Chemical Engineering Journal 355 (2019) 448–456

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Enhanced 2, 4-dichlorophenol degradation at pH 3–11 by peroxymonosulfate via controlling the reactive oxygen species over Ce substituted 3D Mn_2O_3

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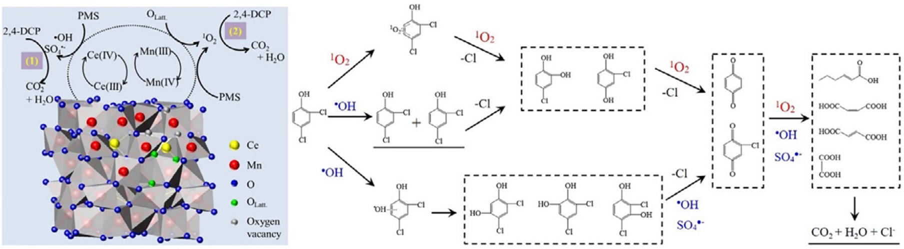
HIGHLIGHTS

- ROS can be regulated by in situ Ce doped Mn_2O_3 for the complete 2,4-DCP degradation.
- Besides $^1O_2$, the contribution of $\cdot OH$ and $SO_4^{\cdot -}$ was controlled by Ce doping amount.
- 2,4-DCP was completely degraded by 4% Ce doped Mn_2O_3 at pH 3–11 with good stability.
- The role of Ce doping in enhancing PMS activation performance of Mn_2O_3 was studied.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Peroxymonosulfate
Activation
Mn oxide
Cerium
Substitution

ABSTRACT

Peroxymonosulfate (PMS) activation has drawn increasing attention in eliminating the recalcitrant organic pollutants in water. Manipulation of generated reactive oxygen species (ROS) over Ce doped Mn_2O_3 during the PMS activation was firstly reported for the complete degradation of 2,4-dichlorophenol (2,4-DCP) in this study. Ce in-situ introduction can greatly enhance the PMS activation performance of Mn_2O_3. For example, 100% of 2,4-DCP degradation can be obtained at 90 min over 4 wt% Ce doped Mn_2O_3 at pH 7 (82.1% for Mn_2O_3 at 90 min). The reaction rate constant (k) was also about 3.6 times higher than that of Mn_2O_3 (0.0668 min^{-1} for Ce doped Mn_2O_3 vs. 0.0186 min^{-1} for Mn_2O_3). Besides $^1O_2$, $\cdot OH$ and $SO_4^{\cdot -}$ were identified and involved in 2,4-DCP degradation process over Ce doped Mn_2O_3, while only $^1O_2$ was detected over 3D Mn_2O_3. Moreover, the contribution of $\cdot OH$ and $SO_4^{\cdot -}$ to 2,4-DCP degradation can be regulated by adjusting the Ce doping amount. The key role of Ce substitution in the regulation of reactive oxygen species was further investigated by XPS and electrochemical experiments. The Ce dopant can lead to a higher current density and greater reductive capability due to the improved charge transfer capability, which is important to the generation of more aggressive $\cdot OH$ and $SO_4^{\cdot -}$ and complete 2,4-DCP degradation.

1. Introduction

2,4-dichlorophenol (2,4-DCP) is a potentially carcinogenic and toxic matter which mainly arising from the wide use of pesticides, herbicides and fungicides [1–4]. It has been listed by the U.S. Environment Protection Agency as a priority control pollutant because of its high toxicity even at a low concentration. However, the conventional technologies such as biological treatment are insufficient to remove this refractory organic pollutant [5–7]. Advanced oxidation processes (AOPs) then provide an alternative method due to the formation of

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https://doi.org/10.1016/j.cej.2018.08.183
Received 10 May 2018; Received in revised form 15 July 2018; Accepted 26 August 2018

highly aggressive reactive oxygen species [8–14]. Although photocatalysis, ozonation and homogeneous catalytic reaction have a high efficiency, the practical application is greatly limited due to the requirements for energy, special equipment and waste of chemical reagents [3,15–21]. Hence, to develop heterogeneous Fenton-like system can solve this problem because it does not require any special energy input but has a good stability.

