



Catalytic oxidation removal of ammonium from groundwater by manganese oxides filter: Performance and mechanisms

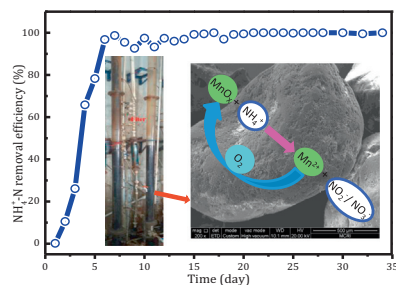
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HIGHLIGHTS

- Long-term filter tests were conducted to investigate NH_4^+ removal by MnO_x .
- Temporospatial evolution of NH_4^+ , NO_2^- and NO_3^- in filter was determined.
- The structural features of MnO_x were systematically investigated.
- NH_4^+ removal mechanisms by MnO_x catalytic oxidation were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

High concentration of ammonium (NH_4^+) often occurs in groundwater. In this study, the behavior of NH_4^+ catalytic oxidation by a manganese oxide (MnO_x) filter was investigated systematically and the formation and evolution of the MnO_x films were characterized extensively. It was found that the MnO_x based filter could be successfully started up within 6 days with the NH_4^+ removal efficiency increasing from 1 to 96%. After start-up, the removal efficiency of NH_4^+ could keep almost constant under different operating conditions, implying the MnO_x filter has a good stability towards NH_4^+ removal. Both X-ray diffraction (XRD) and Raman results suggested that MnO_x was related to hexagonal birnessite which has low crystallinity and small crystallite sizes. The X-ray photoelectron spectroscopy (XPS) spectra of the Mn2p taken on the surface of MnO_x revealed Mn(II), Mn(III) and Mn(IV) species existed in MnO_x materials and their atomic concentrations were 20.2%, 57.8% and 22%, respectively. More importantly, the catalysis of films towards NH_4^+ oxidation was expected to be closely related to its feature structure. Specifically, the ability of manganese to cycle between +2, +3 and +4 oxidation states during catalysis was considered to play important roles in the NH_4^+ conversion on MnO_x surface. Based on the above discussion, three major steps involve in NH_4^+ catalytic oxidation by MnO_x were proposed, which are NH_4^+ adsorption, catalytic oxidation, and desorption of reaction products.

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1. Introduction

High levels of ammonium (NH_4^+) in groundwater, and eventually in drinking water, pose a serious threat to people's health [1]. Many studies have shown that the presence of ammonium in water could not only cause solution odor but also lead to the generation of toxic disinfection byproducts [2–4]. Therefore, the

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removal of ammonium from water has received more and more attentions since the 1970s, and nowadays has become a basic and routine work for most drinking water treatment plants [5].

Many treatment options have been explored for ammonium removal, and these include ammonium stripping [6], adsorption [7], ion exchange [8], and filtration [4]. Filtration, as compared with other ammonium removal methods, possesses many advantages such as low cost, easy operation and no secondary pollution. Thus it is always considered to be one of the best suitable methods for treating ammonium-laden water [4]. In a traditional filtration system, microbe is generally recognized as the major contributor for the removal of ammonium [9–11]. They utilize reduced nitrogen (e.g., ammonium) as an energy source, carbon dioxide as a carbon source, and molecular oxygen as an electron acceptor [9]. Thus ammonium could be bacterially converted to nitrite (NO_2^-)/nitrate (NO_3^-), and/or to nitrogen gas. Although biofiltration has been thought to be an effective and reliable method for ammonium removal, this method also suffers some limitations. For instance, given the microbe used in this process are very sensitive to their growing conditions, it is hard to maintain their reactivity over a wide pH or temperature range. Also some halogen compounds, cyanides and heavy metals co-present in ammonium-containing water would significantly poison the bacteria [12]. Therefore, in order to improve the microbial ammonium removal efficiency in filters, many efforts have been made to culture and domesticate high-activity ammonium oxidizing bacteria [13]. For example, it was found that controlling the dissolved oxygen (DO), pH and oxidation reduction potential (ORP) of the influent or increasing the surface area of filter medias were effective to enhance the growths and reproductions of microbe [4,14].

Nevertheless, these options could not fully overcome the drawbacks of biotic ammonium removal. Therefore, from another perspective, in order to obtain efficient ammonium removal under different conditions, the abiotic oxidation of ammonium in filters may be a good choice. Actually, several chemical oxidation approaches for ammonium removal have been studied in recent years, including photocatalytic, electrochemical and ozone oxidation [12,15,16]. However, these methods are always too expensive for widespread use and may induce secondary pollution. To address this issue, searching for appropriate oxidants or catalysts that are abundant, efficient and cost effective is highly desirable.

