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Interactions in Ternary Mixtures of MnO_2 , Al_2O_3 , and Natural Organic Matter (NOM) and the Impact on MnO_2 Oxidative Reactivity

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Abstract

Our previous work reported that Al_2O_3 inhibited the oxidative reactivity of MnO_2 through heteroaggregation between oxide particles and surface complexation of the dissolved Al ions with MnO_2 (S. Taujale and H. Zhang, “Impact of interactions between metal oxides to oxidative reactivity of manganese dioxide” *Environ. Sci. Technol.* 2012, 46, 2764–2771). The aim of the current work was to investigate interactions in ternary mixtures of MnO_2 , Al_2O_3 , and NOM and how the interactions affect MnO_2 oxidative reactivity. For the effect of Al ions, we examined ternary mixtures of MnO_2 , Al ions, and NOM. Our results indicated that an increase in the amount of humic acids (HAs) increasingly inhibited Al adsorption by forming soluble Al–HA complexes. As a consequence, there was less inhibition on MnO_2 reactivity than by the sum of two binary mixtures (MnO_2 +Al ions and MnO_2 +HA). Alginate or pyromellitic acid (PA)—two model NOM compounds—did not affect Al adsorption, but Al ions increased alginate/PA adsorption by MnO_2 . The latter effect led to more inhibition on MnO_2 reactivity than the sum of the two binary mixtures. In ternary mixtures of MnO_2 , Al_2O_3 , and NOM, NOM inhibited dissolution of Al_2O_3 . Zeta potential measurements, sedimentation experiments, TEM images, and modified DLVO calculations all indicated that HAs of up to 4 mg-C/L increased heteroaggregation between Al_2O_3 and MnO_2 , whereas higher amounts of HAs completely inhibited heteroaggregation. The effect of alginate is similar to that of HAs, although not as significant, while PA had negligible effects on heteroaggregation. Different from the effects of Al ions and NOMs on MnO_2 reactivity, the MnO_2 reactivity in ternary mixtures of Al_2O_3 , MnO_2 , and NOM was mostly enhanced. This suggests MnO_2 reactivity was mainly affected through heteroaggregation in the ternary mixtures because of the limited availability of Al ions.

Graphical Abstract

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ASSOCIATED CONTENT

Supporting Information

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Supporting Information including Texts S1–S5, seven figures and one table is available (PDF)

The authors declare no competing financial interest.

INTRODUCTION

Manganese oxides have a vital role in the fate and transport of organic contaminants in the environment, mostly via adsorption, hydrolysis, and redox reaction of the contaminants.^{1–7} Although numerous work has examined the reactivity of MnO_2 as a single oxide, the obtained results cannot be directly extrapolated to natural soil-water systems because they are more complex mixtures containing various metal oxides and natural organic matter (NOM). A previous study of ours revealed that among the metal oxides examined, Al_2O_3 had the most negative impact on the oxidative reactivity of MnO_2 , mostly through both heteroaggregation between the oxide particles and complexation of the Al ions released from Al_2O_3 with MnO_2 .⁸ Both interactions block the reactive sites on MnO_2 surface to make it less reactive, with the complexation of Al ions with MnO_2 the dominant inhibition mechanism.

NOM is ubiquitous in the environment and can interact extensively with various metal oxides. For instance, sorption of NOM by metal oxides such as aluminum and iron oxides has been extensively reported to occur through ligand exchange, complexation with the acidic ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) functional groups, hydrogen bonding, electrostatic interaction, and cation bridging among others.^{9–13} NOM can also significantly affect the redox reactivity of MnO_2 ^{1,4} and sorption of metal ions by metal oxides. In ternary mixtures of metal ions, NOM, and metal oxides, multiple interactions exist: (i) formation of soluble complexes in solution, (ii) formation of ternary surface complexes, (iii) competition for surface sites, and (iv) changing electrostatic properties of the oxide surface.¹⁴ Metal ions such as Al^{3+} , Fe^{3+} and Cu^{2+} are known to form strong soluble complexes with NOM or NOM model compounds,^{15–18} leading to decrease in their sorption by oxide surfaces.^{19,20} For strongly complexing ions (Me) such as Cu^{2+} , both type A (surface–Me–HA) and type B

(surface–HA–Me) complexes can form, but the relative contribution of each complex depends greatly on the solution condition.¹⁸ For weakly complexing ions such as Ca^{2+} , electrostatic interactions dominate the sorption so there is weak sorption of Ca^{2+} by the positively charged goethite but strong sorption of Ca^{2+} by the negatively charged fulvic acid (FA).^{14,21} Alginate, a widely used model compound for polysaccharides, was also found to complex with divalent metal ions such as Ca^{2+} , Sr^{2+} , and Ba^{2+} .²²

