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A comparison study of the start-up of a MnO_x filter for catalytic oxidative removal of ammonium from groundwater and surface water

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ABSTRACT

As an efficient method for ammonium (NH_4^+) removal, contact catalytic oxidation technology has drawn much attention recently, due to its good low temperature resistance and short start-up period. Two identical filters were employed to compare the process for ammonium removal during the start-up period for ammonium removal in groundwater (Filter-N) and surface water (Filter-S) treatment. Two types of source water (groundwater and surface water) were used as the feed waters for the filtration trials. Although the same initiating method was used, Filter-N exhibited much better ammonium removal performance than Filter-S. The differences in catalytic activity among these two filters were probed using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and compositional analysis. XRD results indicated that different manganese oxide species were formed in Filter-N and Filter-S. Furthermore, the Mn3p XPS spectra taken on the surface of the filter films revealed that the average manganese valence of the inactive manganese oxide film collected from Filter-S (FS-MnO_x) was higher than in the film collected from Filter-N (FN-MnO_x). Mn(IV) was identified as the predominant oxidation state in FS-MnO_x and Mn(III) was identified as the predominant oxidation state in FN-MnO_x. The results of compositional analyses suggested that polyaluminum ferric chloride (PAFC) used during the surface water treatment was an important factor in the mineralogy and reactivity of MnO_x. This study provides the theoretical basis for promoting the wide application of the technology and has great practical significance.

Introduction

Human activity has drastically impacted the global nitrogen cycle, leading to excessive amounts of ammonium (NH_4^+) in groundwater and surface water (Qin et al., 2016). According to monitoring data from recent years, more than 40% of the surface water in China cannot meet the national standard for drinking water sources (<1.0 mg/L NH_4^+-N, Water Quality Standard for Drinking Water Sources (CJ3020-93)), being mainly contaminated by organic matter and ammonium (Feng et al., 2012). The presence of ammonium in water systems leads to oxygen depletion, eutrophication of surface water and toxicity for fish (Hasan et al., 2011; Li et al., 2011). Additionally, during drinking water treatment, ammonium must be removed before disinfection with chlorine because it consumes chlorine and produces chloramines (Cai et al., 2014). The above-mentioned

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situation has threatened the availability of safe drinking water and thus, human health.

To remove ammonium effectively and economically, a great deal of work has been done on ammonium treatment processes and removal pathways (Cheng et al., 2016; Du et al., 2016; Huang et al., 2015). Generally, physicochemical (chlorination, ion exchange, membrane filtration, *etc.*) (Feng and Sun, 2015; Kurama et al., 2002; Leaković et al., 2000; Sprynskyy et al., 2005) and biological methods (biological filter, biological contact oxidation, alga, photosynthetic bacteria, *etc.*) (Cai et al., 2015; Han et al., 2013; Luo et al., 2016; Wen et al., 2016) are the most effective methods for ammonium removal. However, there are both advantages and disadvantages for these methods. Excessive amounts of chlorine may stimulate the formation of undesirable chlorinated by-products in the drinking water (Choi and Valentine, 2002; Yu et al., 2007). The application of ion exchange and membrane filtration are limited due to their high capital and operational costs (Bódalo et al., 2005; Cai et al., 2015). Low temperature is another limiting factor in ammonium removal when using conventional biological approaches, which generally drastically affects the processing rate of nitrifying bacteria (Huang et al., 2013; Zhang et al., 2013). According to the literature (Zhang et al., 2013), the optimal temperature for nitrification in pure culture ranges from 25 to 35 °C. Below 15 °C, the nitrification rate drops sharply, which could result in nitrite accumulation.

More recently, a novel technology was proposed to remove ammonium from groundwater, which was called "contact catalytic oxidation technology". Specifically, a manganese oxide filter was built to remove ammonium from groundwater based on the abiotic transformation of ammonium by manganese oxide catalytic oxidation (Cheng et al., 2017). Enormous effort has been expended on this research (Cheng et al., 2017; Guo et al., 2015, 2017). The technology was able to achieve efficient ammonium removal from groundwater at low temperature (Guo et al., 2017). Additionally, the behavior of ammonium catalytic oxidation by the manganese oxide filter was investigated systematically, and the formation and evolution of the manganese oxide films were characterized extensively during the groundwater treatment (Cheng et al., 2017). However, no studies have been done to explore the feasibility of applying this "contact catalytic oxidation technology" to remove ammonium from surface water. This definitely could have a significant impact in the field of surface water purification, since a large number of water treatment plants use surface water rather than groundwater as a water source. Moreover, traditional drinking water treatment processes are usually ineffective in ammonium removal, especially during the winter when the average temperature is always below 10 °C (Qin et al., 2016; Huang et al., 2013; Zhang et al., 2013). Accordingly, in this study we attempted to apply this manganese oxide filter catalytic oxidation technology to surface water treatment. Unlike groundwater, surface water has some unique properties such as high turbidity, variable temperature and low hardness. All of these factors may affect the formation and/or the performance of manganese oxide films toward ammonium. On the other hand, considering that coagulation is always a necessary step in surface water treatment plants, and some coagulants (*e.g.*, polyaluminum ferric chloride (PAFC)) could remain in water after the coagulation/precipitation process, these residual coagulants may also influence the removal of ammonium by the manganese oxide filter.

In sum, this paper will compare the processes for ammonium removal during the start-up period for ammonium removal in groundwater and surface water treatment, and carries out a preliminary study of the limiting factors for the application of the technology in surface water treatment. This study aims to provide the theoretical basis for promoting the wide application of the technology.

Therefore, in this study, two types of source water (groundwater and surface water) were used as the feed water for the filtration trials. The ammonium removal performance of these two filters was compared during the start-up period. Meanwhile, the structure, composition and morphology of the manganese oxides were also characterized.

1. Materials and methods

1.1. The start-up and operation of filters

Two identical lab-scale gravity filters made of plexiglass were adopted for the start-up phase of ammonium removal. Schematic diagrams of the filter systems are shown in Appendix A Fig. S1. The filter column used in this study had an inner diameter of 100 mm and was filled with virgin quartz sand of size fraction 0.75–1.20 mm, with a height of 1.0 m. The detailed initiating processes of the filters are described in Appendix A. Two types of source water were used as the feed water for the filtration trials. Local raw surface water was used as the influent of the filter (Filter-S) in our lab at the south suburb of Xi'an, and local raw underground water as the influent of the filter (Filter-N) in a lab at the north suburb (Appendix A Fig. S2). The water quality of the raw groundwater and surface water are shown in Table 1. During the start-up period, potassium permanganate (MnO_4^-) and manganese chloride (Mn(II)) with a mole ratio of 0.6 were added to the feed water to form MnO_x, and then the suspension was pumped into the filter. When the influent ammonium could be removed almost completely, a filter was regarded as being successfully started and the addition of potassium permanganate and $MnCl_2$ solution was stopped. Backwashing was performed when filters became clogged. Ammonium was continually added in order to maintain an ammonium

Table 1 – Quality of the raw groundwater and surface water.

Parameters	Groundwater	Surface water
pH	7–8	7–8
Temperature (°C)	15–22	14–20
DO (mg/L)	4–6	4–6
TOC (mg/L)	1–3	1–5
Total hardness ($CaCO_3$)	70–80	190–200
TDS (mg/L)	110–120	460–470
Ca^{2+} (mg/L)	35–40	25–30
Mg^{2+} (mg/L)	23–25	3–5
HCO_3^- (mmol/L)	6	1.35

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