Manganese oxides (MnO_x), usually coated on the filter media in filters for biotic ammonium removal from water, are also the most important naturally occurring reactants or catalysts in the transformation of many organic pollutants in natural environment [17–19]. Owing to the high oxidation potential ($E^0 = 1.23 \text{ V}$), manganese oxides could participate in a wide range of chemical reactions, including the chemical oxidation of ammonium. However, the abiotic transformations of ammonium by manganese oxides catalytic oxidation have been widely overlooked in the field of water treatment. Until recently, our group has confirmed that the effective catalytic oxidation of ammonium by MnO_x film could occur in filters [20], although the traditional wisdom claims that the effect of bacteria dominates the ammonium removal process when MnO_x -based filters are used. It was found that, despite inactivation processes were involved both in the filter film and raw water, 90% ammonium could be removed from water, and the reaction was still effective in a low temperature value (e.g., 6.6°C) [20]. However, with respect to the mechanism of ammonium catalytic oxidation by MnO_x , it has not been extensively investigated. On the other hand, the properties of the MnO_x film were also not characterized thoroughly, which should be quite helpful to understand the chemical reactivity of this manganese oxide.

Accordingly, the objectives of this work were to (i) investigate the catalytic oxidation processes of MnO_x for ammonium removal;

(ii) identify the structure, composition and morphology of the catalytically active MnO_x and (iii) explore the key prerequisites for the catalysis of MnO_x in ammonium oxidation.

2. Materials and methods

2.1. The start-up and operation of the filter

A pilot-scale filter system was set up near a groundwater resource area, which is located in Xi'an City, China. The column experiments were conducted using a plexiglass column (diameter, 10 cm; height, 200 cm) packed with 120 cm of quartz sand (0.75–1.20 mm particle size). As demonstrated in Fig. 1, seven sampling points (located at 0, 10, 25, 40, 60, 85, 120 cm from bottom to top) were attached along the height of the column. Groundwater pumped from a water source well was used as the feeding water for the filtration trials (the water parameters were listed in Table S1). After an aeration process, the concentration of dissolved oxygen (DO) in the influent was between 6.0 and 7.0 mg/L. During the start-up period (i.e., from 1st to 10th day in this work), potassium permanganate and manganese chloride (2 mg/L Mn^{2+}) with a mole ratio of 0.6 were added to the feeding water to produce MnO_x and then the suspension was pumped into the filter. After that, as the MnO_x film coated on the sand ripened, the solutions of potassium permanganate and manganese chloride were no longer added. Considering the ammonium concentration of raw groundwater ranged from 0.5 to 1.5 mg/L (see Table S1), NH_4Cl was sometimes added into the feeding water to obtain a higher ammonium concentration (e.g., 1.5 or 2.5 mg/L) for some specific tests. In order to prevent filter blockage, backwashing was performed every 48 h. The detailed initiating and operating processes of the filter system are described in Supporting Information (SI).

2.2. Analytic methods

During continuous pilot experiments, samples were collected in 500 mL polypropylene bottles and immediately analyzed after sampling. Mn^{2+} , NH_4^+ , NO_2^- , and NO_3^- were detected by spectrophotometry [21]. Temperature (T), DO and pH were determined by a portable instrument (HACH, HQ30d, USA). Alkalinity was determined by acid-base titration. In the batch experiment, the concentration of total dissolved manganese species was determined using an inductively coupled plasma mass spectrometry (ICP-MS, series 200-ElanDRC-e, PE, USA).

2.3. Micro characterization

In order to identify the structures of MnO_x coated on the quartz sands, X-ray diffraction (XRD) tests were performed. XRD data were obtained on Ultiman IV (Rigaku, Japan) at room temperature with $\text{Cu K}\alpha$ (1.54 Å) radiation. The beam voltage and beam current were set to 40 kV and 40 mA, respectively. Continuous scans were taken in a 2θ range of $7\text{--}75^\circ$ with a scan rate of 0.02 deg/s. The measurements of Raman spectra were performed on a JY HR800 Raman spectrometer. Scanning electron microscopy (SEM, FEI Quanta 600) was conducted to characterize the morphology of the MnO_x filter medias and the gold particles were sputtered onto the surfaces of samples before SEM test. X-ray photoelectron spectroscopy (XPS) data were obtained on K-Alpha XPS (Thermo Electron Corporation). All binding energy (BE) measurements were corrected for charging effects with reference to the $\text{C}1s$ peak at 284.6 eV (adventitious carbon). This reference gave BE values with an accuracy of 0.2 eV. The deconvolution method of XPS spectra is fitted by Gaussian function. The element contents of coating films on the surface of quartz sands were tested by energy dispersive

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