

INTRODUCTION AND OBJECTIVES

MnO₂ is a common soil and sediment constituent that demonstrates a high reactivity with many organic pollutants. It has been shown to oxidize a variety of organic contaminants such as phenols, anilines and aromatic amines^[1]. However, a limited amount of information is available about the reactivity of MnO₂ when it co-exists with other commonly found metal oxides such as Al or Fe oxides. So, to properly determine the fate of organic contaminants, it is necessary to study the reactivity of MnO₂ in a more complex system where MnO₂ co-exists with other metal oxides.

Some of the observed interactions between different metal oxides in a mixed system include heteroaggregation, surface complexation and surface precipitation. Our previous work on oxidation of triclosan by MnO₂ in the presence of secondary metal oxides such as Al₂O₃, SiO₂ and TiO₂ showed that these secondary metal oxides lowered oxidative reactivity of MnO₂ due to both aggregation of the metal oxides and the complexation of soluble metal ions with MnO₂^[2].

Besides the metal oxides, natural organic matter (NOM) is another important component of the soil-water environment. NOM have been shown to be adsorbed by different mineral/metal oxides through ligand exchange between the functional groups of the NOM and the oxide surface^[3,4]. The coating of NOM changes the characteristics of the mineral surfaces such as the zeta potential which affects their behavior such as aggregation and adsorption of trace metal ions.

The purpose of this study was to elucidate the effect of NOM on the oxidative reactivity of MnO₂ in binary oxide mixtures. Our hypothesis is that the presence of NOM will affect the oxidation process by interfering with the aggregation process among MnO₂ and the secondary metal oxides and also by forming complex with the soluble metal ions that would otherwise complex with MnO₂.

MATERIALS AND METHOD

Kinetic Experiments

> Kinetic results were obtained from batch reactions of triclosan with MnO₂, secondary metal oxides (Al₂O₃, SiO₂, FeOOH, Fe₂O₃) and OM in amber glass bottles under constant stirring. Reaction aliquots were periodically collected to measure oxidation.

> Reaction was quenched by using NaOH addition to adjust pH to 10 before centrifugation. Adding NaOH releases the triclosan adsorbed by the oxides so the overall loss of triclosan in supernatant is due to oxidation only.

> The concentration of triclosan was measured using the HPLC.

Zeta Potential Measurements

The pH_{ZPC} values and zeta potential measurements of the oxides that are mixed with varying concentrations of OM were measured using the Malvern Zetasizer Nano ZS.

Adsorption of OM

The concentrations of OM in the supernatant were measured using the Agilent 8670 UV-visible spectrophotometer. The wavelength used to measure Aldrich humic acid (AHA) and Leonardite humic acid (LHA) was 254 nm. Pyromellitic acid (PA) was measured at 255 nm.

PROPERTIES OF THE METAL OXIDES

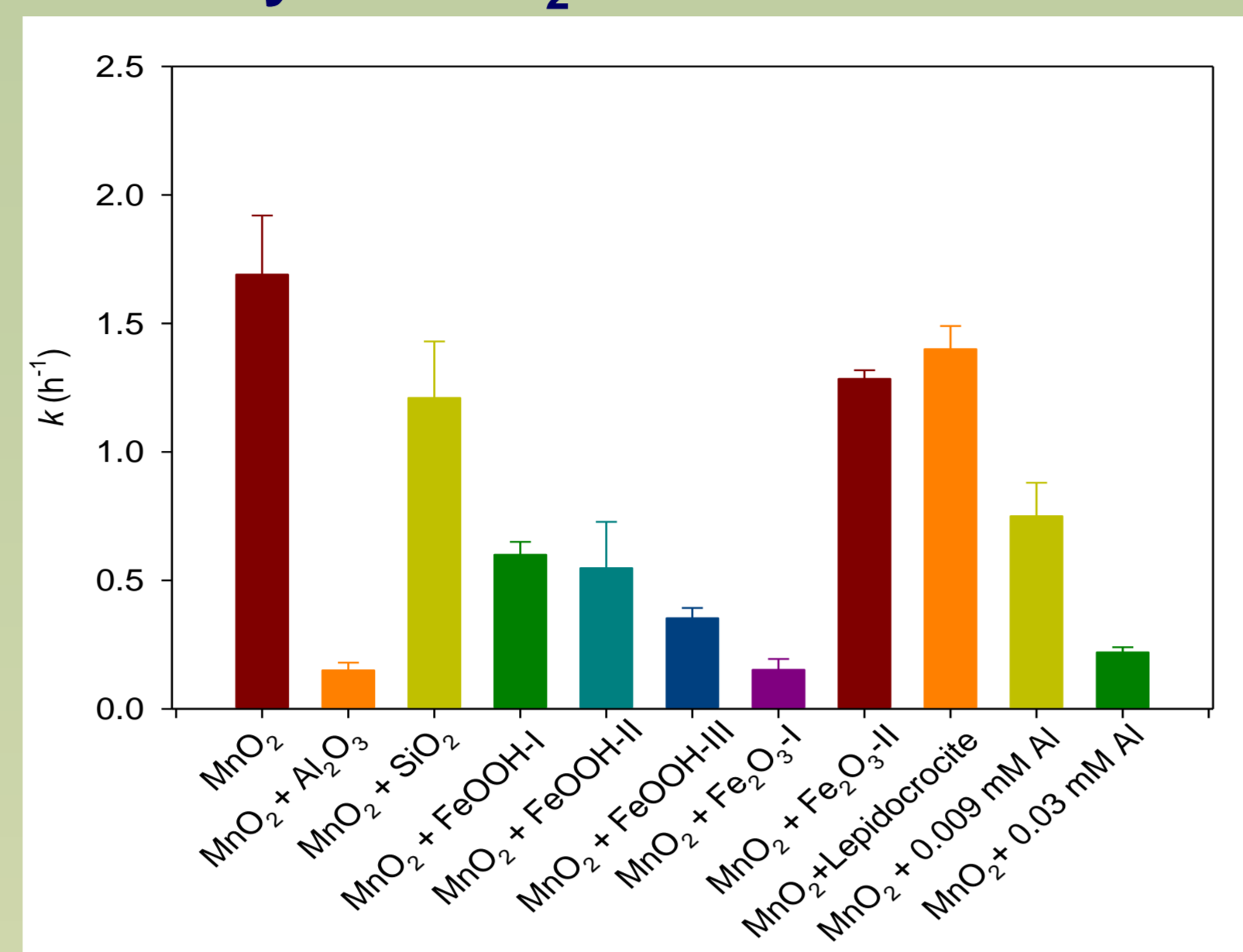
Metal Oxide	BET surface area (m ² g ⁻¹)	average particle size (nm)	pH _{ZPC}
Y-Al ₂ O ₃	180	25	9.3
SiO ₂	440	80	2.4
FeOOH-I	17	100-600	8.0
FeOOH-II	40-60	20-60	8.0
FeOOH-III	136.8	6	7.8
Fe ₂ O ₃ -I	14	100-600	3.4
Fe ₂ O ₃ -II	20-60	90	7.7
Lepidocrocite	18	50-300	7.9
δ-MnO ₂	255	-	2.4

