



Reduction-induced aggregation of manganese dioxide colloids by guaiacol



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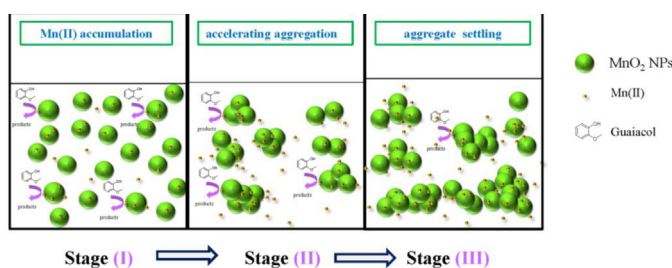
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HIGHLIGHTS

- The effective aggregation of MnO₂ colloids was mainly caused by adsorption of Mn(II).
- Reduction-induced aggregation was observed for MnO₂ colloids with guaiacol.
- The reduction-induced aggregation could be defined as three stages.
- The reduction-induced aggregation slowed down as the increase of pH.
- The decrease of guaiacol concentration retarded the reduction-induced aggregation.

GRAPHICAL ABSTRACT



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ABSTRACT

It is well known that the most abundant oxidizing agent in aquatic environments, manganese dioxide (MnO₂), can be reduced to Mn(II) by organics containing electron-rich moieties such as phenol, aniline, and thiol. It is expected that the redox reactions between MnO₂ colloids and electron-rich moieties may significantly affect the aggregation of MnO₂ colloids. This work, for the first time, reports a potential role of MnO₂ colloid reduction in their aggregation through time-resolved dynamic light scattering with guaiacol (2-methoxyphenol) as a model phenolic monomer. Data on initial aggregation kinetics show that additive Mn(II) exhibit excellent ability to cause MnO₂ colloidal aggregation compared with other divalent ions such as Ca(II) and Mg(II), probably due to its much higher surface affinity. As expected, the introduction of guaiacol results in a reduction-induced aggregation of MnO₂ colloids. As the redox reactions proceeded, the hydrodynamic diameter of MnO₂ colloids first decreased slightly despite the decreased electrostatic repulsion between them, then an accelerated rate aggregation of MnO₂ colloids was observed accompanying a further decrease of electrostatic repulsion, and finally the MnO₂ aggregates settled out. The reduction-induced aggregation slowed down with the increase of pH or decrease of guaiacol concentration. Surface bound Mn(II) might play a primary role in decreasing the electrostatic repulsion between MnO₂ colloids, and thus result in their reduction-induced aggregation.

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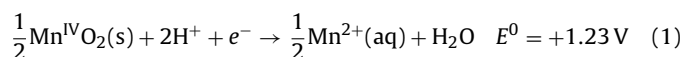
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1. Introduction

The occurrence of manganese dioxide (MnO₂) colloids in both natural waters (e.g., through weathering of minerals and biological catalysis of dissolved manganese(II)) and engineered systems (via permanganate (Mn(VII)) reduction and dissolved manganese(II) oxidation) is well documented [1–3]. Once MnO₂ colloids are formed, aggregation might significantly impact their surface properties (e.g., adsorption and oxidation), and thus affect their aquatic transport as well as that of associated contaminants [4–6].

Recently, the initial aggregation kinetics of MnO₂ colloids have been investigated under various conditions with/without humic substances and biomacromolecules in the presence of both mono- and divalent ions, such as Na(I), Mg(II), and Ca(II) [7]. The aggregation of MnO₂ colloids was more efficient in the presence of Ca(II) than in the presence of Mg(II), as the former has a higher affinity for the MnO₂ surface. It has been reported previously that Mn(II) has increased affinity for MnO₂ surfaces compared with various other divalent cations (e.g., Ca(II), Mg(II), Sr(II), Ni(II), Cd(II), Ba(II), and Zn(II)) [8,9], so it can be expected that Mn(II) may also lead to aggregation of MnO₂ colloids more effectively than other divalent cations. Perez-Benito et al. reported such an observation qualitatively with coagulation experiments. Nevertheless, accurate data on the aggregation of MnO₂ colloids in the presence of Mn(II) is currently not available and might deepen our understanding of their aggregation.

Moreover, MnO₂ is also known as a potential oxidizing agent of natural and xenobiotic organic compounds containing electron-rich moieties such as phenol, aniline, and thiol due to its strong oxidation ability under neutral conditions [10]:



For instance, the oxidation of various phenolic compounds such as humic model monomers (e.g., guaiacol (2-methoxyphenol) and catechol) and man-made pollutants (e.g., triclosan and 2,4-dichlorophenol) by MnO₂ has been widely investigated [11–14]. Also, MnO₂ has been shown to oxidize various anilines (e.g., chloroanilines, toluidine, anisidine) [15,16] and thiols (such as cysteine and glutathione) [5,17]. The low state Mn(II) has been reported to be the final stable product of manganese therein. Thus, the redox reactions between MnO₂ colloids and organic matter containing electron-rich moieties might lead to MnO₂ colloidal aggregation in aquatic environments.