Despite the above knowledge, we know little about how NOM affects oxide redox reactivity in mixed oxide systems. Our recent work examined how NOM affects oxidative reactivity of MnO_2 in the presence of Fe(III) oxides.²³ The primary goal of this study was to examine the reactivity of MnO_2 in ternary mixtures with Al_2O_3 and NOM. To examine how MnO_2 reactivity was affected by heteroaggregation with Al_2O_3 in the presence of NOM, we conducted sedimentation experiments for the extent of aggregation, measured zeta potentials for oxide surface charges, examined transmission electron microscopic (TEM) images of oxide particles, conducted modified DLVO calculations of interaction energy profiles, obtained adsorption isotherms of NOM, and collected ATR-FTIR images of soluble vs adsorbed NOM. To examine how MnO_2 reactivity was affected by Al complexation in the presence of NOM, we measured dissolution of Al_2O_3 in binary and ternary mixtures and examined adsorption of NOM and Al ions in ternary systems of MnO_2 , NOM, and Al ions. Similar to our previous works,^{8,23} the oxidative reactivity of MnO_2 in all mixtures was measured based on the oxidation kinetics of triclosan, a widely used antibacterial agent.

The NOMs used in this study are Aldrich humic acid (AHA), Leonardite humic acid (LHA), alginate, and pyromellitic acid (PA). Alginate, a natural polymer, is commonly studied as a model NOM and has shown to stabilize fullerene nanoparticles. Its reported molecular weight is 12–80 kDa and is composed of blocks of 1,4-linked β -D-mannuronic acid and α -L-guluronic acid. Similar to HA, adsorbed alginate changes the surface charges of metal oxides and affects the stability of the oxides.^{9,10} PA ($\text{C}_{10}\text{H}_6\text{O}_8$) is used as a model NOM, as previous studies have reported its adsorption behavior to be analogous to that of naturally occurring NOM.²⁴ Compared to the other NOM used in this study, PA is a much smaller molecule (molecular weight: 254.15 g/mol).²⁴

MATERIALS AND METHODS

Details on the chemicals, oxide preparation, experimental setup and analysis for triclosan oxidation kinetics, TEM images, sedimentation, zeta potentials, adsorption of NOM, and ATR-FTIR images are shown in Text S1 in the Supporting Information (SI). Briefly, for triclosan oxidation kinetics, the reactors contained 5 mg/L of MnO_2 , 10 μM of triclosan, 0.01 M NaCl, and 25 mM acetic acid to maintain a pH of 5.0. Aliquots of reaction suspensions were added into centrifuge tubes containing enough 1 M NaOH to raise the suspension pH to greater than 10. This was followed by centrifugation at 12 100g for 20 min. Previous studies have shown that triclosan oxidation is very slow at alkaline pH thus quenching the reaction, and also pH > 10 desorbs >98% triclosan from the metal oxides.¹ This method allowed us to measure loss of triclosan due to oxidation only. After centrifugation, the supernatants were transferred to separate vials for triclosan analysis by an Agilent 1200 HPLC.

TEM images were collected on a JEOL (JEM 1400) transmission electron microscope. Details on sample preparation are in SI Text S1. Sedimentation experiments of Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$ in the presence of various NOMs were conducted at pH 5.0 by using a UV–vis spectrophotometer. The optical absorbance by Al_2O_3 or $\text{Al}_2\text{O}_3+\text{MnO}_2$ were measured at 508 nm as a function of time.²⁵ Zeta potentials and pH_{zpc} were measured using a Zetasizer Nano ZS (Malvern Instruments). The observed effects of NOM on the surface charge of Al_2O_3 are in SI Text S3. ATR-FTIR spectra of the soluble and adsorbed PA were collected with a PerkinElmer Spectrum 100 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Details on the instrument conditions, sample preparations along with the results are described in SI Texts S1 and S4.

Adsorption of NOMs by either Al_2O_3 or $\text{Al}_2\text{O}_3+\text{MnO}_2$ was carried out under experimental conditions identical to kinetic experiments while varying the initial concentrations of NOM. The amounts of NOM adsorbed by Al_2O_3 or $\text{Al}_2\text{O}_3+\text{MnO}_2$ were calculated by subtracting the amounts of NOM measured in the filtered samples from the initial NOM concentrations (C_i). Note that our control experiments have showed negligible adsorption of the NOMs by the filters. AHA, LHA, and PA concentrations were measured by UV–vis while alginate concentrations were measured by a TOC analyzer.