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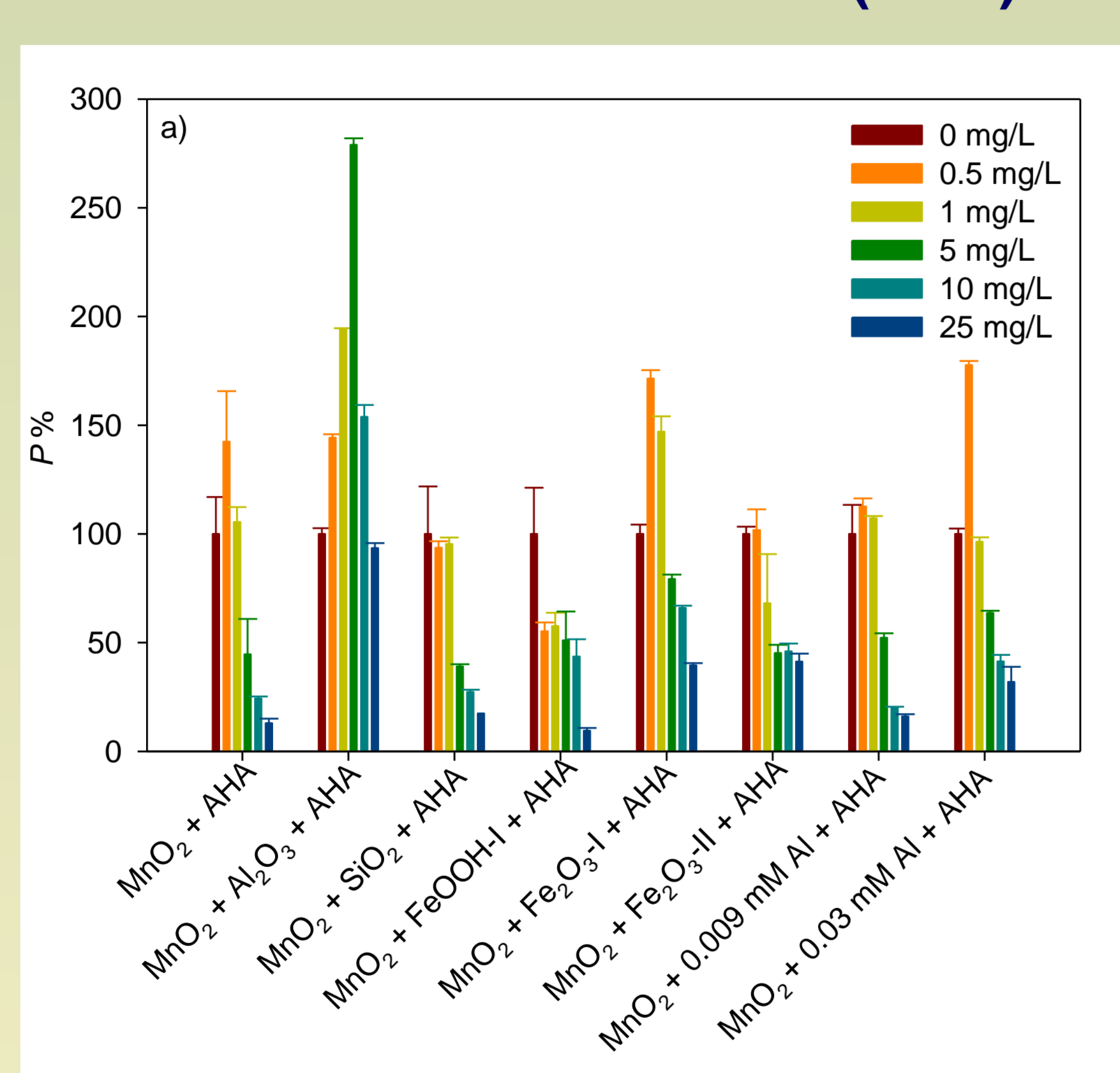
RESULTS AND DISCUSSION