At present, the heterogeneous Fenton-like reaction by activation of H_2O_2 or PMS has drawn increasing attention for eliminating the recalcitrant organic pollutants [22–27]. As reported, $\cdot$OH based mechanism as a result of H_2O_2 activation was responsible to efficient organic pollutants removal [28–30]. $SO_4^{\cdot-}$ and $\cdot$OH was identified as the main ROS when PMS was used as the oxidant [31–34]. Our previous study further proved that $^1O_2$ instead of $SO_4^{\cdot-}$ and $\cdot$OH was generated in $LaMnO_3$/PMS system [35]. It is worthy to note that different ROS have different oxidation capacity, for example, the standard redox potentials of $SO_4^{\cdot-}$, $\cdot$OH, and $^1O_2$ are 3.1 V, 2.8 V, and 2.22 V, respectively, which will greatly affect the degradation efficiency of target pollutants in Fenton-like reaction [32,36,37]. Hence, to provide a Fenton-like catalyst that can modulate the ROS for efficient pollutant removal is interesting and important for its application in practical water treatment. Mn oxides have been regarded as the superior candidates for PMS activation due to the abundance, low-cost and environment friendly properties of Mn [21,38–41]. However, our results show that Mn_2O_3 as the most efficient Mn oxide cannot degrade 2,4-DCP completely (data shown later) in PMS activation. Hence, there are two main concerns need to be investigated in this study: (1) Is it possible to regulate ROS for 2,4-DCP complete degradation by PMS activation? (2) How to manipulate the Mn_2O_3 catalytic property for generation of ROS with different oxidation capacity.

In this work, 3D Mn_2O_3 and in-situ Ce substituted 3D Mn_2O_3 were successfully prepared and their performance in PMS activation for 2,4-DCP degradation was investigated. Compared with 3D Mn_2O_3, 2,4-DCP was completely degraded at a wide pH range of 3.0–11.0 over Ce substituted Mn_2O_3. Besides $^1O_2$, the controlled generation of $SO_4^{\cdot-}$ and $\cdot$OH was realized and their contribution to 2,4-DCP degradation increased with the Ce doping amount. 4% of Ce doping exhibits the highest PMS activation efficiency, in which above 40% of 2,4-DCP was degraded by $SO_4^{\cdot-}$ and $\cdot$OH and the rest 2,4-DCP was degraded by $^1O_2$. Finally, the regulation mechanism for reactive oxygen species was discussed. The findings in this study are very important and provide a promising alternative for the removal of recalcitrant organic compounds in water.

2. Experimental

2.1. Materials

Potassium permanganate ($KMnO_4$, 99.8%), nitric acid (HNO_3, 68%), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$), sodium sulfate (Na_2SO_4), 2,4-dichlorophenol (2,4-DCP, 99%), ethanol (EtOH, 99.9%), tert-butyl alcohol (TBA, 99.9%), sodium azide (NaN_3, 99.5%), acetonitrile, and methanol (MeOH) of HPLC grade were purchased from Sinopharm Chemical Reagent Co., Ltd. 5,5-Dimethyl-1-pyrroline (DMPO, > 99.0%) and 2,2,6,6-Tetramethyl-4-piperidinol (TEMP, 99%) for EPR-spectroscopy were purchased from Sigma-Aldrich. Oxone® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, PMS) was obtained from Aladdin. All chemicals were used as received without further purification.

2.2. Preparation of PMS activation catalysts

In situ Ce substituted 3D Mn_2O_3 was prepared by a modified hydrothermal process with reduction of $KMnO_4$, followed by calcination of obtained precursor. In a typical experiment, 2 mmol potassium permanganate was dissolved in 45 mL deionized water, and 17.4 mg cerium (III) nitrate hexahydrate (about 4 wt%) was added into above solution. Then 0.6 mL nitric acid (68%) was dropped into the solution under vigorously stirring. After stirring for 30 min, the obtained solution was transferred to the Teflon autoclave, and heated at 100 °C in an oven for 12 h. After cooling to room temperature, the obtained precipitates were washed several times with ethanol and deionized water, and dried under vacuum for 6 h. After calcining the collected precursors at 550 °C for 2 h in air, the Ce substituted 3D Mn_2O_3 were obtained and denoted as HPCMO. Similarly, HPCMO with different cerium amount (1 wt%, 2 wt%, and 8 wt%) were also prepared and designated as HPCMO-1, HPCMO-2 and HPCMO-8, respectively.