Adsorption experiments of Al ions by MnO_2 were carried out as a function of NOM concentration. To prepare the reactors, 5 mg/L of MnO_2 was added to 50 mL DI water with 0.01 M NaCl and 25 mM of acetate buffer. Al ion was added to suspensions to maintain an initial concentration of 0.009 mM or 0.03 mM. After equilibrating the mixture for an hour by stirring on a magnetic stir plate, NOM was added to the reactors. After allowing the mixtures to stir overnight, they were filtered using 0.22 μm filters. The filtrates were acidified using 1 M HCl and the Al concentrations in the filtrates were measured using an ICP-MS.

Dissolution experiments of Al_2O_3 in single oxide systems, i.e., only Al_2O_3 , and in binary oxide mixtures of $\text{Al}_2\text{O}_3+\text{MnO}_2$ were carried out as a function of NOM concentration. 0.1 g/L of Al_2O_3 and 5 mg/L of MnO_2 were added to reactors containing 50 mL DI water, 0.01 M NaCl, and 25 mM acetic acid buffer. The reactors were allowed to equilibrate for an hour before adding the NOM. The mixtures were then equilibrated overnight on a magnetic stir plate and centrifuged followed by filtration through 0.22 μm filters. The filtrates were acidified using 1 M HCl and Al concentrations were measured using an ICP-MS.

RESULTS AND DISCUSSION

NOM Adsorption by Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$

NOM adsorption by Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$ was determined while varying the concentration of AHA or LHA from 0 to 52.4 or to 82.9 mg-C/L, respectively. The concentrations of both alginate and PA were varied from 0 to 200 mg/L. For both HAs and the model NOMs, we did not see a significant difference in the amount of NOM adsorbed by Al_2O_3 and by $\text{Al}_2\text{O}_3+\text{MnO}_2$ (Figure 1). This was mostly because of the negligible adsorption of the NOMs by MnO_2 .²³ Therefore, any adsorption of NOM by $\text{Al}_2\text{O}_3+\text{MnO}_2$ is mostly due to Al_2O_3 only. One difference observed among the adsorption trends of the

NOMs was that the HA systems had reached an equilibrium between 20 and 25 mg-C/L, whereas the adsorption trends for both alginate and PA were still linear even at the highest initial NOM concentration of 200 mg/L. A comparison between alginate and PA adsorption reveals a higher alginate adsorption by both systems. A lower adsorption of HAs compared to alginate/PA at high concentrations is most likely associated with the significantly larger size of the HA molecules that prevents further adsorption of HAs on oxide surfaces due to steric effects.

Effects of NOM on the Homo- And Heteroaggregation of Metal Oxides

TEM images were used in analyzing the extent of homo and heteroaggregation between the oxide particles at pH 5.0 and 0.01 M NaCl. Images of single oxides and oxide mixtures were obtained in the presence of different concentrations of NOM. Selected area diffraction (image not shown) indicated that the MnO_2 (SI Figure S3a) used in our study is amorphous, SI Figure S3b shows Al_2O_3 as distinct nanoparticles, and SI Figure S3c suggests intensive heteroaggregation between MnO_2 and Al_2O_3 under the examined conditions. TEM analysis was also conducted for MnO_2 and $\text{MnO}_2+\text{Al}_2\text{O}_3$ in the presence of 0.4 mg-C/L of AHA. Addition of AHA seemed to have little effect on either the homoaggregation between the MnO_2 particles (SI Figure S3d) or the heteroaggregation between Al_2O_3 and MnO_2 (Figure S3e). It must be noted that the air drying process of the sample grids may affect the aggregation between the oxide particles, so the TEM images obtained may not represent the oxide interactions in the aqueous suspension. Therefore, we conducted sedimentation experiments as an alternative method to study the effect of NOMs on the extent of both homo and heteroaggregation. It is also worthwhile to mention that light scattering techniques were not used to study the aggregation due to the wide range of particle size distribution in our systems.