A. Effect of oxides and ions on the oxidative reactivity of MnO₂



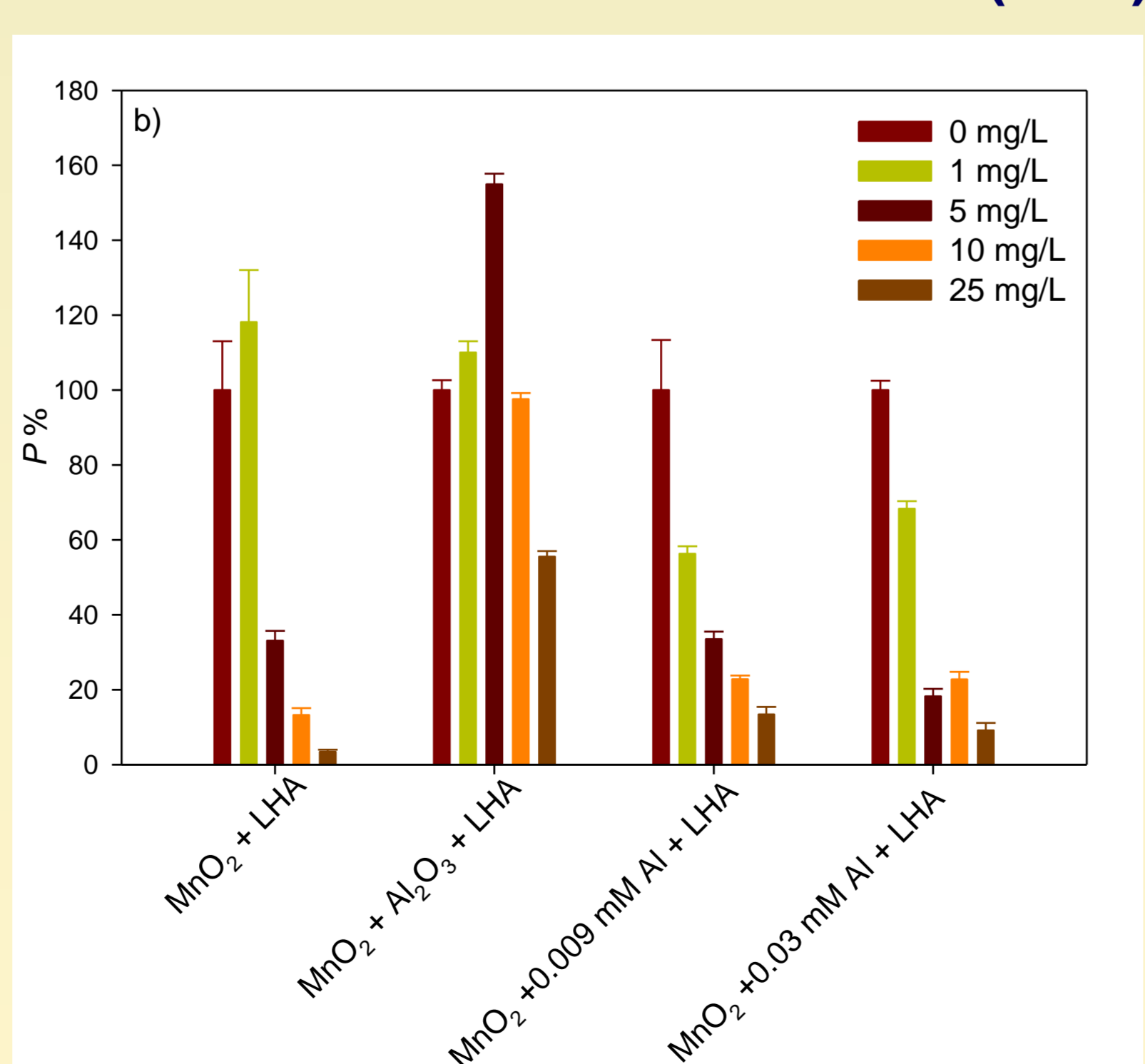
The presence of metal oxides decreases the rate constant and the effect is higher for metal oxides with smaller particle size.

