Reduction of MnO₂ dissolution by doping with ferric ion

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Abstract

MnO₂ nanofiber was found to possess high adsorption capacities for heavy metal ions such as, arsenic and lead, in water due to its high specific surface area (SSA) and high surface activity. However, a significant amount of manganese was found to leach from MnO₂ nanofibers. Reducing MnO₂ dissolution is very important for improving its applications in drinking water treatment. In this study, MnO₂ nanofiber was doped with Fe³⁺ to reduce its dissolution in water. Dissolution tests were conducted on un-doped and Fe-doped MnO₂ nanofibers. The results revealed that doping with Fe³⁺ significantly reduced MnO₂ dissolution. SSA and defects of MnO₂ materials were analyzed by BET and XRD methods. The effects of Fe³⁺ on MnO₂ dissolution were discussed and the optimal dopant amount was identified.

1. Introduction

Natural or synthetic manganese dioxide has been widely used in water filtration applications. It oxidizes ferrous (soluble) ion and manganese ion in water. The oxidized particles form precipitation, and then filtered out from water. Laboratory study by Ghurye and Clifford[1] revealed that manganese dioxide was the preferred oxidant for As(III) to As(V) conversion prior to the removal of arsenic from drinking water. US Filter also reported using hydrous manganese oxide to remove radium[2].

Inframat has developed unique nanofibrous MnO₂ via a wet chemical processing technique[3]. Each fiber is about 15 nm in diameter and a few hundred nanometers in length. The nanofibers randomly weave with each other to form “bird’s nest-like” morphology. Each “bird’s nest” is about 10 μm in diameter and is highly porous. More importantly, by modifying synthesis conditions, the morphology of nanofibers can be further controlled to facilitate the permeability of liquid through the material[4]. There are many potential applications for this unique material. We started to explore its application in water treatment since 2003 and have demonstrated that MnO₂ nanofibers outperformed commercial MnO₂ as oxidant for As(III) to As(V) conversion[5] and it was also an outstanding adsorbent for both As(V) and Pb(II)[6].

Regardless of all the outstanding characteristics of this material as oxidant and adsorbent for water filtration applications, a big concern is whether it is chemically stable in water. It is required by National Sanitation Foundation International, an independent, not-for-profit, non-governmental organization, that materials in contact with drinking water shall not impart levels of extractable contaminants that exceed the maximum contaminant concentration (MCC) or maximum drinking water level (MDWL) values. The MDWL for manganese is 0.3 mg/l and the advisory concentration is 0.05 mg/l[7]. The objective of this study is to reduce MnO₂ dissolution by doping it with Fe³⁺.
2. Experimental details

2.1. Preparation of MnO₂ nanofibers

MnO₂ nanofibers were synthesized via our patented procedure [3,4]. Here, 9.0 g of MnSO₄·H₂O was dissolved in 30 ml deionized water (D.I.W.) and 6.0 g of KMnO₄ was dissolved in 100 ml D.I.W. in separate containers. KMnO₄ solution was atomized and introduced to MnSO₄, resulting in brownish colloidal suspension. The colloidal suspension was then heat-treated in the range from 100 to 120°C for 2–24 h to gradually transform the amorphous particles into a random weave of nanofibers. The resulting nanofibers were filtered and washed with D.I.W. to remove the undesired reaction by-products. Finally, the material was dried in oven at 100°C for 6–12 h. The dried material was very fluffy and can be easily ground into fine powders.

The same procedure was used to synthesize Fe-doped MnO₂. The Fe³⁺ dopant was introduced by mixing proper amount of Fe³⁺-containing solution with MnSO₄ solution.

2.2. MnO₂ dissolution tests

A series of tests were conducted to find out dissolution of un-doped and Fe-doped MnO₂ materials. The test methods were adapted from NSF/ANSI 53-2002e as described in Table 1. Local tap water containing 0.5±0.05 mg/l free chlorine and with a pH of 6.75±0.25 was used as test water. First, 1.68 g powder was soaked in 100 ml test water for 24 h. Water was then separated from media using 0.2μm disc filter for analysis. The water samples were analyzed for manganese concentration by ICP–OES method at the Center of Environmental Science and Engineering at the University of Connecticut.

