible light irradiation using OMS-2 as the catalyst. In order to improve its performance, PMS was added into the system. This heterogeneous catalysis method seems to be an economically attractive and environmentally friendly oxidation technology for the treatment of organic pollutants. The reaction mechanism and the effect of several major facts were also discussed.

2. Materials and methods

2.1. Preparation of OMS-2 catalyst

A reflux method was employed to synthesize OMS-2 [31]. In a typical reaction, 60 mmol manganese sulfate hydrate was placed in

30 mL double deionized water (DDW) with three milliliter of nitric acid. A second solution was then prepared by dissolving 38 mmol KMnO_4 in 100 mL DDW. This solution was subsequently added dropwise into the MnSO_4 solution under vigorous stirring to form a dark brown precipitate at 110°C . The resultant slurry was heated overnight at reflux temperature, washed with DDW, and dried at 120°C for 12 h to obtain OMS-2.

2.2. Characterization

X-ray powder diffraction (XRD) pattern was obtained on a Bruker D8 powder X-ray Diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The beam voltage and current used were 40 kV and 40 mA, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 spectrometer. The sample was mixed with solid KBr, then ground into powder and dried before pressed into a KBr wafer. The surface morphology was characterized on a JSM-5610LV scanning electron microscope (SEM) instrument (JEOL Ltd. Japan). UV-vis diffuse reflectance spectra were recorded on a Shimadzu UV-2450 spectrometer in the range of 200–800 nm with BaSO_4 as a reference. TG characterization was carried on a TGA/DSC 1 instrument (METTLER TOLEDO Co., Ltd.) in nitrogen atmosphere. Temperature-programmed reduction (TPR) was performed in a 5% H_2 -95% N_2 flow system. The sample was pretreated at 200°C for 2 h. The zeta potentials of OMS-2 under different solution pH were measured by Zetasizer Nano-ZS (Mavlern Instruments, UK).

The chemical oxidation states of Mn species in OMS-2 were investigated by X-ray photoelectron spectra (XPS) on a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with $\text{AlK}\alpha$ radiation as the exciting source (300 W). Charging effects were corrected by adjusting the binding energy of C1s to 284.6 eV. Electron spin resonance (ESR) spectra were recorded at room temperature using a Bruker ESR A-300 spectrometer with the following parameters: center field 3450 G, sweep width 1500 G, microwave frequency 9.86 G, modulation frequency 100 kHz, microwave power 1 mW.

2.3. Catalytic degradation experiment

All batch experiments were performed in a 100 mL reactor at about 25°C without irradiation or under irradiation by a 300 W xenon lamp (CHF-XM-300W, Beijing Trusttech Co.). After the desired amounts of AO7 and PMS (Oxone®, DuPont's triple salt: $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, Aladdin) in 50 mL of the aqueous solution were added into the reactor, the reaction was initialized by adding OMS-2. Each reaction solution was constantly stirred with a PTFE coated magnetic stirrer. Since PMS is an acidic oxidant, the addition of PMS led to a significant decrease of pH, and the experiment was conducted at acidic medium (pH 4.41, no adjustment). For studying the effect of solution pH on the rate of AO7 degradation, H_2SO_4 (20 mM) and NaOH (20 mM) was used to adjust the solution pH after PMS was added into the solution.

To monitor the degradation process of AO7, solution samples were taken out at given time intervals and measured immediately on a Varian Cary 50 Scan UV-vis spectrophotometer under the maximum absorption wavelength (484 nm). For identification of degradation products, the samples were analyzed by mass spectrometry, and the experiments were performed on an Esquire LC-ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an orthogonal geometry ESI source. Nitrogen was used as the drying (3 L/min) and nebulizing (6 psi) gas at 300°C . The spray shield was set to 4.0 kV and the capillary cap was set to 4.5 kV. Scanning was performed from m/z 70 to 800 in the standard resolution mode at a scan rate of 13 kDa/s. Before analysis, each sample was diluted ten times.

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