B. Effect of Aldrich Humic Acid (AHA)



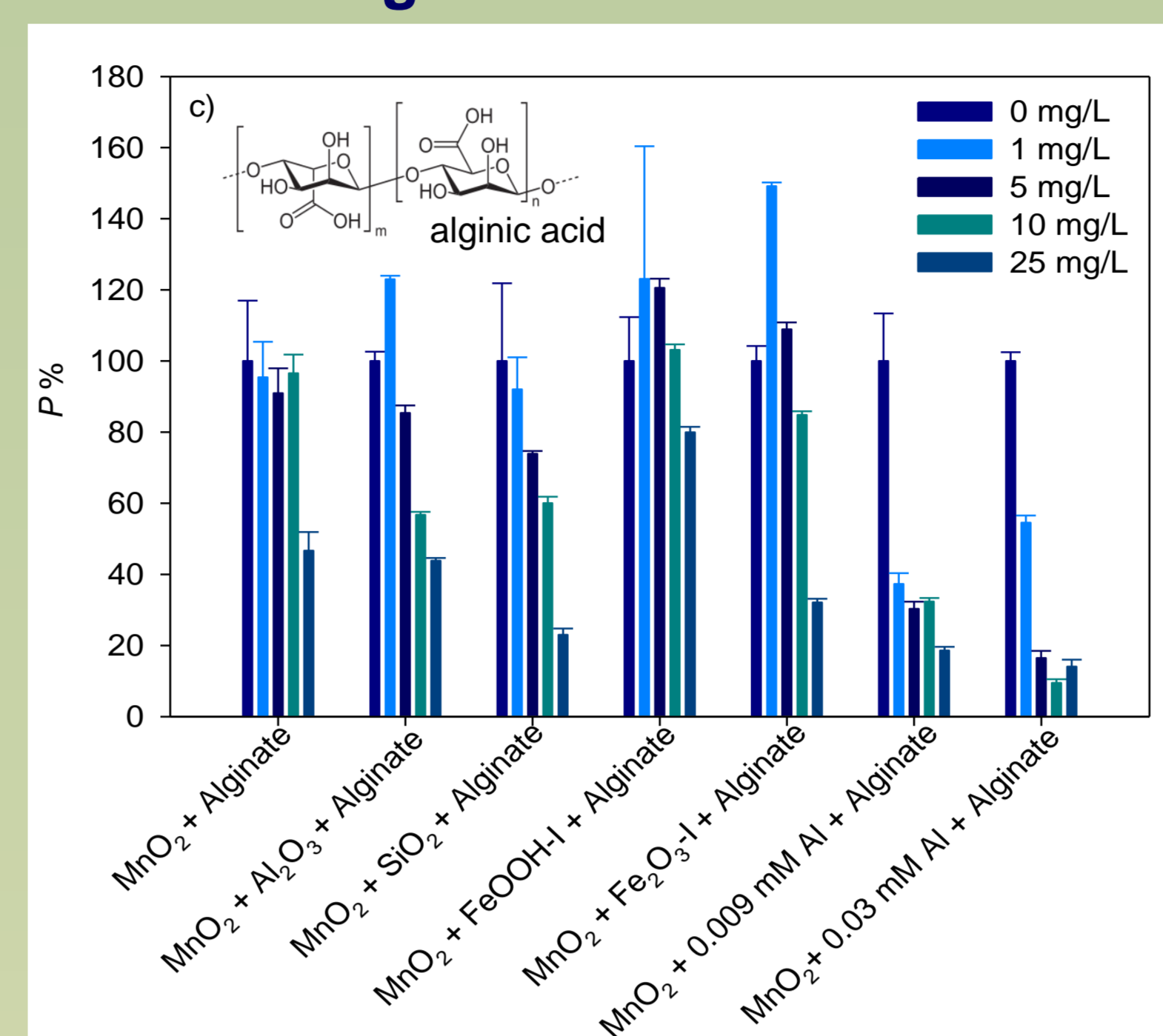
The presence of AHA most likely causes less aggregation between MnO₂ and the metal oxides (Al₂O₃, FeOOH-I and Fe₂O₃-I) hence increasing the number of reactive surface sites on MnO₂.