For comparison, the synthetic procedure of the pure 3D Mn_2O_3 was similar to the above method except for no addition of $Ce(NO_3)_3{\cdot}6H_2O$. The obtained sample was denoted as HPMO.

2.3. Characterization

The chemical composition of the samples was determined by the Thermo Scientific iCAP Qc inductively coupled plasma-mass spectroscopy (ICP-MS). XRD patterns were collected on a Bruker AXS D8-Focus X-ray diffractometer using a Cu Kα ray radiation source ($\lambda = 1.5406$ Å) with a scanning step of 0.05 s. The morphology and structure of the catalysts were observed using the high-resolution transmission electron microscope (HRTEM, JEM-2010FEF) and the field-emission scanning electron microscope (FE-SEM, Hitachi SU8010). The pore size distribution and N_2 adsorption isotherms of the catalysts were tested on the Micromeritics ASAP 2020 type apparatus, and the N_2 adsorption–desorption isotherms used the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectra (XPS) of catalysts were collected using a VG MULTILAB 2000 X-ray photoelectron spectrometer with Al Kα radiation at 300 W. Cyclic voltammetry (CV) measurements were carried out between −0.4 and 1.0 V (vs. Ag/AgCl) at the scan rate of 100 mV/s in 0.1 M Na_2SO_4 and 1 g/L PMS solution, and electrochemical impedance spectroscopy (EIS) data were collected at a frequency from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV using a CHI 660D electrochemical workstation.

2.4. Catalytic degradation of 2,4-DCP and analysis methods

The 2,4-DCP removal experiments were all carried out at 25 °C in a batch reactor containing 50 mg/L 2,4-DCP solution under the constant stirring. In a typical experiment, before the addition of PMS, 0.2 g/L of catalyst was added into 2,4-DCP solution for 60 min to achieve adsorption–desorption equilibrium. Then, the desired amount of PMS was added to trigger the Fenton-like reaction. At each time interval, the reaction solution was withdrawn, filtered and injected into a HPLC vial. After each run, the catalysts were recycled, washed by water and ethanol several times, and dried in an oven at 60 °C overnight for reuse. For the effect of leached ions on the catalytic oxidation process, the similar experimental procedure is carried out without adding PMS. After that, the suspension was filtrated to separate the catalyst, and then PMS was added to the solution to test the role of potential leached ions on the activation PMS by Ce substituted 3D Mn_2O_3.

The 2,4-DCP concentration was analyzed by an Agilent 1220 high performance liquid chromatography (HPLC) with UV lamp at 280 nm with a C18 column. The mobile phase was made of 60% methanol and 40% ultrapure water at a flow rate of 0.8 mL/min. Total organic carbon (TOC) was measured with a Shimadzu TOC-L CPH CN200 analyser. Ion chromatography (761 Compact IC, Metrohm, Switzerland) was used to determine the concentration of chloride ions (Cl^-) throughout the catalytic experiment. The eluent was 3.5 mM Na_2CO_3 with a flow rate of 1.0 mL/min. A JEOL JES-FA200 spectrometer was used for ESR analysis: temperature = 298 K, microwave frequency = 9.146 GHz, microwave power = 3 mW, and modulation amplitude = 0.5 mT. 5,5-Dimethyl-1-pyrroline (DMPO) was employed as the spin trapping agent in the EPR experiment for the detection of hydroxyl and sulfate radicals by measuring the DMPO-$^{\cdot}$OH and DMPO-$SO_4^{\cdot-}$ adducts. On the other