Previously, aggregation and dissolution have been widely investigated for various metal nanoparticles (NPs), such as zero valent silver (nAgNPs), ZnO, SiO₂, and quantum dots (QDs) [18–24]. These results have shown that the aggregation and dissolution behavior of these NPs depend on not only the characteristics of the colloid (e.g., size, elemental components, aggregate structure, and coating) but also those of the surrounding environment (e.g., organic matter, pH, and irradiation). Only limited work has focused on the interplay between aggregation and dissolution of NPs [25,26]. For example, Di et al. [26] reported the effect of the aggregate structure of nAgNPs on their dissolution rate. Zhang et al. [25] examined the relationship between the dissolution kinetics of nAgNPs and their primary particle size and concentration. However, to our knowledge, data on the role of the product ions originating from MnO₂ colloidal redox reactions on their aggregation have not been reported yet.

In this work, we examine the initial aggregation kinetics of MnO₂ colloids driven by Mn(II) at environmentally relevant pH by time-resolved dynamic light scattering (TR-DLS). Moreover, the reduction-induced aggregation of MnO₂ colloids was assessed using guaiacol as a model phenolic monomer, and further explored mechanistically. Finally, the effects of water pH and guaiacol concentration on aggregation were investigated.

2. Materials and methods

2.1. Materials

All chemicals were used as received. KMnO₄, Na₂S₂O₃, MnCl₂·4H₂O, sodium borate (Na₂B₄O₇·10H₂O), NaOH, and HNO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-(*N*-Morpholino)-ethanesulfonic acid (MES, pK_a = 6.1), 3-(*N*-morpholino)-propanesulfonic acid (MOPS, pK_a = 7.2), and guaiacol were purchased from Sigma–Aldrich Company. The guaiacol stock solution (1 mM) was prepared in deionized (DI) water (>18.2 MΩ cm) and stored at 4 °C and used in one week. The pH was buffered at 6.00 ± 0.05 by MES, 7.00 ± 0.05 by MOPS, or 8.50 ± 0.05 by sodium borate. These buffers were selected because their inertness in reducing MnO₂ [27,28], as confirmed in our preliminary studies (Figs. S1–S3).

2.2. Synthesis and characterization of MnO₂ colloids

MnO₂ colloids were synthesized and characterized following the method used in our previous study [7]. Details on the synthesis and characterization of MnO₂ colloids were provided in the SI (Text S1). The dark brown MnO₂ colloidal stocks were stored in the dark at 4 °C. The mean oxidation state of Mn in synthesized colloids was ~4.0. Important colloidal characteristics described as average diameter and Zeta potential were about 55 nm and –42 mV, respectively.

2.3. Aggregation experiments, electrophoretic mobility (EPM) measurements, and determination of dissolved Mn(II)

The Mn(II)-induced aggregation of MnO₂ colloids was conducted following the similar processes used in our previously [7]. Details on these experiments and determination of aggregation kinetics were provided in SI (Text S2). Aggregation of MnO₂ colloids in the presence of guaiacol was conducted on Zetasizer (Nano ZS90, Malvern, UK) operating with a He–Ne laser at a wavelength of 633 nm. The changes of MnO₂ colloidal intensity-weighted averaged hydrodynamic diameter with time were measured using TR-DLS. In these experiments, a certain amount of guaiacol solution was added into the DLS cuvette containing a predetermined volume of diluted MnO₂ colloidal suspension so that the total volume of the final suspension was 2 mL. The concentration of MnO₂ colloids in DLS vial was controlled at 300 μM. The quartz cuvette was then immediately vortexed for 1 s and placed into the light scattering unit. Immediately, the hydrodynamic diameter measurement was started. All the aggregation measurements were conducted at a scattering angle of 90° and each autocorrelation function was accumulated for 1 min. For all determination of average hydrodynamic diameter of MnO₂ colloids in aggregation experiments, the polydispersity index (PDI), reported directly from the Zetasizer Nano ZS instrument could also be recorded to interpret the broadness of the size distribution.

The EPM measurements were conducted on a Zetasizer (Nano ZS90, Malvern, UK) operating with a He–Ne laser at a wavelength of 633 nm. To determine the impact of added Mn(II) concentration on the MnO₂ colloidal EPM of suspensions, the identical procedure used in the Mn(II)-induced aggregation experiments was employed. The EPM values of MnO₂ colloids in reduction-induced aggregation experiments were also obtained in the presence of 60 μM guaiacol at different time and pH.

The dissolved Mn(II) concentrations in the reduction-induced aggregation were quantified using an inductively coupled plasma mass spectrometer (ICP-MS, NexION 300Q, PerkinElmer Corp.) after

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