C. Effect of Leonardite Humic Acid (LHA)

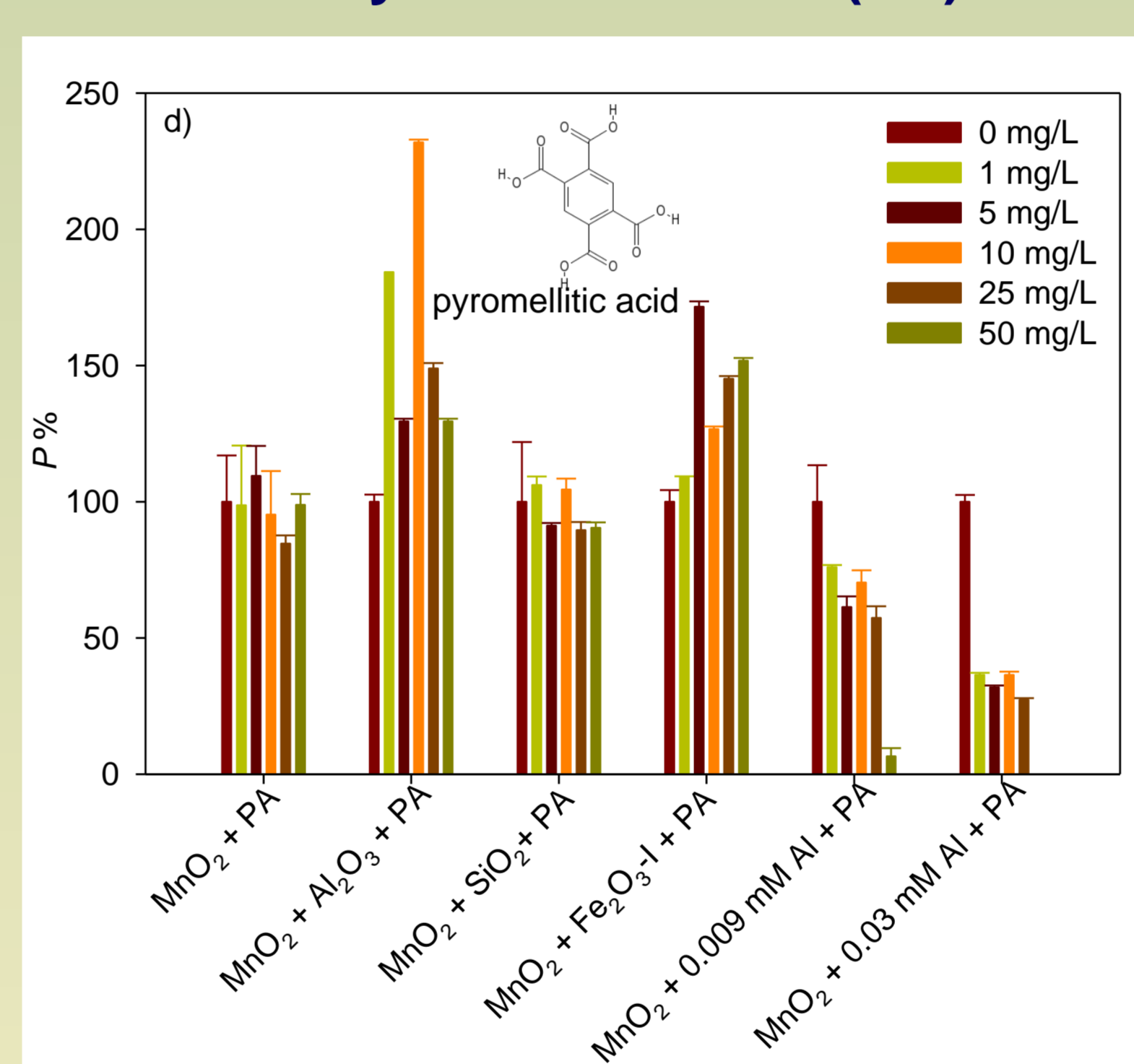


LHA exhibits similar effects as that of AHA when added to a system containing Al₂O₃ or Al.

D. Effect of Alginate



E. Effect of Pyromellitic Acid (PA)



Alginate decreases the aggregation among metal oxides by adsorption on their surface. There is less adsorption of PA by the metal oxides and hence it does not affect the aggregation between the metal oxides.