The effect of NOM on the homo and heteroaggregation of the oxide particles was studied by monitoring the sedimentation rates of Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$ at varying NOM concentrations. To measure the extent of homo or heteroaggregation between the oxide particles, rather than the rate of aggregation, the systems were allowed to equilibrate for overnight before UV-vis analysis. Therefore, the systems had reached a pseudo steady-state of aggregation after the pre-equilibrium. The rate of sedimentation is correlated to the size of the aggregates. Faster sedimentation corresponds to a higher extent of aggregation and slower sedimentation corresponds to a lesser extent of aggregation. As shown in Figure 2a and c, AHA and LHA affected the sedimentation rates of Al_2O_3 to a certain extent. Sedimentation of Al_2O_3 increased as the concentrations of AHA were increased. In the case of LHA, the sedimentation rate was higher when the concentration of LHA was less than 4.6 mg-C/L but much lower when LHA concentration reached 12.5 mg-C/L. The sedimentation of the Al_2O_3 particles occurs as a result of homoaggregation. The higher sedimentation rate when the HAs were added is likely due to the neutralization of surface charges of Al_2O_3 by the adsorbed HA molecules, leading to more aggregation. Upon further increase in the concentration of the HAs, there was enough HA to reverse the surface charge (SI Figure S1b) such that the colloids were electrostatically stabilized.

$\text{Al}_2\text{O}_3+\text{MnO}_2$ had higher sedimentation rates at 0 to 2 mg-C/L AHA as compared to the sedimentation rates at 4–10 mg-C/L AHA (Figure 2b). Similar results were seen in sedimentation of the binary oxide at varying concentrations of LHA (Figure 2d). Given the opposite surface charges of Al_2O_3 and MnO_2 at pH 5 (SI Figure S1a), in the absence of HA or at low HA concentrations, a higher extent of heteroaggregation is expected to occur between the oxides. At HA concentration 10 mg-C/L, the binary oxide suspensions did not sediment over time indicating there was negligible homo or heteroaggregation between the particles. Although there was sedimentation in the Al_2O_3 system at 10 mg-C/L HA, the $\text{Al}_2\text{O}_3+\text{MnO}_2$ system with 10 mg-C/L of HAs was more stable. The difference in the stabilities of the two systems is most likely due to the difference in Al_2O_3 concentration (0.2 vs 0.1 g/L in single Al_2O_3 vs binary oxide systems). Since there is insignificant AHA adsorption by MnO_2 , there is a higher amount of AHA adsorbed by Al_2O_3 in the binary oxide system which imparts more negative charge on the oxide surface and hence decreases the homoaggregation within the Al_2O_3 . As shown in Figure 1a, the majority of AHA at concentrations less than 10 mg-C/L was adsorbed by 0.1 g/L of Al_2O_3 . With 0.2 g/L of Al_2O_3 , majority of AHA should be adsorbed as well. Therefore, the adsorption density of AHA is less for 0.2 g/L of Al_2O_3 , which would lead to less impact of AHA on the surface charge of Al_2O_3 at 0.2 g/L than at 0.1 g/L.

Sedimentation results with alginate are similar to those with the HAs (SI Figures S4e,f). In both single and binary oxide systems, sedimentation rates initially increased with increasing alginate concentration but decreased again when alginate concentration was above 10 mg/L. These results show that there was a decrease in the extent of heteroaggregation between MnO_2 and Al_2O_3 when a larger amount of alginate (10 mg/L) was added to the system. SI Figures S4g,h show that, although PA adsorption by the oxides is only slightly lower than alginate adsorption, varying concentrations of PA did not affect the sedimentation rates of Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$. One of the possible reasons for the difference in sedimentation patterns is the steric hindrance effect in the case of alginate. This effect could be lower for PA due to its much smaller molecular size. However, further studies are needed to confirm this possibility.

Extended DLVO Calculations

The DLVO theory has been widely used to examine the interaction mechanisms between particles in aqueous systems. The overall interaction energies between the particles are determined based on the sum of two forces *viz.* electrostatic repulsive forces and van der Waals attractive forces. However, in the presence of NOM, steric repulsion due to the large NOM molecules attached on the oxide surfaces also contributes to the overall interaction between the particles. Therefore, in our systems the net energy between the particles was determined based on the sum of the three forces. As shown in our previous work,²³ the modified DLVO theory can better explain the aggregation patterns between metal oxides in the presence of NOM.