2.3. Other characterizations

SSA, crystal structure, and defects are material properties that are known to affect dissolution of iron oxides [8]. These properties are also expected to affect MnO₂ dissolution. The phases of the synthesized manganese oxides were determined by Bruker D5005 and D8 X-ray diffractometer. SSA was determined by N₂ adsorption, according to the BET method using Quantachrome NOVA 4200e surface area and pore size analyzer.

3. Results and discussion

3.1. MnO₂ dissolution tests

MnO₂ dissolution test results are listed in Table 2. Under the test condition described in Section 2.2, 8454 μg/l manganese was detected in water sample collected from dissolution test of un-doped MnO₂ (sample A), while only 4 μg/l manganese was detected in dissolution test of sample B (Fe-doped MnO₂). The difference was more than 2000 times. Usually doping may create crystal defects, such as vacancies, and accelerate dissolution, but this was not observed on Fe-doped MnO₂. According to Nesbitt and Banerjee, [9] synthesis of MnO₂ by reaction of Mn²⁺ with an oxidant (KMnO₄ used as oxidant) include two electron transfer steps: (1) oxidation of Mn²⁺ to produce Mn³⁺ oxyhydroxide as an intermediate reaction product on the surface and (2) subsequent oxidation of Mn³⁺-oxyhydroxide surface species to produce MnO₂. Some surface Mn³⁺ ions remain unoxidized and incorporated into MnO₂ structure. These Mn³⁺ ions are the sources of severe dissolution in un-doped MnO₂. Fe³⁺ is the ideal dopant for this system because it has the identical ion radius and same charge as Mn³⁺. When Fe³⁺ replaced Mn³⁺, the sources of MnO₂ dissolution was removed while the structure remained intact. Thus, MnO₂ dissolution was reduced dramatically.

Comparison of dissolution results among doped MnO₂ revealed that dissolution increased in some extent with the increase of Fe³⁺ amount in precursor solution. In general, dissolution of material depends on factors such as surface area, substitution ions and crystallinity. How the properties

| Sample ID | Fe(III):Mn(II) ratio in precursor solution | Mn extraction (μg/l) | Fe extraction (μg/l) |
|-----------|------------------------------------------|---------------------|---------------------|
| A         | 0                                        | 8454                | NA                  |
| B         | 0.04                                     | 4                   | ND                  |
| C         | 0.08                                     | 10                  | ND                  |
| D         | 0.16                                     | 42                  | ND                  |
| E         | 0.33                                     | 108                 | ND                  |

Note: NA, not available; ND, not detectable.
of the sample influence its dissolution behavior is still not fully understood. As these factors are interrelated, it is often difficult to isolate the effect of any one of them. As was discussed in the previous paragraph, no defects were expected when Fe\(^{3+}\) substituted Mn\(^{3+}\) in MnO\(_2\). However, when Fe\(^{3+}\) dopant amount exceeds Mn\(^{3+}\) in MnO\(_2\), excess Fe\(^{3+}\) ions will replace Mn\(^{4+}\) and create defects because (1) Fe\(^{3+}\) radius is bigger than Mn\(^{4+}\) radius and (2) oxygen vacancies may be created to maintain charge balance. These defects affect crystallinity and SSA of MnO\(_2\) and are expected to affect its dissolution in some extent. More results and discussions are on the next section.