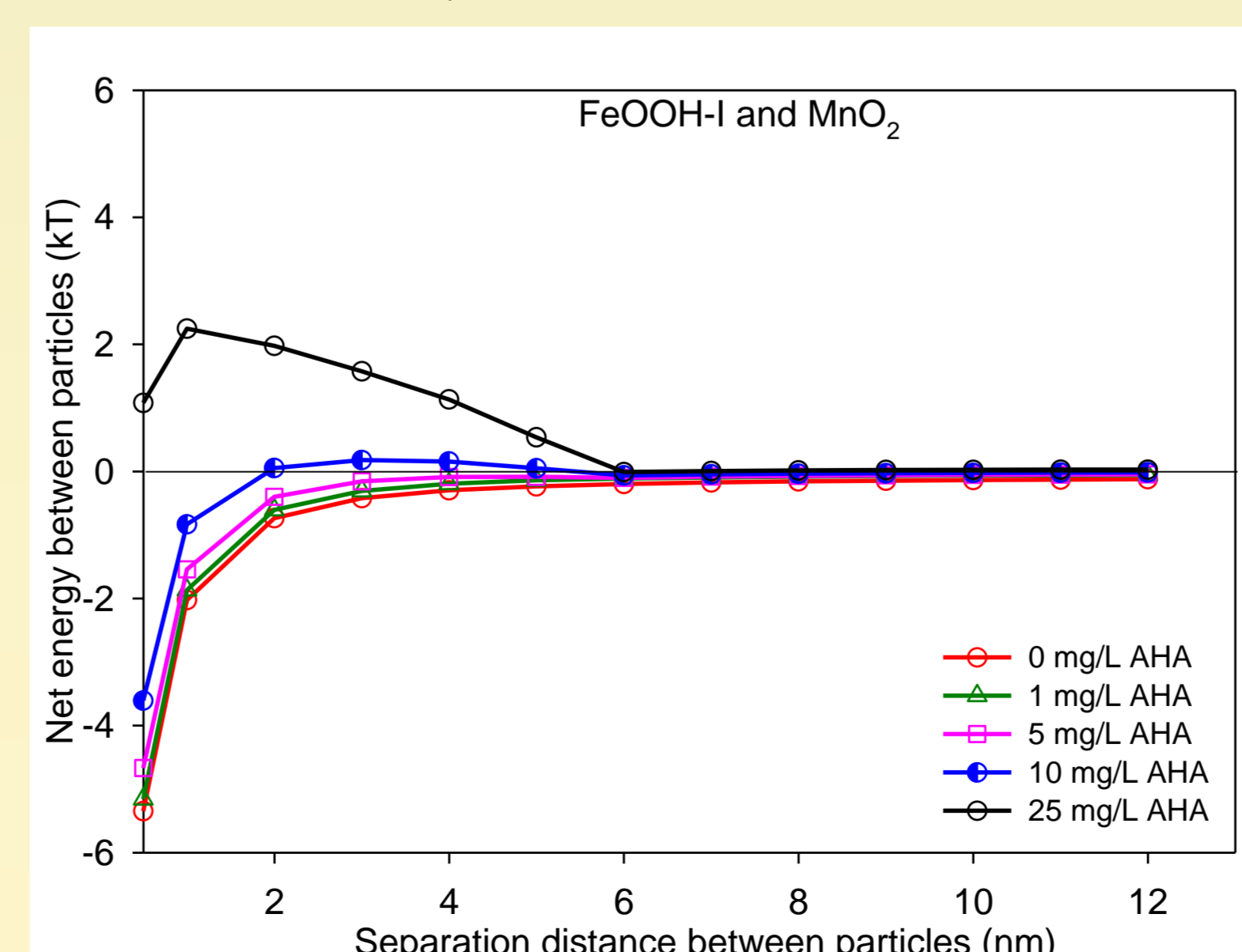
F. Extended DLVO theory [5]

$$\Phi_{Total} = \Phi_{EDL} + \Phi_{VDW} + \Phi_{V_{ST}(h)}$$

$$EDL = \pi \epsilon \frac{a_1 a_2}{(a_1 + a_2)} (\psi_1^2 + \psi_2^2) \times \left[\frac{2\psi_1 \psi_2}{\psi_1^2 + \psi_2^2} \ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) + \ln(1 - e^{-2\kappa h}) \right]$$

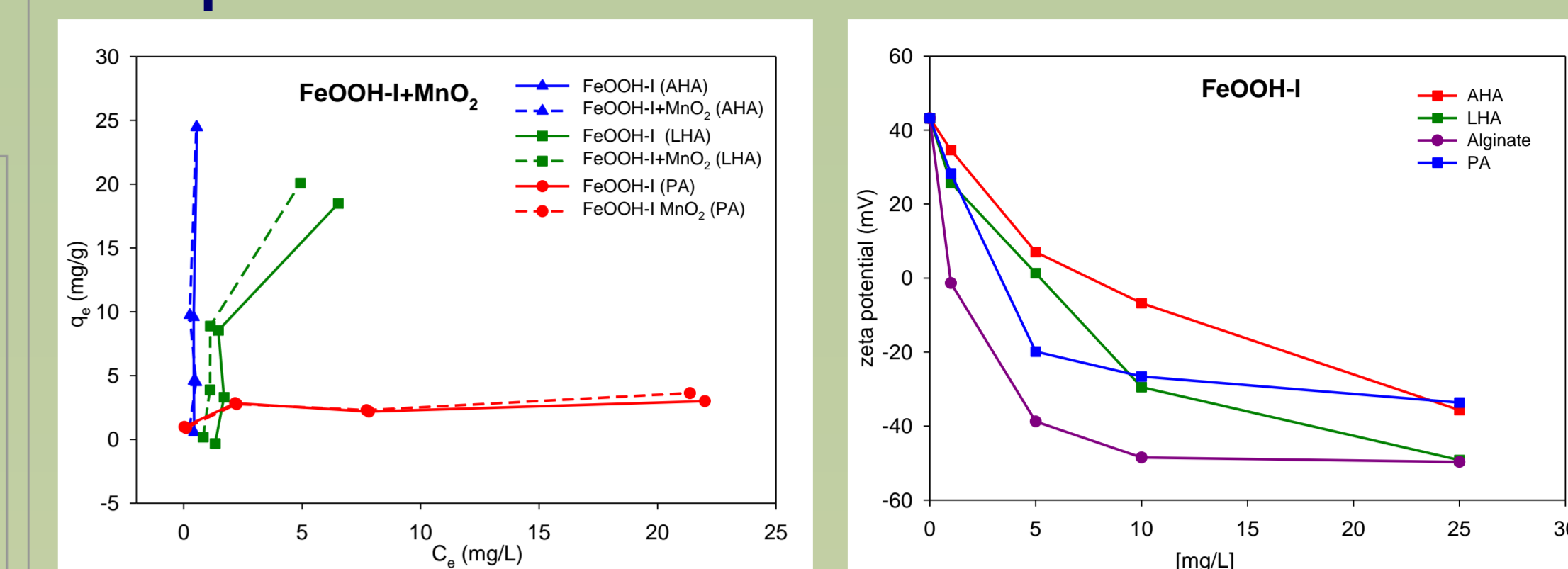
$$VDW = -\frac{A}{6} \left[\frac{2a_1 a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1 a_2}{r^2 - (a_1 - a_2)^2} + \ln \left(\frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2} \right) \right]$$