The interaction energy profiles shown in SI Figure S5a are based on the classical DLVO theory, which does not consider the steric repulsive energy. They indicate net negative interaction energies of zero at all concentrations of AHA. However, based on the

information gathered from the sedimentation experiments, there was a negligible amount of aggregation in the mixed oxide system at higher HA concentrations. This shows the inadequacy of the classical DLVO theory in explaining the stable behavior of the oxides at higher concentrations of AHA. For the calculation purpose, the reported estimated values of 7 nm²⁶ or 5.7 nm²⁷ for the thickness of HA adsorbed on the surface of hematite and TiO₂, respectively, were used to represent the thickness of the adsorbed AHA layer (SI Text S5). The energy profiles for the interaction between MnO₂ and Al₂O₃ based on these values (SI Figures S5b,c) show the overall interaction energies to be positive at 4 and 10 mg-C/L AHA. These results are in agreement with the results seen in our sedimentation experiments, supporting the mixed oxide system to be stable at higher concentrations of HA.

Dissolution of Al₂O₃ in the Presence of NOM

To understand the importance of Al ions on MnO₂ reactivity in ternary MnO₂+Al₂O₃+NOM mixtures, we measured the amount of Al dissolved from Al₂O₃ in the mixtures. The detected Al ion concentrations in the single and binary oxide systems as a function of NOM are shown in Figure 3. Figure 3a shows that the amount of Al dissolved in the single Al₂O₃ suspension mostly decreased as the concentration of NOM was increased. In the absence of NOM, a much lower concentration of Al ions was measured in the binary oxide system (Figure 3b) than in the single oxide system. This is mainly a result of intense heteroaggregation between Al₂O₃ and MnO₂ as well as the adsorption of Al ions by MnO₂.⁸ After the addition of NOM to the binary oxide mixture, there was a slight decrease in Al ion concentration with increase in most of the NOMs (Figure 3b). This is again due to the passivation of Al₂O₃ surfaces upon NOM adsorption to inhibit its dissolution. Indeed, outer-sphere ligands such as PA and HA are known to inhibit dissolution of Al oxides.^{28–30} Addition of alginate of >10 mg/L led to a significantly increased dissolution of Al₂O₃ in both single and binary oxide systems, further research is however needed to elucidate the Al ion release mechanism.

Adsorption of Al Ions by MnO₂ With or Without NOM

Because of the dissolution of Al₂O₃ to form soluble Al ions, we had to examine ternary mixtures of MnO₂, Al ion, and NOM to fully understand the role of Al ions in ternary mixtures of MnO₂, Al₂O₃, and NOM. This included examining how soluble Al is adsorbed by MnO₂ in the absence and presence of NOM, how Al ions affect NOM adsorption, and how Al ions affect oxidative reactivity of MnO₂, as shown in the following three sections.

Our previous work showed that Al ions can sorb strongly to the MnO₂ surface which significantly lowered the oxidative reactivity of MnO₂.⁸ The sorption of a number of divalent metal cations on a hydrous Mn oxide has been modeled based on a 2-site diffuse double layer model.³¹ We adopted the same modeling approach to provide macroscopic information on the formed surface complexes. As details shown in the SI Table S1 and Figure S6, there are mainly two types of surface complexes formed:

where $\equiv \text{XOH}$ and $\equiv \text{YOH}$ are the strong and weak surface sites, and $\equiv \text{XAl}^{2+}$ and $\equiv \text{YAl}^{2+}$ are the two types of inner-sphere surface complexes formed. Based on the obtained complexation constants, Al ions can be strongly sorbed by MnO_2 .³¹ Al ions have also been reported to be able to form strong complexes with NOM and NOM model compounds.^{16,32}

At both 0.009 and 0.03 mM Al ions, the adsorption of Al ions by MnO_2 decreased with the increase in AHA or LHA concentration (Figure 4). This is likely due to (1) competition of the HAs and Al ions for the limited number of surface sites and (2) formation of soluble Al–HA complexes that resist adsorption by MnO_2 . As reported, the enhanced oxidative reactivity of MnO_2 in the presence of metal ions and 0.1–1 mg/L of HA was attributed to the strong binding ability of HA for the ions and thus less “occupied” surfaces of MnO_2 by the ions.⁴ In addition, in the presence of FA, sorption of Cu^{2+} by hematite decreased at $\text{pH} > 6$ due to an increasing concentration of soluble Cu–FA complexes.¹⁹ The decrease in the amount of Al adsorbed with an increasing amount of LHA and AHA is thus at least partly due to soluble Al–HA complexes formed. Because the effect of LHA on the amount of Al sorbed is more significant than AHA, LHA might have formed stronger complexes with Al ions than AHA.

Adsorption of Al ions by MnO_2 was only slightly lowered by the presence of a large amount of alginate or PA (Figure 4). This could be mainly due to the poor ability of alginate and PA to form soluble complexes with Al ions. Indeed, PA was reported to only form outer-sphere complexes with Al and Fe oxides.^{28,30} The less adsorption of alginate and PA by MnO_2 when their concentrations are not too high (Figure 1b) could be another reason, which allows little competition for surface sites.