3.2. Crystallinity, SSA and pore characteristics of MnO\(_2\) materials

X-ray analyses of un-doped and Fe-doped MnO\(_2\) are shown in Fig 1. Un-doped MnO\(_2\) possessed \(\alpha\)-MnO\(_2\) structure. Small amount of iron dopant (Fe\(^{3+}\): Mn\(^{2+}\) ratio in precursor solution up to 0.08) did not seem to affect MnO\(_2\) structure, as both samples B and C remained XRD pattern of \(\alpha\)-MnO\(_2\) in Fig. 1. However, crystallinity of MnO\(_2\) was severely degraded in samples D and E in which Fe\(^{3+}\):Mn\(^{2+}\) ratio in precursor solutions increased to 0.16 and 0.33, respectively. As was discussed in Section 3.1, when high dosage of Fe\(^{3+}\) was used, excess Fe\(^{3+}\) ions replaced Mn\(^{4+}\) and defects were created to maintain charge balance and accommodate radius difference between Fe\(^{3+}\) and Mn\(^{4+}\) ions. These defects degraded crystallinity and increased MnO\(_2\) dissolution to some extent. More defects are expected in sample E than any other sample because the highest Fe\(^{3+}\) dosage was used in sample E. Material dissolution involves the solid/solution interface reaction and is expected to increase with the increase of SSA. SSA and pore characteristics of MnO\(_2\) samples are listed in Table 3. Comparison among Fe\(^{3+}\)-doped MnO\(_2\) revealed that the SSA increased with the increase of Fe\(^{3+}\) dopant amount, so does the dissolution. SSA of any Fe\(^{3+}\)-doped MnO\(_2\) was higher than that of un-doped MnO\(_2\). However, this study revealed that dissolution of Fe\(^{3+}\)-doped MnO\(_2\) was much lower than that of undoped-MnO\(_2\), which suggested that the dissolution caused by higher SSA resulted from doping effect is far less significant than dissolution caused by Mn\(^{3+}\) in un-doped MnO\(_2\). So, although Fe-doped MnO\(_2\) has higher SSA (as high as 503 m\(^2\)/g for sample E), its dissolution was much lower than un-doped MnO\(_2\). The data on Table 3 also showed that high Fe\(^{3+}\) dosage-doped MnO\(_2\) materials, samples D and E, possess a substantial amount of micropores. Definition of micropore is the pore with diameter smaller than 20 Å. These micropores were related to defects resulted from substitution of Mn\(^{4+}\) by Fe\(^{3+}\). The creation of micropores significantly degraded crystallinity and increased SSA. Consequently, MnO\(_2\) dissolutions from sample D and E were found to be higher than low dosage Fe\(^{3+}\)-doped MnO\(_2\).

4. Summary

This study has showed that MnO\(_2\) dissolution was dramatically reduced, by doping with Fe\(^{3+}\). The primary cause of severe dissolution in un-doped MnO\(_2\) was unoxidized Mn\(^{3+}\) in the material. No structure defects were expected when Fe\(^{3+}\) replaced Mn\(^{3+}\), because Fe\(^{3+}\) has the identical ion radius and same charge as Mn\(^{3+}\). The ideal Fe\(^{3+}\) dosage should equal to the amount of Mn\(^{3+}\) in MnO\(_2\). When Fe\(^{3+}\) dopant amount exceed the unoxidized Mn\(^{3+}\) in MnO\(_2\), excess Fe\(^{3+}\) would replace Mn\(^{4+}\) and defects were created in MnO\(_2\) to maintain charge balance and accommodate size difference between Fe\(^{3+}\) and Mn\(^{4+}\). These defects degraded crystallinity and increased SSA, which increased dissolution to some extent. By optimizing Fe\(^{3+}\) dosage, the effects of crystal defects and SSA can be reduced. Based on this study, the optimal Fe\(^{3+}\) dosage was

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Table 3
Specific surface area and pore analysis results

| Sample ID | Fe(III):Mn(II) ratio in precursor solution | SSA (m\(^2\)/g) | Pore volume (cc/g) | Micropore volume (cc/g) | Sur. area from micropore (m\(^2\)/g) |
|-----------|------------------------------------------|-----------------|-------------------|-------------------------|--------------------------------------|
| A         | 0                                        | 112             | 0.37              | 0.001                   | 2.7                                  |
| B         | 0.04                                      | 172             | 0.32              | 0                       | 0                                    |
| C         | 0.08                                      | 203             | 0.33              | 0                       | 0                                    |
| D         | 0.16                                      | 431             | 0.39              | 0.13                    | 213                                 |
| E         | 0.33                                      | 503             | 0.44              | 0.19                    | 319                                 |

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Fig. 1. XRD patterns of MnO\(_2\) synthesized with different ratio of Fe\(^{3+}\): Mn\(^{2+}\) in precursor solutions: (A) 0, (B) 0.04, (C) 0.08, (D) 0.16, and (E) 0.33.
achieved by adding 0.04 mole of Fe$^{3+}$ for every mole of Mn$^{2+}$ in precursor solution. MnO$_2$ dissolution of the material made in such condition (sample B) was almost non-detectable (4µg/l).

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