$$V_{ST}(h) = -2\pi \left(\frac{a_1 a_2}{a_1 + a_2} \right) \left(\frac{kT}{S^3} \right) \left[\frac{16I^2}{5} \left(h^{-1/4} - I^{-1/4} \right) + \left[\frac{16I^{-3}}{17} \left(h^{1/4} - I^{1/4} \right) \right] - \left[\frac{48I}{35} (h - I) \right] \right]$$



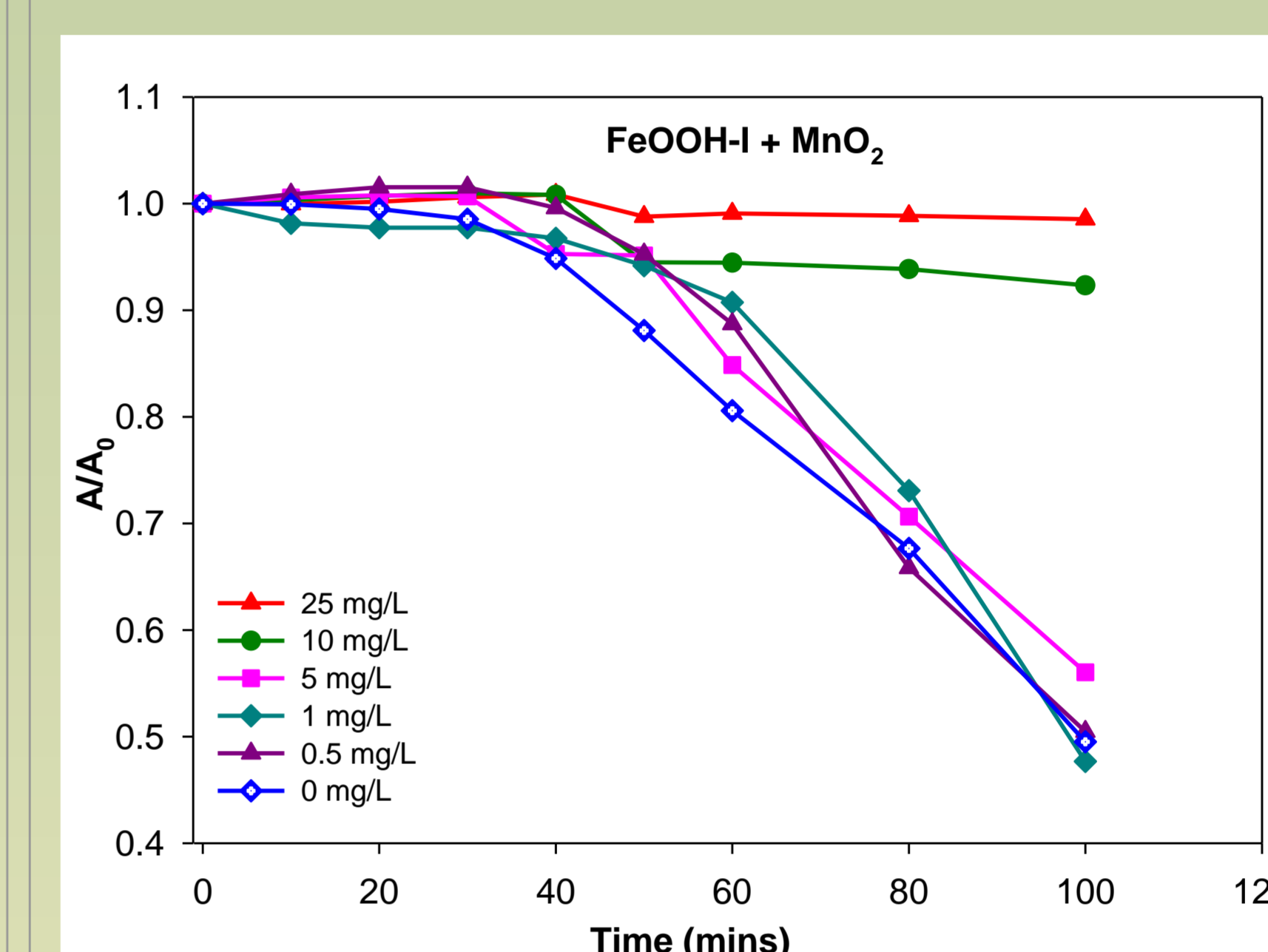
The increase in AHA concentration decreases the surface charge on both MnO₂ and FeOOH-I leading to a higher net energy barrier between the particles. Hence the aggregation is less between them.