Effect of Al Ions on NOM Adsorption by MnO_2

The presence of Al ions could also affect the extent of NOM adsorbed by MnO_2 . As the results show in Figure 5a,b, the adsorption of AHA and LHA by MnO_2 increased when the concentration of soluble Al was increased from 0 to 0.009 mM. There was an even higher increase in the adsorption of both AHA and LHA by MnO_2 when the concentration of soluble Al was increased to 0.03 mM. The higher adsorption of both HAs by MnO_2 in the presence of Al ions is likely due to the neutralization of MnO_2 negative surface charge upon adsorption of the positively charged Al ions. This results in more adsorption of the negatively charged HAs.^{16–18} Addition of Ca^{2+} and Cu^{2+} was found to increase the amount of FA adsorbed by goethite.^{14,21} There is also a likelihood of surface ternary complex formation. Given the fact that Al ions can form strong complexes with both MnO_2 and HA, and HA is typically only adsorbed as outer-sphere complexes,^{20,28–30} the observation that Al ions slightly enhanced HA sorption is likely partly due to the formation of ternary A complex ($>\text{Mn}-\text{Al}-\text{HA}$).³³

Adsorption of alginate and PA by MnO_2 was not affected or slightly lower upon the addition of 0.009 mM Al ions, but increased in the presence of 0.03 mM Al ions than in the absence

of the Al ions (Figure 5c,d). Together with the observation that alginate and PA did not affect Al adsorption (Figure 4), there seemed to be only minor electrostatic effects between alginate/PA and Al ions in affecting each other's adsorption by MnO₂.

Reactivity of MnO₂ with Al Ions and NOM

Rate constants (k) for triclosan oxidation by MnO₂ were calculated using pseudo first-order kinetics for the initial reaction period (typically <1 h at pH 5, examples in SI Figure S7).¹ k will be used as an indicator for MnO₂ oxidative reactivity throughout this work.

Similar to our previous work,²³ the obtained k values were converted to term “ P ”. P values will be used to distinguish the effects of NOM on MnO₂ reactivity from those of Al₂O₃ or Al ions. This is done by normalizing the reactivity of MnO₂ in the presence of NOM ($k_{\text{with_NOM}}$) by that in the absence of NOM ($k_{\text{without_NOM}}$):

$$P = \frac{k_{\text{withNOM}}}{k_{\text{withoutNOM}}} \times 100\% \quad (3)$$

For example, k_{withNOM} of MnO₂+Al₂O₃+NOM vs $k_{\text{withoutNOM}}$ of MnO₂+Al₂O₃. P values can suggest how the addition of NOM affects the reactivity of MnO₂. A P value of greater than 100% would indicate an enhancing effect of NOM while a P value of lower than 100% would indicate an inhibition effect of NOM. Moreover, we can compare the P values of ternary mixtures to those of the respective binary mixture of MnO₂+NOM to see the effect of Al₂O₃/Al ions. For instance, if the P value of MnO₂+Al₂O₃+AHA is greater than that of MnO₂+AHA under otherwise identical conditions, it suggests there is less inhibition on the MnO₂ reactivity in the ternary mixture than the sum of two binary mixtures: MnO₂+AHA and MnO₂+Al₂O₃. In other words, there are additional interactions in the ternary mixture to alleviate the inhibition effects in the binary mixtures.

Similar to our previous work,²³ the reactivity of MnO₂ is slightly higher in the presence of 0.2 mg-C/L of AHA or 0.5 mg-C/L of LHA (Figures 6a,b). This is mostly due to the formation of soluble HA-Mn complexes which inhibits the adsorption of the produced Mn²⁺ during MnO₂ reaction.⁴ Addition of more than 2 mg-C/L of AHA and LHA increasingly inhibited the MnO₂ reactivity, mostly due to more HAs adsorbed by MnO₂.²³ Some previous studies have made similar observations which have been attributed to the blockage of MnO₂ surface sites.¹ As presented in our previous paper,²³ both alginate and PA did not affect MnO₂ reactivity, likely because of their poor adsorption by MnO₂ under the experimental conditions. The effect of alginate was only seen at a very high concentration of 25 mg/L when a significant amount of alginate was adsorbed (Figure 1b).