G. Adsorption of OM by FeOOH-I and their effect on zeta potential



Both AHA and LHA showed much higher adsorption capacity toward FeOOH-I than PA. The zeta potential values for FeOOH-I decreased with an increasing amount of NOM adsorbed.

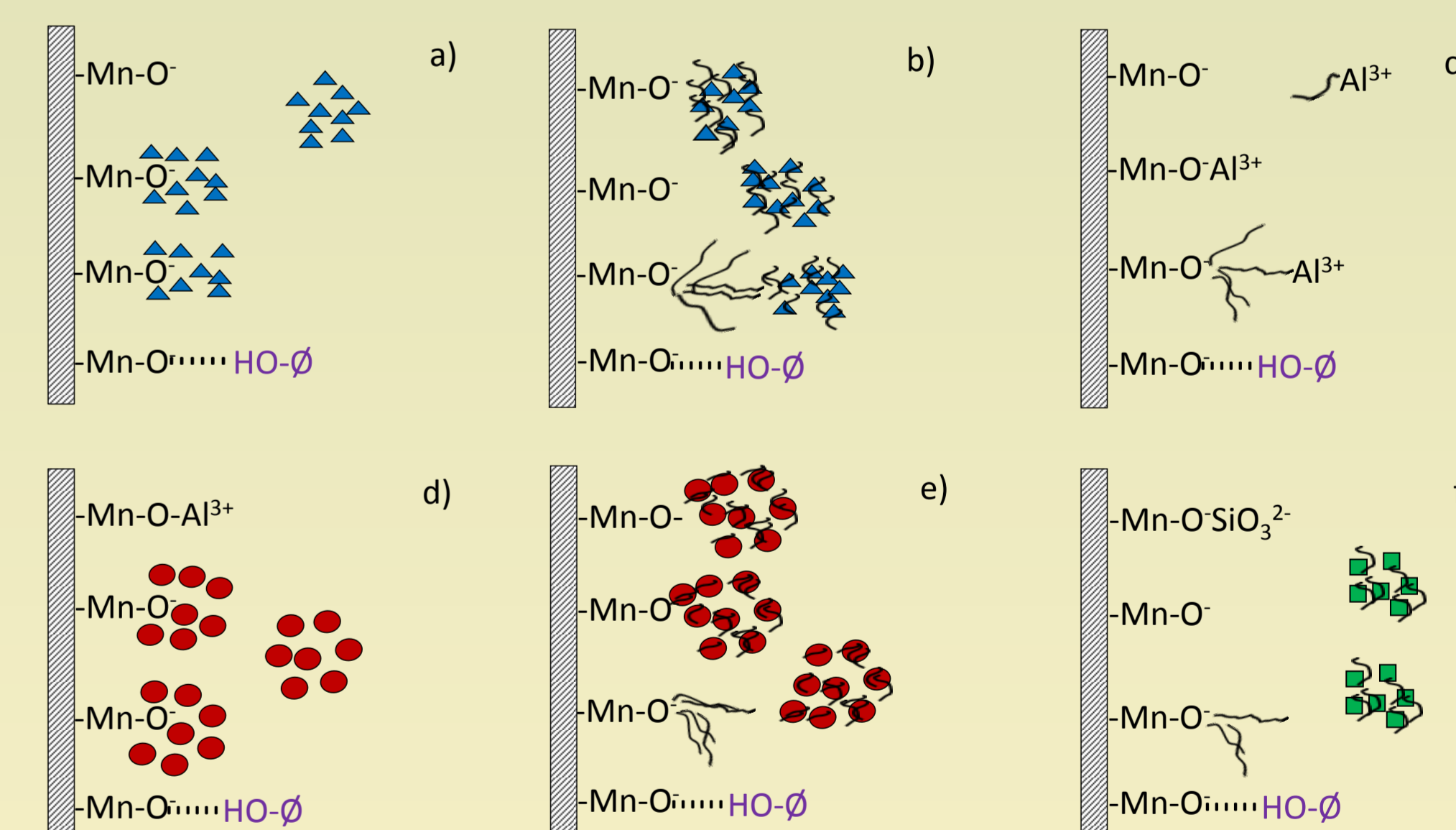
H. Sedimentation



Increasing concentration of AHA increases the stability of the FeOOH-I and MnO₂ mixture indicating that there is less aggregation among the two metal oxides.

CONCLUSIONS

▲ Fe Oxide ● Al₂O₃ ■ SiO₂ ◊ OM HO-φ Organic Compound



Proposed interaction mechanisms: a) MnO₂+Fe oxide, b) MnO₂+Fe oxide+OM, c) MnO₂+Al³⁺+OM, d) MnO₂+Al₂O₃, e) MnO₂+Al₂O₃+OM, and f) MnO₂+SiO₂.

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