When only a small amount of HA (i.e., 0.2–0.4 mg-C/L of AHA or 0.5 mg-C/L of LHA) was added to the mixture of Al ions and MnO₂, MnO₂ reactivity was mostly comparable to that of the respective binary mixture of MnO₂+HA (Figure 6a–b). This correlates well with the negligible effect of HAs on the amount of Al adsorbed when HA concentrations are low (Figure 4). The addition of 2.0–12.5 mg-C/L of AHA or LHA to the mixture of Al ion (0.009 mM) and MnO₂, however, yielded generally greater P values than the respective

mixture of MnO_2 +HA (Figure 6a,b). The effect was more significant when Al ion concentration reached 0.03 mM. This again agrees well with the decreasing amount of Al sorbed by MnO_2 with increasing HA loading (Figure 4). Although the higher amount of HA adsorbed in the presence of Al ions (Figure 5a–b) would likely inhibit MnO_2 reactivity, it did not seem to compete well with the above enhancing effect.

The presence of a wide range of alginate (1–25 mg/L) or PA (1–50 mg/L) in ternary mixtures of MnO_2 , NOM, and Al ion, surprisingly, yielded smaller P values than those of the respective MnO_2 +NOM (Figure 6c,d). The effect was more drastic when soluble Al concentration reached 0.03 mM. Under these conditions, similar amounts of Al were sorbed in the binary vs ternary systems (Figure 4). Our previous work also showed poor aggregation within MnO_2 ,²³ so the most likely reason for the observed lower P values is the enhanced adsorption of the NOMs once the oxide surfaces partially complex with Al ions (Figure 5c,d). Once Al ions complex with MnO_2 , the surface becomes less negatively charged. This would facilitate further adsorption of the negatively charged NOM and hence more inhibition of the MnO_2 reactivity. The presence of Cu^{2+} has also been reported to markedly increase FA adsorption by goethite.²¹

Upon understanding the dominant interactions in the ternary MnO_2 +Al+NOM mixtures and how the interactions affect MnO_2 reactivity, we are now ready to examine ternary MnO_2 + Al_2O_3 +NOM mixtures to see how important Al ions and heteroaggregation are in affecting MnO_2 reactivity in the later mixtures.

Reactivity of MnO_2 with Al_2O_3 and NOM

Comparison of the P values of ternary mixtures of MnO_2 + Al_2O_3 +HA to those of binary mixtures of MnO_2 +HA show comparable to slightly lower P values at 0.2 to 0.4 mg-C/L of AHA or 0.5 mg-C/L of LHA (Figure 6a,b). Higher P values for the ternary mixtures, however, were observed at 2.0–10 mg-C/L of AHA or 2.0–12.5 mg-C/L of LHA.

The effects of HAs on MnO_2 reactivity in ternary mixtures with Al_2O_3 are very different from those observed for ternary mixtures of MnO_2 +Al+HA (Figure 6). If complexation of Al ions plays an important role in MnO_2 + Al_2O_3 +HA, the effect of HAs should be comparable to that of MnO_2 +Al+HA. The different trends observed in Figure 6 thus suggest that Al ions play a much less significant role in affecting MnO_2 reactivity in ternary MnO_2 + Al_2O_3 +HA mixtures than in binary MnO_2 + Al_2O_3 mixtures. Indeed, the trend can be well explained by the inhibited dissolution of Al_2O_3 in the presence of HAs (Figure 3) so that only a small amount of Al ions is now available to complex with MnO_2 . As a result, heteroaggregation between MnO_2 and Al_2O_3 has become the dominant interaction mechanism in MnO_2 + Al_2O_3 +HA such that increasing the concentration of HAs to 2 mg-C/L increased the stability of the oxide mixtures (or decreased the extent of heteroaggregation between the two metal oxides), as shown in Figure 2 and SI Figure S4. The end result is enhanced MnO_2 reactivity at higher concentrations of HAs. When the concentration of HA was low (0.2–0.4 mg-C/L of AHA or 0.5 mg-C/L of LHA), the enhanced extent of heteroaggregation as observed in Figure 2 and SI Figure S4 can also explain the slightly inhibited MnO_2 reactivity in Figure 6a,b. Similar effects of the extent of

heteroaggregation on MnO₂ reactivity due to NOM adsorption have been observed for MnO₂ and iron oxides when heteroaggregation was the major interaction mechanism.²³

In the presence of 1–25 mg/L of alginate or 1–50 mg/L PA, higher *P* values were observed for all ternary mixtures with Al₂O₃ than the respective binary MnO₂+NOM mixture. This trend, again, is opposite to what was observed for ternary MnO₂+Al+NOM, suggesting the effect of Al complexation with MnO₂ was minor at most. Similar to the HAs, alginate and PA mainly affected the extent of heteroaggregation between MnO₂ and Al₂O₃ to affect MnO₂ reactivity.

Environmental Significance

Currently, the literature on the oxidative transformation of organic contaminants (OCs) focuses on model systems where only pure oxidants are present. However, complex environmental conditions prevent us from quantitatively extrapolating the results obtained from model systems to environmental systems. As a result, we are far from developing environmental fate models that can be used to predict the redox behavior of OCs in the environment. Given the fact that (1) mechanistic understanding of the redox transformation of many OCs by *single* Mn oxides has been achieved, yet (2) little information is available regarding the redox transformation of OCs in soil-water environments, it is important to investigate more complex model systems that are based on the existing single oxide systems but are more representative of the environment, so that further examination of the environment is feasible. Mixtures of metal oxides are ubiquitous in soils and aquatic environments, among which Al, Fe, and Si oxides are among the most important components mixing with Mn oxides.^{34–37} Our current work examined how an Al oxide interacted with a Mn oxide in the presence of NOM and how the redox reactivity of MnO₂ was affected by the interactions. Together with our recent work on binary Fe/Al/Si and Mn oxide mixtures⁸ and ternary MnO₂, Fe oxides, and NOM mixtures,²³ the gap between single oxide systems and complex environmental systems is narrower. This makes it more realistic to incorporate redox transformation, which is lacking in the existing models, into a new generation of environmental fate models.

In addition to being important in redox transformation of OCs, Mn oxides, the most abundant Mn form in many sedimentary environments, affect a wide range of geological processes, including anaerobic degradation of organic matter, biogeochemical cycling of trace elements, and the development of anoxic conditions in soils.^{38–43} Our findings will also allow a more accurate modeling of the redox activity of Mn oxides in geological environments, which in turn will enable better modeling of the redox cycling of Mn oxides and the corresponding cycling of many other elements under geological conditions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Adsorption isotherms of (a) AHA and LHA and (b) PA and alginate by Al_2O_3 and $Al_2O_3+MnO_2$. Q_e is the amount adsorbed and C_e is the equilibrium solution concentration.

Conditions: 0.1 g/L Al_2O_3 , 5 mg/L MnO_2 , 0.01 M NaCl, 25 mM acetate buffer, pH 5.0.

Figure 2. Sedimentation of Al_2O_3 and $\text{Al}_2\text{O}_3+\text{MnO}_2$ in the presence of varying concentrations of AHA (a and b) and LHA (c and d). Conditions: 0.1 g/L MnO_2 , 0.1 g/L Al_2O_3 , 0–10 mg-C/L AHA, 0–12.5 mg-C/L LHA, 0.01 M NaCl, and pH 5.0.

Figure 3.

Soluble Al ions measured in a) Al_2O_3 and b) $\text{Al}_2\text{O}_3 + \text{MnO}_2$ in the presence of NOMs.

Experimental conditions: 5.0 mg/L MnO_2 , 0.1 g/L Al_2O_3 , 0–12.5 mg-C/L AHA and LHA, 0–50 mg/L alginate and PA, 0.01 M NaCl, pH 5.0.

Figure 4. Sorption of (a) 0.009 mM and (b) 0.03 mM of Al ions by MnO₂ in the presence of different amounts of NOM. Experimental conditions: 5.0 mg/L MnO₂, 0–50 mg/L NOM, 0.01 M NaCl, pH 5.

Figure 5. Effect of Al ions on the adsorption of (a) AHA, (b) LHA, (c) alginate, and (d) PA by MnO_2 . Conditions: 5 mg/L MnO_2 , 0–0.03 mM of Al ions, 0–12.5 mg-C/L AHA and LHA, 0–50 mg/L alginate and PA, 0.01 M NaCl, pH 5.0.

Figure 6.

Effects of (a) AHA, (b) LHA, (c) alginate, and (d) PA on the oxidative reactivity of MnO_2 with or without Al_2O_3 or Al ion. Reaction conditions: 0.1 g/L Al_2O_3 , 0.009 or 0.03 mM Al ions, 10 μM triclosan, 5.0 mg/L MnO_2 , 0.01 M NaCl, 25 mM acetic buffer, and pH 5.0. The legends indicate the concentrations of NOM in mg-C/L for AHA and LHA and mg/L for alginate and PA. Error bars indicate standard deviations of duplicate experiments.